CHAPTER 1

Determining the Glass Transition in Polymer Melts

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INTRODUCTION

In the last 15 years, computer simulation studies of the glass transition in polymer melts have contributed significantly to advance our understanding of this phenomenon, which is at the same time of fundamental scientific interest and of great technical importance for polymer materials, most of which are amorphous or at best semi-crystalline. This progress has been possible, on the one hand, because of improved models and simulation algorithms and, on the other hand, because of theoretical advances in the description of the structural glass transition in general.1 Much of this development has been mirrored in a series of conferences on relaxations in complex systems the proceedings of which might serve as a good entry point into the literature on the glass transition in general.2,3

Instead of providing a detailed overview of all simulation work performed on the glass transition in polymer melts, this review has two goals. The first goal is to provide a novice to the field with the necessary background to understand the model building and choice of simulation technique for studies of the polymer glass transition. In particular, a novice modeler needs to be aware of the strengths and limitations of the different approaches used in the simulation of glass-forming polymers and to be able to judge the validity of the original literature. The second goal is to present a personal view of the
contribution that computer simulations have made to our understanding of different aspects of the polymer glass transition, ranging from thermodynamic to dynamic properties. This part of the review will present our current understanding of glass transitions in polymeric melts based on simulation, experiment, and theory. We will illustrate this understanding based mainly on our own contributions to the field.

In the next section, a short summary of the phenomenology of the glass transition is presented. The following section on models then explains the various types of models employed in the simulation of polymer melts, and the ensuing section on simulation methods introduces the algorithms used for such simulations. We will then describe simulation results on concepts relating to the thermophysical properties of the polymer glass transition. Finally, the main section of this review will present an overview of simulations of the slowdown of relaxation processes in polymer melts upon approaching the glass transition, and in the conclusions, we summarize what has been learned about how to identify the glass transition in polymer melts.

PHENOMENOLOGY OF THE GLASS TRANSITION

The defining property of a structural glass transition is an increase of the structural relaxation time by more than 14 orders in magnitude without the development of any long-range ordered structure. Both the static structure and the relaxation behavior of the static structure can be accessed by scattering experiments and they can be calculated from simulations. The collective structure factor of a polymer melt, where one sums over all scattering centers $M$ in the system

$$S(q) = \frac{1}{M} \sum_{i,j=1}^{M} \langle \exp[iq \cdot (\bar{r}_i - \bar{r}_j)] \rangle$$

resembles the structure factor of small molecule liquids (we have given here a simplified version of a neutron structure factor: all scattering lengths have been set to unity).

In Figure 1, we show an example of a melt structure factor taken from a molecular dynamics simulation of a bead-spring model (which will be described later). The figure shows a first peak (going from left to right), the so-called amorphous halo, which is a measure of the mean interparticle distance in the liquid (polymer melt). Upon lowering the temperature to the glass transition, the amorphous halo shifts to larger momentum transfers as the mean interparticle distance is reduced by thermal expansion. The amorphous halo also increases in height, which indicates smaller fluctuations of the mean interparticle distance, but no new structural features are introduced by this cooling.
The thermal expansion, however, changes behavior at the glass transition, which is a phenomenon that was first analyzed in detail in a careful study by Kovacs. In the polymer melt, the thermal expansion coefficient is almost constant, and it is again so in the glass but with a smaller value. At the glass transition, there is therefore a break in the dependence of density on temperature that is the foremost thermophysical characteristic of the glass transition.

The decay of the structural correlations measured by the static structure factor can be studied by dynamic scattering techniques. From the simulations, the decay of structural correlations is determined most directly by calculating the coherent intermediate scattering function, which differs from Eq. [1] by a time shift in one of the particle positions as defined in Eq. [2]:

\[ S(q, t) = \frac{1}{M} \sum_{i,j=1}^{M} \langle \exp[i\vec{q} \cdot (\vec{r}_i(t) - \vec{r}_i(0))] \rangle \]  

The Fourier transform of this quantity, the dynamic structure factor \( S(q, \omega) \), is measured directly by experiment. The structural relaxation time, or \( \alpha \)-relaxation time, of a liquid is generally defined as the time required for the intermediate coherent scattering function at the momentum transfer of the amorphous halo to decay to about 30%; i.e., \( S(q_{ah}, \tau_\alpha) = 0.3 \).

The temperature dependence of the \( \alpha \) time scale exhibits a dramatic slowdown of the structural relaxation upon cooling. This temperature dependence...
This macroscopic measure of the relaxation time in the melt serves to define the so-called viscosimetric glass transition $T_g$ as the temperature at which the viscosity is $10^{13}$ Poise. This result corresponds to a structural relaxation time of approximately 100 s. In Figure 2, we show three typical temperature dependencies of the viscosity in the form of an Angell plot. The upper curve is an Arrhenius law defining so-called “strong glass formers.” The two other curves follow Vogel–Fulcher laws (Eq. [3]) observed for “fragile glass formers,” a category to which most polymeric systems belong, displaying a diverging viscosity at some temperature $T_0 < T_g$. Around $T_g$, the relaxation time of fragile glass formers increases sharply. The definition of $T_g$ is thus based on the fact that at this temperature the system falls out of equilibrium on typical experimental time scales. As a result of this falling out of equilibrium, one also observes a smeared-out step in the temperature dependence of the heat capacity close to $T_g$ defining the calorimetric $T_g$ (similar to the behavior of the thermal expansion coefficient). The calorimetric $T_g$ and the viscosimetric $T_g$ need not agree exactly. For crystallizable polymers, one can define a “configurational entropy” of the polymer melt by subtracting the entropy of the corresponding crystal from the entropy of the melt. A monotonous decrease is predicted in the configurational entropy to a value at $T_g$, which is about one third of the corresponding value of the configurational entropy at the melting temperature of the crystal. Extrapolating to lower temperatures, one finds the configurational entropy to vanish at the Kauzmann temperature $T_K$, which is typically 30–50 K lower than $T_g$. It is interesting to note that

Figure 2 Sketch of typical temperature dependencies of the viscosity $\eta$ of glass-forming systems. The viscosimetric $T_g$ of a material is defined by the viscosity reaching $10^{13}$ Poise. Strong glass formers show an Arrhenius temperature dependence, whereas fragile glass formers follow reasonably well a Vogel–Fulcher (VF) law predicting a diverging viscosity at some temperature $T_0$. 
$T_k$ is often close to the Vogel–Fulcher temperature $T_0$ discussed in connection with Figure 2, which is determined by fitting the Vogel–Fulcher relation\textsuperscript{5–8} to the temperature dependence of the structural relaxation time of the melt\textsuperscript{9} using Eq. [3]:

$$\tau = \tau_\infty \exp [E_{\text{act}}/k_B(T - T_0)]$$  \hspace{1cm} [3]$$

where $\tau_\infty$ is a time characterizing microscopic relaxation processes at high temperatures and $E_{\text{act}}$ is an effective activation energy.

Up to this point the phenomenological characterization of the glass transition is the same for a polymer melt and for a molecular liquid. In a polymer melt, however, one must also have knowledge of both the conformational structure and the relaxation behavior of a single chain to characterize the system completely, be it in the melt state or in the glassy state. Flexible linear macromolecules in the melt adopt a random coil-like configuration; i.e., their square radius of gyration is given by\textsuperscript{10–12} Eq. [4]:

$$R_g^2 = C_\infty \ell N^2 = Nb^2$$  \hspace{1cm} [4]$$

where $N$ ($N \gg 1$) is the degree of polymerization and $\ell$ is the length of a segment. The characteristic ratio $C_\infty$ describes short-range orientational correlations among subsequent monomer units along the backbone of the polymer chain, and $b = \sqrt{C_\infty \ell}$ is the statistical segment length of the chain. On intermediate length scales, the structure of a polymer coil is well described by the Debye function\textsuperscript{10} of Eq. [5]:

$$S_p(q) = \frac{1}{N} \sum_{i,j=1}^{N} \langle \exp [i \vec{q} \cdot (\vec{r}_i - \vec{r}_j)] \rangle = N f_D(q R_g^2)$$

$$f_D(x) = \frac{2}{x^2} [\exp(-x) - 1 + x]$$  \hspace{1cm} [5]$$

where $q b \ll 1$ is assumed for the momentum transfer and we again set all scattering lengths to unity.

In the dense melt, these coils interpenetrate each other. Thus, their diffusive motion is slow even at temperatures far above the glass transition. If the chain length $N$ is smaller than the “entanglement chain length” $N_e$, above which reptation-like behavior sets in,\textsuperscript{12–15} the relaxation time describing how long it takes a coil to renew its configuration is given by the Rouse time

$$\tau_R = \zeta(T) N^2 C_\infty \ell^2 / (3 \pi^2 k_B T)$$  \hspace{1cm} [6]$$

where $\zeta(T)$ is the friction coefficient experienced by the segments of the chain in their Brownian motion, $k_B$ is Boltzmann’s constant, and $T$ is the temperature.
The Rouse model\textsuperscript{12} that yields Eq. \( [6] \) also shows that the self-diffusion constant of the chains scales inversely with chain length

\[
D_N = \frac{k_B T}{(N\zeta(T))} \tag{7}
\]

whereas the melt viscosity is proportional to the chain length

\[
\eta = c\zeta(T)b^2N/36 \tag{8}
\]

with \( c \) being the number of monomers per volume.\textsuperscript{14,15}

Ample experimental evidence exists\textsuperscript{10–13} that Eqs. \([4]\)–\([8]\) capture the essential features of (nonentangled) polymer chains in a melt; however, recent simulations and experiments\textsuperscript{16,17} have shown that the relaxation of coils on length scales smaller than \( R_g \) is only qualitatively described by the Rouse model. The glass transition manifests itself in the temperature dependence of the segmental friction coefficient \( \zeta \). Within the Rouse model, this quantity captures the influence of the specific chemistry on the dynamics in the melt, whereas the statistical segment length \( b \) captures its influence on the static properties. This result explains the two types of models used to study the properties of polymer melts (the glass transition being one of them). Coarse-grained models, like a bead-spring model in the continuum or lattice polymer models, can reproduce the chain length scaling of static and dynamic properties in polymer melts when they correctly capture the determining physics. That physics involves the excluded volume between all segments and the connectivity of the chains. Chemically realistic models are needed when one either tries to reproduce experimental data quantitatively or to describe polymer properties on length and time scales that are still influenced by the detailed chemistry.

A particular characteristic feature of dynamic processes in the vicinity of the glass transition is the ubiquity of the Kohlrausch–Williams–Watts (KWW) stretched exponential relaxation:\textsuperscript{1,7–9}

\[
\phi(t) \propto \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right], \quad 0 < \beta < 1 \tag{9}
\]

Relaxation functions \( \phi(t) \), which are observable via mechanical relaxation, dielectric relaxation, multidimensional nuclear magnetic resonance (NMR) spectroscopy, neutron-spin echo scattering, and so on, can be described in their long-time behavior by Eq. \( [9] \). The exponent \( \beta \) typically lies in the range \( 0.3 \leq \beta < 1 \) and depends on what is relaxing. Although the relaxation time \( \tau \) depends strongly on temperature, \( \beta \) is often approximately independent of temperature in some temperature interval. In this regime, \( \phi(t) \) exhibits a scaling property called the “time-temperature superposition principle.”\textsuperscript{7–9}

Polymers are very good glass formers, with a few notable exceptions. For some polymers, such as atactic polypropylene or random copolymers like...
cis-trans polybutadiene, no possible crystalline state is known, so in these cases it is not clear at all whether we can speak about a super-cooled liquid on approaching the glass transition. Even when there is an ordered ground state (crystalline or only liquid crystalline) for a specific polymer, we can easily understand that a kinetic hindrance for ordering exists. In order to crystallize, a chain must change its random-coil-like state in favor of one of its possible energetic ground state conformations. Because of the packing constraints in a dense melt, this must happen (presumably) in a synchronized fashion with the surrounding chains. Thus, it is understandable that polymers are hard to crystallize. Accordingly, whether no known ordered state exists or whether that state is only kinetically inaccessible, it is easy to observe and measure metastable thermal equilibrium properties of polymer melts (e.g., specific heat or entropy) from the high-temperature melt to the low-temperature glass.

MODEL BUILDING

Our aim is to better understand the glass transition phenomenon in polymer melts by using computer simulations. The discussion of the glass transition phenomenology in the previous section made it clear that we can distinguish several levels of specificity in our computational quest: (1) We can try to model generic features of the structural glass transition, i.e., those features that are independent of whether we are considering a polymer melt or, e.g., an organic liquid. (2) We can try to determine features of the structural glass transition that are specific to polymeric materials as compared with, e.g., silica glasses. (3) We can try to understand quantitatively the glass transition for a specific polymeric material. If the aim of our work falls into category (1) and partly (2), it is most efficient from the modeling perspective to use coarse-grained models that capture only generic polymeric properties like monomer connectivity and excluded volume. If the aim of our work falls into category (3) and partly (2), we will need to employ a chemically realistic model for which quantitative input on the local geometry and energetics, i.e., a well-calibrated force field, is required. Below we consider first chemically realistic models and then we describe two classes of coarse-grained models.

CHEMICALLY REALISTIC MODELING

If we are aiming for a quantitatively correct prediction of the behavior and properties of a specific polymer, we need to employ an optimized and carefully validated force field for this specific polymer. In the literature one often finds simulation work using force fields that do not fulfill these criteria but where instead the authors use “polymer-xy-like” models. Although these models fail to reproduce the properties of the polymer they claim to model
quantitatively, the qualitative conclusions drawn from these simulations are often valid, especially when they concern more general polymeric properties. However, even qualitative conclusions pertaining only to a specific polymer or to a class of similar polymers can be problematic when derived from simulations employing inaccurate or unvalidated potentials. Various forms of classical potentials (force fields) for polymers can be found in the literature and have been reviewed in this book series. We are concerned in this chapter with reproducing the static, thermodynamic, and dynamic (transport and relaxational) properties of non-reactive organic polymers, and for this reason, the potential must represent accurately the molecular geometry, nonbonded interactions, and conformational energetics of the macromolecules of interest.

The classical force field represents the potential energy of a polymer chain, made of $N$ atoms with coordinates given by the set $\{\vec{r}\}$, as a sum of nonbonded interactions and contributions from all bond, valence bend, and dihedral interactions:

$$V(\{\vec{r}\}) = V_{\text{nb}}(\{\vec{r}\}) + V_{\text{pol}}(\{\vec{r}\})$$

$$= V_{\text{nb}}(\{\vec{r}\}) + \sum_{\text{bonds}} V_{\text{bond}}(r_{ij}) + \sum_{\text{bends}} V_{\text{bend}}(\theta_{ijk}) + \sum_{\text{dihedrals}} V_{\text{tors}}(\Phi_{ijkl})$$

More complicated cross-terms between the different intramolecular degrees of freedom are also employed in some force fields, but we will not consider them in the following. The dihedral term may also include four-center improper torsion or out-of-plane bending interactions that occur at $sp^2$ hybridized centers.

The nonbonded interactions commonly consist of a sum of two-body repulsion and dispersion energy terms between atoms that are often of the Lennard–Jones form in addition to the energy from the interactions between fixed partial atomic or ionic charges (Coulomb interaction)

$$V_{\text{nb}}(\{\vec{r}\}) = \sum_{i,j=1}^{M} 4\epsilon \left[ \frac{\sigma}{r_{ij}} \right]^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

The dispersion interactions are weak compared with repulsion, but they are longer range, which results in an attractive well with a depth $\epsilon$ at an interatomic separation of $\sigma_{\text{min}} = 2^{1/6}\sigma$. The interatomic distance at which the net potential is zero is often used to define the atomic diameter. In addition to the Lennard–Jones form, the exponential-6 form of the dispersion-repulsion interaction,

$$V_{\exp-6}(\{\vec{r}\}) = \frac{1}{2} \sum_{i,j=1}^{M} A_{ij} \exp \left\{ -B_{ij} r_{ij} \right\} - \frac{C_{ij}}{r_{ij}^6}$$
is often used in atomistic models. Nonbonded interactions are typically included in the force field calculations for all atoms of different molecules and for atoms of the same molecule separated by more than two bonds or by three bonds when the nonbonded “1-4” interaction has been included in the parameterization of an effective torsional interaction.  

The Coulomb interaction is long-range, which necessitates use of special numerical methods for efficient simulation. When one tries to understand the glass transition in a chemically realistic model, these long-range Coulomb interactions add further numerical overhead so that the most extensive glass transition simulations of realistic models were done for apolar molecules.

In atomistic force fields, the contributions from bonded interactions included in Eq. [10] are commonly parameterized as

\[
V_{\text{bond}}(r_{ij}) = \frac{1}{2} k_{ij}^{\text{bond}} (r_{ij} - r_{ij}^0)^2
\]

\[
V_{\text{bend}}(\theta_{ijk}) = \frac{1}{2} k_{ijk}^{\text{bend}} (\theta_{ijk} - \theta_{ijk}^0)^2 \sim \frac{1}{2} k_{ijk}^{\text{bend}} (\cos \theta_{ijk} - \cos \theta_{ijk}^0)^2
\]

\[
V_{\text{tors}}(\Phi_{ijkl}) = \frac{1}{2} \sum_n k_{ijkl}^{\text{tors}} \left[ 1 - \cos(n \Phi_{ijkl}) \right] \quad \text{or}
\]

\[
V_{\text{tors}}(\Phi_{ijkl}) = \frac{1}{2} \sum_n k_{ijkl}^{\text{oop}} \phi_{ijk}^2
\]

Here, \(r_{ij}^0\) is an equilibrium bond length and \(\theta_{ijk}^0\) is an equilibrium valence bend angle, whereas \(k_{ij}^{\text{bond}}\), \(k_{ijk}^{\text{bend}}\), \(k_{ijkl}^{\text{tors}}(n)\), and \(k_{ijkl}^{\text{oop}}\) are the bond, bend, torsion, and out-of-plane bending force constants, respectively. The indices indicate which (bonded) atoms are involved in the interaction. These geometric parameters and force constants, combined with the nonbonded parameters \(q_i\), \(\epsilon\), and \(\sigma\), constitute the classical force field for a particular polymer.

Although there are existing standard force fields in the literature like AMBER, OPLS-AA, COMPASS, CHARMM, and PCFF to name but a few (see also Refs. 24–28), one will typically find that they are only a qualitative or at best a semi-quantitative representation of a polymer one might want to study. The quantitative modeling of a given polymeric material has to start from high-level quantum chemistry calculations as the best source of molecular level information for force field validation and parameterization. Although such calculations are not yet possible on high polymers, they are feasible on small molecules that are representative of polymer repeat units and for oligomers. These calculations can provide the molecular geometries, partial charges, polarizabilities, and the conformational energy surface needed for accurate prediction of structural, thermodynamic, and dynamic properties of polymers. A general procedure for deriving quantum chemistry–based potentials can be found in the literature. The intermolecular dispersion interactions can also, to a certain extent, be determined from these calculations.
However, it has turned out that the most accurate way of fixing these parameters is through matching of simulated phase equilibria to those derived from experiment. As a final step, the potential, regardless of its source, should be validated through extensive comparison with available experimental data for structural, thermodynamic, and dynamic properties obtained from simulations of the material of interest, closely related materials, and model compounds used in the parameterization. The importance of potential function validation in simulation of real materials cannot be overemphasized.

For nonpolar, simple hydrocarbon chains that we will discuss later we can employ a simple force field of the form

\[
V(\{r\}) = \sum_i V(l_i) + \sum_j V(\theta_j) + \sum_k V(\Phi_k) + \sum_{n,m} V_{nb}(r_{nm})
\]  

where the sums run over all bonds, bends, torsions, and nonbonded interacting atoms, respectively. One often does not treat the hydrogen atoms explicitly in simulations of hydrocarbon chains but instead combines them with the carbon atoms to which they are bound to create “united atoms.” This approximation not only reduces the number of force centers for the calculation of the nonbonded interactions, but it also removes the highest frequency oscillations \((C-H)\) bond length and \(H-C-H\) and \(H-C-C\) bond angles) from the model. This approximation works well when one wants to study structure and relaxational properties in amorphous polymers without any specific local interactions (i.e., strong electrostatic interactions or hydrogen bonding). In the latter cases, internal degrees of freedom of the united atoms and a model for their interaction may be added, but no reliable way exists so far to determine the parameters entering such a description quantitatively for a given polymer, so one generally loses the ability to obtain quantitative predictions using such models. A final approximation often employed in large-scale polymer simulations is to neglect the \(C-C\) bond length oscillations and to perform the simulation with constrained bond lengths. The approximations discussed in the last paragraph are motivated by computational expediency. However, they reflect our understanding of the relevant physical processes that must be included in the computer simulation for us to obtain a quantitative reproduction of the structure and dynamics of a realistic polymer melt. Such approximations are imposed on us by the huge spread of relaxation times one has to cover in the simulation, which range from local relaxations to conformational changes of unentangled chains requiring substantial computational efforts when one is striving to perform simulations in thermodynamic equilibrium. The simulation studies of dynamic processes are generally conducted using molecular dynamics (MD) methods. Equilibrating the starting configurations for these studies, however, can profit from the use of Monte Carlo (MC) techniques where moves generating global conformational rearrangements are included.
COARSE-GRAINED MODELS

Coarse-grained polymer models neglect the chemical detail of a specific polymer chain and include only excluded volume and topology (chain connectivity) as the properties determining universal behavior of polymers. They can be formulated for the continuum (off-lattice) as well as for a lattice. For all coarse-grained models, the repeat unit or monomer unit represents a section of a chemically realistic chain. MD techniques are employed to study dynamics with off-lattice models, whereas MC techniques are used for the lattice models and for efficient equilibration of the continuum models.\textsuperscript{36–42} A tutorial on coarse-grained modeling can be found in this book series.\textsuperscript{43}

Coarse-Grained Models of the Bead-Spring Type

These models retain the form of the nonbonded interaction used in the chemically realistic modeling, i.e., they use either an interaction of the Lennard–Jones or of the exponential-6 type. The repulsive parts of these potentials generate the necessary local excluded volume, whereas the attractive long-range parts can be used to model varying solvent quality for dilute or semi-dilute solutions and to generate a reasonable equation-of-state behavior for polymeric melts.

The inclusion of chain connectivity prevents polymer strands from crossing one another in the course of a computer simulation. In bead-spring polymer models, this typically means that one has to limit the maximal (or typical) extension of a spring connecting the beads that represent the monomers along the chain. This process is most often performed using the so-called finitely extensible, nonlinear elastic (FENE) type potentials\textsuperscript{44} of Eq. [17]

\[
U_F(l) = -\frac{1}{2} k l^2 \max \ln[1 - l(l/l_{\max})^2] \quad 0 \leq l \leq l_{\max}
\]

but also with harmonic spring length potentials with a length cut-off\textsuperscript{45} or very stiff force-constants.\textsuperscript{46} Beyond this bond length potential, one may typically include a bending energy term to reduce local flexibility. Because the bending energy and geometry on this length scale do not derive from chemical hybridization, one typically takes the equilibrium bond angle to be 180°. Dihedral energy terms are generally not included in coarse-grained models. Instead, the chains are treated on mesoscopic scales as freely rotating.

The Bond-Fluctuation Lattice Model

The large-scale structure of polymer chains in a good solvent is that of a self-avoiding random walk (SAW), but in melts it is that of a random walk (RW).\textsuperscript{11} The large-scale structure of these mathematical models, however, is
independent of whether one studies them in the continuum or on a lattice, and because of this, MC simulations of lattice models for polymers have a long history.

Later in this tutorial we will use results from simulations of the bond-fluctuation lattice model. This model represents the repeat units of the coarse-grained polymer not as single vertices on some space lattice but as unit cubes on a simple cubic lattice (see Figure 3 for the three-dimensional version of the model). The bonds connecting consecutive monomers are from the class \([2,0,0],[2,1,0],[2,1,1],[3,0,0],[2,2,1],[3,1,0]\), where the square brackets indicate all vectors obtainable from the given vector by lattice symmetry operations. There are a total of 108 bonds with 5 different lengths and 87 different bond angles for this model. The model thus introduces some local conformational flexibility while retaining the computational efficiency of lattice models for implementing excluded volume interactions by enforcing a single occupation of each lattice vertex. Intramolecular potentials are chosen as bond length and/or bond angle dependent according to the physical problem one wants to model. Note that, as in all coarse-grained models, the potentials in the bond-fluctuation model do not correspond physically to bond stretches and valence angle bending potentials in a chemically realistic polymer chain.

When one implements an MC stochastic dynamics algorithm in this model (consisting of random-hopping moves of the monomers by one lattice constant in a randomly chosen lattice direction), the chosen set of bond vectors induces the preservation of chain connectivity as a consequence of excluded volume alone, which thus allows for efficient simulations. This class of moves

Figure 3 Sketch of the bond-fluctuation lattice model. The monomer units are represented by unit cubes on the simple cubic lattice connected by bonds of varying length. One example of each bond vector class is shown in the sketch.
allows for a physical interpretation of the obtained stochastic dynamics\textsuperscript{41} that generates Rouse-like motion of the chains\textsuperscript{12} in the simulation of dense polymer melts.

**SIMULATION METHODS**

The simulation methods most commonly used for atomistic or coarse-grained molecular models are MD simulations and MC simulations. In MD simulations, Newton’s equations of motion are integrated to generate a trajectory (a history) of the model system. The method can capture all vibrational and relaxational processes contained in the chosen model Hamiltonian. MC is a stochastic simulation method that can capture relaxational and diffusive processes. MC is commonly used to generate equilibrium configurations for either sampling of thermodynamic and structural properties or to provide starting configurations for ensuing MD runs that are used to evaluate the dynamics of the model system. In the following discussion, we will examine the two methods with regard to their two main applications—equilibration and generation of trajectories for dynamic measurements, respectively.

**Monte Carlo Method**

The MC method considers the configuration space of a model and generates a discrete-time random walk through configuration space following a master equation\textsuperscript{41,51}

\[
P(x, t_n) = P(x, t_{n-1}) + \sum_{x'} W(x' \rightarrow x)P(x', t_{n-1}) - \sum_{x'} W(x \rightarrow x')P(x, t_{n-1})
\]

[18]

Here \(x, x'\) denote two configurations of the system (specified, for instance, by the set of coordinates of all atoms \(\{r_n\}\) or the position of one chain end for all chains and all bond lengths, bond angles, and torsion angles \(\{r_i^\alpha, l_i^\alpha, \theta_j^\alpha, \phi_k^\alpha\}\), where \(\alpha = 1, \ldots, M\) runs over all chains and the indices \(i, j, k\) run over all internal degrees of freedom of one chain). The transition rates \(W(x \rightarrow x')\) are chosen to fulfill the detailed balance condition

\[
W(x' \rightarrow x)P_{eq}(x') = W(x \rightarrow x')P_{eq}(x)
\]

[19]

which ensures an equal probability flow from \(x'\) to \(x\) as in the reverse direction in equilibrium. Here

\[
P_{eq}(x) = \frac{1}{Z} \exp\{-\beta H(x)\}
\]

[20]
where $\beta = 1/k_B T$, $H(x)$ is the Hamiltonian of the system, and $Z$ is the canonical partition function

$$Z = \sum_x \exp\{-\beta H(x)\}$$

Equation [19] ensures that the thermodynamic equilibrium distribution of Eq. [20] is the stationary (long-time) limit of the Markov chain generated by Eq. [18]. It does not specify the transition rates uniquely, however. Let us write them in the following way:

$$W(x \to x') = W_0(x \to x') W_T(x \to x')$$

where $W_0$ is the probability suggesting $x'$ as the next state, i.e., to suggest a certain MC move, and $W_T$ is the thermal acceptance probability chosen to fulfill Eq. [19]. This requires the suggestion probabilities to be reversible

$$W_0(x \to x') = W_0(x' \to x)$$

Only a few choices for $W_T$ exist in the literature, i.e., Metropolis rates, Glauber rates, or heat-bath, but there is an unlimited variety of possible choices for $W_0$, and this is the great advantage of the MC method. Only some choices for $W_0$ result in physically reasonable dynamics (in general, local moves like selecting a monomer at random and then moving it into a randomly chosen direction by a small distance), but all reversible choices lead to the correct equilibrium distribution of states. One can therefore invent MC moves targeted at overcoming the main physical barriers leading to slow equilibration of a model system.

The two main sources for slow relaxation in polymers are entanglement effects and the glass transition. The first is entropic in origin, whereas the second—at least in chemically realistic polymer models—is primarily enthalpic. We write the largest relaxation time in the melt as

$$\tau_l(T, N) = \tau_{\text{mes}}(T) N^x$$

where $\tau_{\text{mes}}$ is a mesoscopic time scale. The chain length dependence crosses over from $x = 2$ for Rouse behavior to $x = 3.4$ for repeating chains. Every simulation method that performs configuration changes typical for the mesoscopic time scale $\tau_{\text{mes}}$, i.e., local rearrangements, leads to a relaxation of the large-scale structure of the polymer chains in the melt only after $O(N^x)$ such configuration changes. This in turn quickly limits the range of chain lengths one can treat in thermodynamic equilibrium. To circumvent this problem,
one has to use advanced MC techniques that implement global configurational changes within a single Monte Carlo step.

A class of these advanced MC techniques consists of the so-called “connectivity altering moves” like the cooperative motion algorithm\textsuperscript{52} and the end-bridging algorithm\textsuperscript{53–55} and its newest variant, the double-bridging algorithm,\textsuperscript{56,57} which is sketched in Figure 4. The latter two algorithms have been developed with chemically realistic polymer models in mind, and we will now briefly discuss the concepts behind, and properties of, these algorithms.

In the original end-bridging algorithm,\textsuperscript{53–55} an end monomer $i$ of one chain in the melt attacks a backbone atom $j$ of another chain that is sufficiently close in proximity and tries to initiate a change in connectivity of the two involved chains by forming a trimer bridge to this backbone atom. In the event of a successful bridging, the attacking chain grows by a part that is cut off of the attacked chain, and the attacked chain shrinks by a corresponding amount. This description already exhibits the main drawbacks of the algorithm: It generates polydisperse polymer melts, and it needs a sufficient number of chain ends to be efficient. It was found empirically that the efficiency of the algorithm dropped considerably (1) as the stiffness of the chains was increased and (2) in the presence of chain orientation. The algorithm was nonetheless applied successfully to polyethylene melts\textsuperscript{58,59} and cis-1,4 polyisoprene melts,\textsuperscript{60,61} for example.

In the double-bridging algorithm, an inner monomer of a chain attacks an inner monomer of another chain (or the same chain) and tries to form a

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{double_bridging_algorithm.png}
\caption{Sketch of the double-bridging algorithm. Starting from monomer $i$ on the white chain, a trimer bridge to monomer $j$ on the black chain is initiated. If the formation of this connection is geometrically possible, then a bridge between monomers $i'$ and $j'$ has to be built, as they are four monomers removed from $i$ and $j$, respectively. If both bridges can be formed, the intermediate monomers are excised. Two new chains with the same chain length as the original ones are created.}
\end{figure}
trimer bridge (see Figure 4). Simultaneously another bridge is formed between two monomers that are four steps apart from the first two monomers along the two chains, thereby generating two new chains with exactly the same length as the original chains. These requirements understandably put heavy geometric constraints on the configurations of the two chains for which this type of move is feasible (because only special choices of involved monomers \((i,j)\) and excised trimers conserve the chain lengths in the move). The trimer bridge is made of three monomers (atoms) connected by bonds of fixed lengths \(l\) making a fixed angle, which is chosen to be the maximum value of the bond-angle distribution of the model.Whenever the monomers \(i\) and \(j\) are at a distance less than the maximum bridgeable distance of \(4l \cos((\pi - \theta_{\text{max}})/2)\), this geometric problem is in principle solvable.

Connectivity changing algorithms are especially efficient in decorrelating large-scale structure in the melt. These algorithms are typically augmented by local moves and reptation moves (a randomly chosen end monomer of a chain is cut off and reattached to the opposite end of the same chain with a random orientation) to equilibrate the local structure.\(^{41}\) An alternative method for overcoming the entropic slowdown in a polymer melt caused by packing and connectivity is the so-called "4d-algorithm." The idea of this algorithm\(^{62}\) is to turn some monomers into ghost particles (alternatively, one can think of removing some particles into the fourth dimension, which is similar to desorbing and readsorbing particles from a two-dimensional film into the third dimension) and then forcing those particles back into the three-dimensional structure by applying an external field in an extended ensemble simulation. The algorithm is similar to other suggestions to reduce the packing effects.\(^{63–65}\) So far it has been tested on the structural relaxation of a collapsed polymer globule where the connectivity of the chains and the high density inside the globule lead to a dramatic increase in the structural relaxation time of the globule.

True equilibration in a polymer melt is only reached when the largest length scales (e.g., the end-to-end orientation of the chains) are decorrelated. The connectivity altering moves overcome the chain length dependence of this time scale, and the extended ensemble simulations overcome some packing effects influencing the prefactor, but we have not yet discussed any method that can overcome completely the slowing down in the prefactor of Eq. [24], i.e., the deceleration of the structural relaxation accompanying the glass transition. No efficient MC algorithm exists yet to overcome the slowdown of structural relaxation connected with the glass transition! All MC moves employed thus far share the same fate as MD simulations, which face an increase of relaxation time (that is, the simulation time needed) by 14 orders of magnitude on approaching \(T_g\). Because this range of relaxation times is not be covered by modern computing machinery, one is limited to follow the glass transition in equilibrium over about 3-4 orders of magnitude in the relaxation time.
Molecular Dynamics Method

MD involves integrating Newton’s equation of motion, which we write in the Hamiltonian form

\[
\begin{align*}
\frac{d\vec{r}_i}{dt} &= \vec{v}_i \\
\frac{d\vec{v}_i}{dt} &= \frac{\vec{F}_i}{m_i}
\end{align*}
\]  

where \( m_i \) is the mass of particle \( i \), \( \vec{r}_i \) is its position, \( \vec{v}_i \) is its velocity, and \( \vec{F}_i = -\nabla V \) is the force acting on it, where \( V \) is the force field in the Hamiltonian. Because of its conceptual simplicity, the MD method is contained in almost all commercial simulation packages and is therefore widely used. To use it correctly and efficiently, however, requires having some knowledge about the integrators employed and the strengths and limitations of the method.

The numerical solution of Eq. [25] is typically performed using the velocity Verlet integrator,\(^{37,38}\) which is a second-order symplectic integrator.\(^6\) Symplectic integrators conserve phase space volume and are therefore reversible, endowing them with an excellent stability even for relatively large time steps and making them good at conserving energy along a microcanonical trajectory. The time step in the MD integrator is limited by the fastest degrees of freedom in the material being modeled. When we denote with \( \tau_f \) a typical vibrational period of such a fast degree of freedom, the integration step \( \Delta t \) has to be of the order of \( 1/30\tau_f - 1/10\tau_f \). The theory of symplectic integrators is also the starting point to derive multiple time-step integrators,\(^{67,68}\) which increase the efficiency of the MD simulation scheme by calculating weak forces less frequently than strong forces. One can also constrain certain fast degrees of freedom using methods that ensure that constraints are conserved.\(^{34,69,70}\)

Between MC and MD methods, Brownian dynamics (sometimes called stochastic dynamics) methods exist:\(^7\)

\[
\begin{align*}
\frac{d\vec{r}_i}{dt} &= \vec{v}_i dt \\
\frac{d\vec{v}_i}{dt} &= \left(\frac{\vec{F}_i}{m_i} - \gamma \vec{v}_i\right) dt + \sigma d\vec{W}_i(t)
\end{align*}
\]

The \( d\vec{W}_i \) are Gaussian white noise processes, and their strength \( \sigma \) is related to the kinetic friction \( \gamma \) through the fluctuation-dissipation relation.\(^7\) When deriving integrators for these methods, one has to be careful to take into account the special character of the random forces employed in these simulations.\(^7\) A variant of the velocity Verlet method, including a stochastic dynamics treatment of constraints, can be found in Ref. 74. The stochastic
simulation methods introduce an additional, external dissipation mechanism into the simulation and that alters the native dynamics of the model system under study on time scales larger than the typical $1/\gamma$ time scale for this external dissipation mechanism.

This is also true for MD simulations in ensembles other than the microcanonical ensemble. The Nosé–Hoover method\(^{75,76}\) for MD simulations in the canonical ensemble introduces a time-dependent friction $\gamma_{NH}$ as an additional dynamical variable. Because its average value along the trajectory is small, $\langle \gamma_{NH} \rangle \ll 1$, it affects only very slow processes. This is not true, however, for MD simulations in the NpT ensemble, where the additional barostat dynamics\(^{77}\) strongly changes the intrinsic dynamics of the system. The safest approach is to work in the microcanonical ensemble, if possible. Starting from an equilibrated configuration, the MD method is used to generate a trajectory of the model system, and one typically stores configurations along the trajectory for a postsimulation analysis of the relaxation processes.

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**THERMODYNAMIC PROPERTIES**

In this section we will discuss two approaches commonly used by scientists to study the glass transition in polymers when they determine the temperature dependence of thermodynamic properties. These properties include the specific volume and the specific entropy. As discussed in the Introduction, the break in the temperature dependence of the specific volume served as one of the first experimental measures of the glass transition.\(^{4}\) In the experiment by Kovacs, a very careful study was performed of the cooling rate dependence of the glass transition temperature. The break in the temperature dependence of the specific volume signifies that the system’s internal relaxation times have reached the time scale of the experiment (inverse cooling rate), at which point, the system is no longer in equilibrium. With simulations one can also use the temperature dependence of other properties. These properties include the internal energy or the size of the polymer chains as determined from the radius of gyration of the chains,\(^{78}\) both of which are readily accessible via computation.

When using an atomic scale MD simulation of this cooling process, the integration time step $\delta t$ is typically as small as 1 fs ($10^{-15}$ s), and accordingly, even very long runs (on the order of $10^7$ or $10^8$ time steps) will not exceed a time interval of 100 ns. It is not even clear that on such short time scales the true physical traits of the glass transition can emerge fully. The “glass transition” that was claimed to be observed in an atomistic model for polyethylene chains from simulation time periods less than 1 ns\(^{79,80}\) implied that a freezing of individual jumps between the energy minima of the torsional potential of the chains took place, rather than a more collective behavior (“cooperatively rearranging units”\(^{81}\) that might occur in the system at somewhat lower
temperatures and on much longer time scales. Even if one takes the view that
the only influence the short-time window (ns) of MD simulation has is to shift
the apparent glass transition temperature $T_g$ (MD) upward in comparison
with that of experiment $T_g$ (expt), one still has to assess the amount of this
upward shift.

Practitioners of MD simulation studying glass forming fluids often
compare MD results on glass transition temperatures directly with experimen-
tal data,\textsuperscript{82–84} ignoring this systematic difference between $T_g$ (MD) and $T_g$
(expt). For “strong” glass formers such as molten SiO\textsubscript{2}, this issue has been
studied carefully.\textsuperscript{83} A very strong dependence of $T_g$ (MD) on the cooling
rate $\Gamma$ was found (which in the case of SiO\textsubscript{2} was in the range $10^{12}$ K/s $< \Gamma < 10^{15}$ K/s, which is many orders of magnitude higher than in the experi-
ments).\textsuperscript{86}) The computed $T_g$ (MD) differed from $T_g$ (expt) $\approx 1450$ K by
more than 1000 K! Because of the much steeper variation of the structural
relaxation time $\tau$ with $T$ near $T_g$ (expt), one does not expect such dramatic
effects for fragile glass formers like most polymers, and indeed for simul-
tations,\textsuperscript{82–84} it was found that $T_g$ (MD) agreed with $T_g$ (exp) reasonably well.

One reason for ignoring the cooling rate dependence of the simulated $T_g$
in these publications is because MD simulations of chemically realistic models
are generally too time consuming for a systematic study of different cooling
rates (for an exception, see Ref. 87), especially when one takes into account
that for each cooling rate one must average over several independent cooling
runs for each rate as will be described later. To evaluate cooling rate depen-
dence, one therefore best uses a coarse-grained model, as was done for the
bead-spring model suggested in Refs. 88 and 89. In the latter paper, the melt-
ing temperature of the bead-spring model was determined to be $T = 0.76$ in
Lennard–Jones units. Upon cooling at a fixed rate in a MD simulation at
constant temperature and pressure (NpT) employing a Nosé–Hoover thermo-
stat\textsuperscript{75,76} and an Andersen barostat,\textsuperscript{77} one observes the temperature-dependent
specific volumes shown in Figure 5. In the top panel, the temperature depen-
dence of the specific volume is shown for a cooling rate of $\Gamma = 52.083 \cdot 10^{-6}$.
Straight line fits in the melt and in the glassy phase assume a constant thermal
expansion coefficient in both phases. The intersection point between the
straight lines defines the glass transition temperature $T_g(\Gamma)$ for this cooling
rate. In the lower panel, the fit curves are shown for different cooling rates.
The melt curve does not depend on the cooling rate, but the glass curves
show a systematic shift, although, within the uncertainty of the data, the
slope of the curves (the thermal expansion coefficient) is independent of the
cooling rate also in the glass. It is obvious from the plot that only a small
(but systematic) variation in $T_g(\Gamma)$ exists in the range of cooling rates that
was accessible in the simulation ($3.3 \cdot 10^{-6} < \Gamma < 8.3 \cdot 10^{-4}$ in Lennard–Jones
units).

To interpret the cooling rate dependence of the glass transition tem-
perature, one can use the Vogel–Fulcher law discussed in the section on the
phenomenology of the glass transition. If one assumes that the break in the observed temperature dependencies occurs when the internal relaxation time is equal to the time scale of the cooling experiment $t_{\text{exp}}$, one obtains

$$t_{\text{exp}} = \tau_\infty \exp\{E_A/(T_g(\Gamma) - T_0)\}$$  \[27\]
In a stepwise cooling experiment, \( t_{\text{exp}} \) is equal to the time spent at every temperature step

\[
t_{\text{exp}} = \Delta T / \Gamma
\]

so that one obtains

\[
T_g(\Gamma) = T_0 - E_A / \ln(\Gamma \tau_\infty / \Delta T)
\]

Applying this prediction to the cooling rate dependence of a break points in the specific volume curves, one obtains a Vogel–Fulcher temperature of \( T_0 = 0.35 \) that agrees well with that determined from the temperature dependence of the diffusion constant in this model, which is \( T_0^D = 0.32 \).

From these results obtained from MD simulations with a coarse-grained model, the following picture emerges. When one cools down a model system in a computer simulation, the break in the temperature dependence of the specific volume indicates the temperature at which the time scale of those internal relaxation processes involved in volume relaxation equals the time scale of the cooling process. In strong glass formers, where the typical time scales at a high temperature increase in an Arrhenius fashion with an activation energy that is much higher than for the fragile glass formers, this means that the system falls out of equilibrium on the time scales accessible in an MD simulation at temperatures that are much higher than the experimental glass transition temperature and that consequently we obtain a very bad estimate for this temperature. For fragile glass formers, in contrast, the high-temperature increase of relaxation times is in general slow, thus often allowing the simulations to approach more closely to the experimental \( T_g \) before falling out of equilibrium. As a result, the glass transition temperatures can be in reasonable agreement with the experimental data. For polymers, where a larger high-temperature activation energy for volume relaxation exists, arising from a coupling to conformational rearrangements involving activated jumps over large dihedral barriers, for example, one anticipates the cooling method to be incapable of locating the experimentally relevant \( T_g \) on typical simulation time scales.

This reasoning also means that we were not really describing a thermodynamic measurement of the glass transition in a polymer melt but instead a macroscopic determination of the temperature dependence of volume-related internal relaxation processes, i.e., a dynamic measurement in the disguise of a thermodynamic measurement.

Let us now turn to a discussion of the relation of the temperature dependence of the polymer melt’s configurational entropy with its glass transition and address the famous paradox of the Kauzmann temperature of glass-forming systems.\(^{90}\) It had been found experimentally that the excess entropy of super-cooled liquids, compared with the crystalline state, seemed
to vanish when extrapolated to low temperatures. The extrapolated temperature of vanishing excess entropy, the so-called Kauzmann temperature \( T_K \), is generally in close agreement with the extrapolated Vogel–Fulcher temperature \( T_0 \) derived from the temperature dependence of relaxation times. A theoretical derivation of the Kauzmann temperature for polymeric glass formers was given by Gibbs and Di Marzio.\(^9^1\) Consider the canonical partition function of \( K \) polymer chains of chain length \( N \) in a volume \( V \),

\[
Z = \sum_E \Omega(E, K, N, V) \exp(-E/k_BT) \tag{30}
\]

where \( E \) is the internal energy of the system and \( \Omega \) is the microcanonical partition function (i.e., the total number of states). For simplicity, a lattice with \( M \) sites is considered with

\[
M = \frac{L^3}{8} = (KN + H) \tag{31}
\]

with \( H \) being the number of vacant sites (holes). Equation [31] is valid for a simulation of the glass transition in the bond-fluctuation lattice model where each repeat unit occupies the eight lattice vertices of a unit cube. The glass transition in this model was studied by employing a Hamiltonian that singled out the bonds of the class \([3,0,0]\) giving them zero energy\(^9^2\)

\[
\mathcal{H} = \begin{cases} 0 & \text{if } b \in [3, 0, 0] \\ \epsilon & \text{otherwise} \end{cases} \tag{32}
\]

The entropy density \( s \) is then

\[
s = \frac{(\ln \Omega)}{M} \tag{33}
\]

In the thermodynamic limit \( M \to \infty \), one can consider \( s = s(e, \rho) \), where \( e = E/M \) is the internal energy per lattice site and \( \rho = KN/M \) is the monomer density. We can also do this as a function of temperature because \( e \) can be replaced by \( T \) via the appropriate Legendre transformation.

Variants of an approximate calculation of the configurational entropy of lattice chains have been developed by Flory,\(^9^3\) Gibbs and Di Marzio,\(^9^1\) and Milchev.\(^9^4\) All three treatments write \( \Omega \) as a product of an intrachain (\( \Omega_{\text{intra}} \)) contribution and an interchain (\( \Omega_{\text{inter}} \)) contribution

\[
\Omega = \Omega_{\text{intra}} \Omega_{\text{inter}} \tag{34}
\]

In Flory’s original treatment, \( \Omega_{\text{intra}} \) accounts for the increase of the chain stiffness when the temperature is lowered. Flory\(^9^3\) described this chain stiffening by
an energy $\varepsilon$ if two consecutive bonds along a chain are not collinear, whereas no energy is assigned if they are collinear. In essence, this calculation relies on the fact that one has a two-level system for the internal degrees of freedom as was realized in the choice of Hamiltonian in Eq. [32].

If we denote by $f$ the probability of finding a bond in the excited state, we get for the intramolecular part of the partition function, neglecting excluded volume effects but assuming a nonreversal random walk, Eq. [35]

$$
\Omega_{\text{intra}} = \left( \frac{K(N - 1)}{fK(N - 1)} \right) \left( 1 - f \right)^{K(N - 1)} \left( \frac{z - 2}{z - 1} \right)^{fK(N - 1)}
$$ [35]

where $z$ is an effective coordination number in the melt. The last term in this equation is obviously correct for the original Flory model where $z - 1$ possibilities exist for the next bond, only one of which is straight and does not carry an energy penalty. For the bond-fluctuation model with the Hamiltonian given by Eq. [32], 1 in 12 bonds does not carry an energy penalty. Furthermore, the effective coordination number in the melt is around 12, so again one can assume that one of the $z - 1$ neighbor bonds is in the ground state.

The treatments of Flory, Gibbs and Di Marzio, and Milchev differ in the way they calculate the second factor $\Omega_{\text{inter}}$. This microcanonical partition function describes the number of ways in which the $K$ chains can be put on the lattice,

$$
\Omega_{\text{inter}} = 2^{-K(1/K!)} \prod_{k=0}^{K-1} v_{k+1}
$$ [36]

with $v_{k+1}$ being the total number of configurations of the $(k + 1)$th chain if there are already $k$ chains on the lattice that can be approximated by

$$
v_{k+1} \approx (M - kN) N_{\text{empty}}^{N-1} z(z - 1)^{N-2}
$$ [37]

Here, $M - kN$ is the number of empty sites after $k$ chains have been placed on the lattice and constitutes the number of potential starting points for the $(k + 1)$th chain. The factor $z(z - 1)^{N-2}$ represents the number of possibilities to place the remaining $N - 1$ monomers of the chain after the first monomer has been placed, forbidding only the immediate back-folding of the walk. The factor $N_{\text{empty}}^{N-1}$, which for the bond-fluctuation model counts the number of empty unit cubes, accounts approximately for the chains being self-avoiding and mutually avoiding and is approximated in the three approaches as in Eqs. [38]–[40]:

$$
N_{\text{empty}} = 1 - kN/M \quad \text{(Flory)}
$$ [38]
or
\[
N_{\text{empty}} = \frac{(1 - kN/M)}{(1 - k(N - 1)Mz/2)} \quad \text{(Gibbs–DiMarzio) [39]}
\]
or
\[
N_{\text{empty}} = \frac{(1 - kN/M)}{(1 - k/K)} \quad \text{(Milchev) [40]}
\]

The idea behind these corrections is to recognize that not all empty lattice sites can serve as starting points for the new polymer; only those lying outside of the volume already consumed by the other \(k\) chains can be used. Unfortunately, neither Eq. [37] nor the expressions for \(N_{\text{empty}}\) can be justified with mathematical rigor. For both the Flory\(^93\) and the Gibbs and Di Marzio\(^91\) approximations, the entropy at low temperatures is negative (in the limit \(N \to \infty\) and \(\rho \to 1\))

\[
s(T \to 0) = -1 \quad \text{(Flory) [41]}
\]

\[
s(T \to 0) = \left(\frac{Z}{2} - 1\right) \ln \left(1 - \frac{2}{z}\right) < 0 \quad \text{(Gibbs–Di Marzio) [42]}
\]

whereas Milchev’s\(^94\) entropy remains non-negative \((s(T \to 0) = 0)\). A comprehensive account of these different mean-field-like theories has been given by Wittmann.\(^95\)

To test these theoretical approaches in a computer simulation, one needs to proceed in several steps. In the first step, one determines the entropy per monomer in the simulation by measuring the energy per monomer \(e(\rho, T)\) and by calculating the free energy per monomer through thermodynamic integration of the excess chemical potential\(^96\)

\[
s(\rho, T) = \frac{e(\rho, T)}{T} - \frac{\rho}{N} \ln \left(\frac{N}{\rho} - 1 - \ln \frac{Z_\rho(N, T)}{N}\right) - \frac{1}{N} \int_0^\rho \mu_{\text{ex}}(\rho', T) d\rho' \quad [43]
\]

where \(Z_\rho(N, T)\) is the partition function of a single chain of length \(N\). The excess chemical potential can be measured according to

\[
\mu_{\text{ex}}(\rho, T) = -T \ln p_{\text{ins}}(\rho, T) \quad [44]
\]

by evaluating the insertion probability for a chain of length \(N\) into a solution at density \(\rho\).\(^97,98\) In the second step, one measures the fraction of bonds in the excited state \(f\), the effective coordination number \(z\) (the number of monomers around a given monomer in the melt that are within a distance given by the maximum bond length), and the number of holes \(H\) (the fraction of the empty lattice sites where one can put another monomer of the bond-fluctuation model)
and inserts these temperature-dependent quantities into Eqs. [38]–[40] for the specific entropy. A comparison between the three theories and computer simulation is shown in Figure 6.

The theories of Flory and Gibss–Di Marzio result in practically identical predictions, both leading to a Kauzmann paradox (negative excess entropy) around $T = 0.18$, which is a temperature in the vicinity of the Vogel–Fulcher temperature, $T_0 \sim 0.13$, determined for this model. Both theories, however, strongly underestimate the value of the configurational entropy, which is always positive. The reason is that an underestimation of the intermolecular part of the partition function exists. This underestimation can be observed when comparing the behavior at $1/T = 0$ with the simulation data and with the results of Milchev’s theory, which agrees more closely with the simulation data and stays positive throughout the whole temperature range. All theories reproduce the shape of the simulated curve reasonably well, which explains why the Gibbs–Di Marzio theory is so successful in predicting experimental results on the glass transition in polymer melts that depend only on derivatives of the specific entropy. From the simulations we conclude, however, that the Kauzmann paradox of vanishing excess entropy is an extrapolation artifact and that the theoretical descriptions reproducing this finding are based on inappropriate approximations. These studies therefore have not revealed any evidence for a phase transition underlying the glass transition in polymer melts.

The strong reduction in specific entropy that is observable in experiment as well as in simulation, i.e., the reduction in configuration space available to

Figure 6 Entropy per monomer in the bond-fluctuation model as a function of inverse temperature. The results from the simulation (filled circles) are compared with the theoretical predictions discussed in the text.
the chains in the melt, has been linked by Adam and Gibbs [81] to the slowing down of the dynamics of the system. In the Adam–Gibbs theory, the center of mass self-diffusion coefficient of the chains is related to the entropy by

$$D(T) = D(\infty) \exp\left\{ -\frac{A}{TS(T)} \right\}$$

[45]

Using the specific entropy determined in the simulations, one can test this theoretical approach by fitting this expression to the temperature dependence of $D$ observed in the simulations. It has been concluded that the Adam–Gibbs theory cannot predict the temperature dependence of the dynamics from the thermodynamic information contained in the temperature dependence of the entropy.92

In the next sections we will focus on analyzing the dynamics of supercooled liquids in more detail and discuss our findings in terms of the mode-coupling theory of the glass transition, which is a liquid state theory that predicts the dynamics from the structural properties of the liquid.

**DYNAMICS IN SUPER-COOLED POLYMER MELTS**

It is not easy to obtain a crystalline polymeric material. In order to crystallize, a homopolymer chain built of simple regular building blocks like, e.g., a bead-spring polymer model, can arrange the beads on some regular cubic lattice and have the chains run along one of the lattice directions.89 To do this, the bead-spring chain must change its random-coil-like state into a stretched out state. In real polymer chains, the repeat units will attempt to obtain locally ground state conformations given by the dihedral conformer energies. These conformers may result in non-space-filling structures. Additionally there is polydispersity or chemical randomness, as in the 1,4-polybutadiene (PB) example that we will be discuss in the section on “Dynamics in 1,4-Polybutadiene.”

Polymers, therefore, in principle, should be good candidates for (quasi-)equilibrium theories of super-cooled liquids. A liquid state theory that can describe the onset of slowdown in super-cooled liquids successfully is the mode coupling theory (MCT).99–101 It is a microscopic approach to the glass transition starting from the observation of the freezing-in of the structural relaxation in the glass transition. The theory assumes density fluctuations to be the dominating slow variables in glass-forming systems. Although the theory was formulated originally for simple (monatomic) fluids only, it is believed to be of much wider applicability and it has been applied to interpret experiments on the polymer glass transition.

Starting from the Liouville equation as the fundamental microscopic evolution equation for the dynamics of all phase-space variables, MCT uses
well-established projection operator techniques that are used for eliminating the fast variables to arrive at an equation for the correlation functions of density fluctuations in Fourier space, i.e., the intermediate scattering functions.

\[
\frac{\partial^2}{\partial t^2}S(q, t) + \Omega_q^2 S(q, t) + \zeta_q \frac{\partial}{\partial t} S(q, t) + \Omega_q^2 \int_0^t m_q(t - t') \frac{\partial}{\partial t'} S(q, t') dt' = 0 \quad [46]
\]

In this generalized oscillator equation, the frequency \(\Omega_q\) is related to the restoring force acting on a particle and \(\zeta_q\) is a friction constant. The key quantity of the theory is the memory kernel \(m_q(t - t')\), which involves higher order correlation functions and hence needs to be approximated. The memory kernel is expanded as a power series in terms of \(S(q, t)\)

\[
m_q(t) = \sum_{i=1}^{i_0} \frac{1}{i!} \sum_{k_1...k_i} V^{(i)}(q, k_1, \ldots, k_i) S(k_1, t) \ldots S(k_i, t) \quad [47]
\]

The coefficients \(V^{(i)}\) of this mode-coupling functional are the basic control parameters of this idealized version of MCT. One sees that Eqs. [46] and [47] amount to a set of nonlinear equations for the correlators \(S(q, t)\) that must be solved self-consistently.

The basic qualitative prediction of MCT is that, upon lowering the temperature or increasing the density of a melt, one observes a separation of time scales between the microscopic dynamics and the structural relaxation leading to a two-step decay of all relaxation functions. One imagines the molecules to be trapped within a cage formed by their neighbors for some time span between the short time dynamics and the large-scale structural relaxation that comes about when particles leave their cages. The long-time behavior is the structural (or \(\alpha\)-) relaxation and the plateau regime occuring between vibrational dynamics, and this \(\alpha\)-relaxation is termed the \(\beta\)-regime in the theory. For a well-developed intermediate plateau regime between microscopic and structural relaxation, MCT predicts solutions of the type

\[
S(q, t) = f_q^c + h_q G(t/t_0, \sigma) \quad [48]
\]

in a time window \(t_0 \ll t \ll t'_\sigma\), where \(f_q^c\) is the nonergodicity parameter, \(h_q\) is some wave-vector dependent amplitude, \(G\) is a \(q\)-independent scaling function of time, and \(t_0\) is the microscopic scale. The separation parameter \(\sigma \propto 1 - \frac{T}{T_c}\) measures the distance from the singularity representing the “ideal” glass transition. For \(\sigma \geq 0\), one has

\[
\lim_{t \to \infty} S(q, t) = f_q^c + h_q \sqrt{\sigma/(1 - \lambda)} + O(\sigma) \quad [49]
\]
where the parameter $\lambda (\lambda < 1)$ is called the “exponent parameter.” For $\sigma < 0$, on the other hand, one has $\lim_{t \to -\infty} \phi_q(t) = 0$. For $\sigma \to 0$, the function $G(t/t_0, \sigma)$ can be linked to a universal correlation function $g_{\pm}(t/t_\sigma)$, where “+” indicates $\sigma > 0$ and “−” indicates $\sigma < 0$

$$G(t/t_0, \sigma) = |\sigma|^{1/2} g_{\pm}(t/t_\sigma), \quad \sigma > 0(< 0)$$ [50]

where

$$t_\sigma = t_0 |\sigma|^{-1/2a}$$ [51]

and the exponent $a$ is related to $\lambda$ by

$$\lambda = [\Gamma(1-a)]^2/\Gamma(1-2a)$$ [52]

For short times, one has a power law decay

$$g_{\pm}(t/t_\sigma) = \frac{t}{t_\sigma}^{-a} \pm A_1 \frac{t}{t_\sigma}^a + \ldots$$ [53]

where $A_1$ is some amplitude. For large $t/t_\sigma$, $g_{+}(t/t_\sigma \to \infty) = 1/\sqrt{1-\lambda}$, consistent with Eq. [49], the correlator approaches structural arrest. The liquid phase solution, on the other hand, exhibits another power law, the so-called von Schweidler law,

$$g_{-}\left(\frac{t}{t_\sigma}\right) = -B \frac{t}{t_\sigma}^b, \quad \left(\frac{t}{t_\sigma} \gg 1\right)$$ [54]

where $B$ is another amplitude, and the von Schweidler exponent $b$ is related to $\lambda$ as

$$[\Gamma(1+b)]^2/\Gamma(1+2b) = \lambda$$ [55]

One can rewrite the von Schweidler law using Eqs. [48], [50]–[52], [54], and [55] as follows:

$$S(q, t) = f_q c - h_q B(t/t'_\sigma)^b$$ [56]

where $t'_\sigma$ is a characteristic time scale that diverges as the ideal glass transition is approached from above,

$$t'_\sigma = t_0 |\sigma|^{-\gamma}, \quad \gamma = 1/(2a) + 1/(2b)$$ [57]
This time \( t'_\sigma \) actually is the maximum time for which Eq. [48] is valid, \( t_0 \ll t \ll t'_\sigma \). The exponent \( \gamma \) characterizes the behavior of the \( \alpha \)-relaxation or structural relaxation. Typical \( \alpha \) time scales diverge as

\[
\tau_\alpha \sim (T - T_c)^{-\gamma}
\]

As indicated, the power law approximations to the \( \beta \)-correlator described above are only valid asymptotically for \( \sigma \to 0 \), but corrections to these predictions have been worked out.\(^{102,103}\) More important, however, is the assumption of the idealized MCT that density fluctuations are the only slow variables. This assumption breaks down close to \( T_c \). The MCT has been augmented by coupling to mass currents, which are sometimes termed “inclusion of hopping processes,” but the extension of the theory to temperatures below \( T_c \) or even down to \( T_g \) has not yet been successful.\(^{101}\) Also, the theory is often not applied to experimental density fluctuations directly (observed by neutron scattering) but instead to dielectric relaxation or to NMR experiments. These latter techniques probe reorientational motion of anisotropic molecules, whereas the MCT equation describes a scalar quantity. Using MCT results to compare with dielectric or NMR experiments thus forces one to assume a direct coupling of orientational correlations with density fluctuations exists. The different orientational correlation functions and the question to what extent they directly couple to the density fluctuations have been considered in extensions to the standard MCT picture.\(^{104-108}\)

Of the available experimental techniques, the various neutron scattering methods most directly measure structural relaxation. Like simulation techniques, however, their dynamic range is limited and several experimental setups have to be combined to obtain information on polymer relaxation from the picosecond scale up to the longest time accessible in neutron spin echo experiments (~ 100 ns depending on momentum transfer), with all the experimental correction and normalization issues involved in matching results from different experiments. To our knowledge, the reconstruction of a single relaxation curve \( S(q,t) \) out of experimental information for the different frequency and time windows has not yet been tried. Therefore, simulation studies of the glass transition still provide us with the most detailed information of the structural relaxation processes.\(^{109}\)

Before we examine in more detail the dynamics of a super-cooled melt of coarse-grained chains and of PB chains, respectively, let us first compare the structure of these two glass-forming systems. Structure is obtained experimentally from either the neutron or the X-ray structure factors. The melt (or liquid) structure factor is given as\(^{110}\)

\[
S_m(q) = \frac{1}{M} \sum_{n,m}^M b_n(q)b_m(q)\langle e^{i\vec{q} \cdot (\vec{r}_n - \vec{r}_m)} \rangle
\]
Here the angular brackets indicate thermal as well as isotropic averages, and the sum runs over all \( M \) scattering centers in the melt. The quantities \( b_n(q) \) are the scattering form factors of the different scatterers in the sample. For X-ray scattering, momentum transfer (\( q \)) dependence of the form factor of the electronic clouds must be taken into account. For neutron scattering, the form factors reduce to \( q \)-independent scattering lengths, \( b_n(q) = b_n \). Neutron scattering studies of the melt structure are typically performed on perdeuterated samples, i.e., where all H atoms have been replaced by D atoms, because for deuterium and carbon atoms, coherent scattering dominates (they have about the same coherent scattering lengths), whereas hydrogen atoms scatter neutrons incoherently. X-ray scattering is most sensitive to the positional correlations of the heavy atoms in the sample with their large associated electron clouds.

Performing neutron scattering not on perdeuterated samples but on a single deuterated chain in a protonated matrix (or vice versa; both ways provide the same contrast) gives the single-chain structure factor,

\[
S_{\text{ch}}(q) = \frac{1}{N} \sum_{n,m} b_n b_m \langle e^{i \tilde{q} \cdot (\tilde{r}_n - \tilde{r}_m)} \rangle
\]  

where now the sum runs only over all monomers of a single chain.

When we think of simulations involving bead-spring models, all scatterers can be assigned the same scattering lengths [that are absorbed into arbitrary units for \( S(q) \)], and for united atom models like the one used for PB, we can consider scattering from the united atoms in the same way. This simplifies the scattering functions of Eqs. [59] and [60] to be

\[
S_{\text{m}}(q) = \frac{1}{M} \sum_{n,m} \langle e^{i \tilde{q} \cdot (\tilde{r}_n - \tilde{r}_m)} \rangle
\]  

and

\[
S_{\text{ch}}(q) = \frac{1}{N} \sum_{n,m} \langle e^{i \tilde{q} \cdot (\tilde{r}_n - \tilde{r}_m)} \rangle
\]

The structure factors are Fourier transforms of radial pair-distribution functions for the complete melt or the single chain, respectively,

\[
S_{\text{m}}(q) = 1 + 4\pi \rho \int_0^\infty r^2 g_m(r) \frac{\sin(qr)}{qr} \, dr
\]  

\[
S_{\text{ch}}(q) = 1 + 4\pi (N - 1) \int_0^\infty r^2 g_{\text{ch}}(r) \frac{\sin(qr)}{qr} \, dr
\]
where we already performed the angular average. The pair-distribution functions $g_m(r)$ and $g_{ch}(r)$ measure structural correlations directly in real space and are, of course, also observables in the simulations.

We show typical examples for the melt structure factor and for the single-chain structure factor in Figure 7. The upper panel is for a chemically realistic simulation of PB,\textsuperscript{111} where the scattering was calculated with the
united atoms as scattering centers of unit scattering length. The lower panel is for a simulation of a bead-spring model.\textsuperscript{88} Recall that the first maximum in the melt structure factor is called the first sharp diffraction peak or amorphous halo. The position of the amorphous halo for the PB simulation agrees well with experimental data.\textsuperscript{112,113}

We can see from Figure 7 that for momentum transfers larger than about 3 A\textdegree\textdegree in PB, i.e., starting around the second maximum, one observes only intramolecular correlations in the melt structure factor\textsuperscript{112–114} when one considers only scattering from the united atom centers. The melt structure factor can always be decomposed into a chain contribution ($S_{ch}(q)$) and a contribution that captures the correlations between distinct melt chains ($S_{md}(q)$).

$$S_m(q) = S_{ch}(q) + S_{md}(q)$$  \[65\]

where

$$S_{md}(q) = 4\pi\rho \int_0^\infty r^2(g_{md}(r) - 1) \frac{\sin(qr)}{qr} dr$$  \[66\]

contains only scattering contributions from scattering centers belonging to different chains ($g_{md}(r)$ is the pair correlation function for atoms belonging to different chains). Intermolecular scattering is responsible for only half of the intensity of the first sharp diffraction peak. For the intermolecular contribution to the scattering, the position of the amorphous halo is given approximately by $2\pi/d$, where $d$ is the typical intermolecular distance between scattering centers.

The behavior of the bead-spring model is different from that of PB. The melt structure factor and the single-chain structure factor depicted in Figure 7 only start to agree at the third peak in the melt structure factor. For smaller momentum transfer, they oscillate with the same wavelength but with a phase shift. The intramolecular structure factor has a minimum preceding the amorphous halo and a maximum shifted slightly with respect to, but still within, the amorphous halo. For the chemically realistic united atom chain, we observe a shoulder in the intramolecular structure factor at the position of the amorphous halo and a first minimum where the melt structure factor also has its first minimum. The shoulder tells us that an intramolecular correlation exists in the PB chain on a scale given by the typical intermolecular distance of about 4–5 A, which agrees with the size of a repeat unit comprising the chain. Pictorially, one can think of the bead-spring chain having the local structure of a pearl necklace with the beads touching each other, whereas the PB chain consists of overlapping spheres with a distance between their centers that is roughly a third of their diameter. The local packing in a hydrocarbon melt like PB, therefore, resembles more the packing of spaghetti than of billiard balls.
This specific local packing can give rise to scattering behavior that might be puzzling at first glance. When one imagines the packing in a polymer melt to be that of billiard balls, one would predict that upon increasing the pressure a better defined packing will result in sharper radial distribution functions and, consequently, in a sharpening and increase in height of the amorphous halo. Moreover, that halo would move to large $q$ because of the overall compression of the melt. However, a series of experiments on the structure and dynamics of polymers under pressure\textsuperscript{115–118} has been reported, showing a very different behavior of the first sharp diffraction peak: It shifted to larger momentum transfer values as expected, but it simultaneously broadened and decreased in height. This behavior has been reproduced in a simulation of a chemically realistic model of PB\textsuperscript{119} under pressure as shown in Figure 8.

To understand the experimental behavior of PB, one has to take into account the fact that the scattering was performed on a perdeuterated sample and that carbon and deuterium have about the same coherent scattering length. Therefore, instead of having one melt structure factor one must actually consider three partial structure factors, $S_{CC}$, $S_{DD}$, and $S_{CD}$, that are weighted by the appropriate combination of scattering lengths (see Ref. 110). The partial structure factor $S_{CC}$ is the one we used in Figure 7. To calculate the structure factor shown in Figure 8, in contrast, we used the trick of

![Figure 8](image_url)

Figure 8 Behavior of the first sharp diffraction peak of PB with experimental scattering lengths for carbon and deuterium. The deuterium atoms are placed at their mechanical equilibrium positions determined by the positions of the united atom centers and the equilibrium CH bond length and HCH and HCC bond angles along a united atom MD trajectory. With increasing pressure (values given in the legend, simulation performed at $T = 293$ K), the first sharp diffraction peak shifts to larger $q$ as expected but unexpectedly decreases in height.
reinserting deuterium atoms into a time series of stored united atom configurations that have been sampled along the MD trajectory. By knowing the equilibrium CH bond length and the equilibrium HCH and HCC bond angles, the hydrogen (deuterium) positions can be uniquely determined from the backbone configuration of the united atom polymer chain.\textsuperscript{120,121}

Knowing all the partial structure factors, we can conclude that the unexpected behavior of the scattering function has been induced by the $q$-dependence of the carbon-deuterium cross correlations (which contribute positively when the amorphous halo is located at smaller momentum transfers but negatively at larger ones) and by a different $q$-dependence of intramolecular and intermolecular contributions.\textsuperscript{119} We caution the reader to be careful with the interpretation of experimental structure factors, and not just for polymers. Given the same molecular packing, neutron scattering on a perdeuterated sample, on a partially deuterated sample, or on a protonated sample and X-ray scattering may yield different experimental structure factors. On the other hand, careful analysis of results obtained from different scattering techniques and/or isotopic substitution can offer a way to glean information on partial structure factors from experiment.

We now turn to a characterization of the dynamics in a polymer melt where, as it is supercooled, it approaches its glass transition temperature. We begin by looking at the translational dynamics in a bead-spring model and consider its analysis in terms of MCT.

**DYNAMICS IN THE BEAD-SPRING MODEL**

Early simulation studies on the structural aspects of the glass transition in polymer melts were performed using the simple bond-fluctuation lattice model.\textsuperscript{122–125} The missing inertial regime of the short-time dynamics and the discreteness of the lattice, however, limited the information that one could obtain on structural relaxation using this model. The next simplest polymer models are hard-sphere chains, studied by Rosche et al.\textsuperscript{126} using MC simulations, and the bead-spring off-lattice model that was studied along an isobar using MD simulations in an NVT ensemble\textsuperscript{88} (see also Refs. 127 and 128 for reviews). Using MD as the simulation method has the advantage of capturing the short-time vibrational dynamics when compared with MC simulations.

Our analysis of the melt dynamics begins by looking at large length and long time scales where we can assess the temperature dependence of the center of mass self-diffusion coefficient of the chains. This self-diffusion is measured in the simulations by monitoring the average mean-squared center of mass displacement of all chains and then employing the Einstein relation

\[
D(T) = \lim_{t \to \infty} \frac{\langle (\vec{R}_{cm}(t) - \vec{R}_{cm}(0))^2 \rangle}{6t}
\]

[67]
For a polymer chain, the long time limit in Eq. [67] means that one has to be able to simulate the model system for times on the order of several Rouse times or, to put it in another way, enough time for the chains to diffuse over a spatial range a few times their size. This simulation is possible for a bead-spring model down to rather low temperatures, but for a chemically realistic model with reasonably long chains, one typically cannot perform such lengthy simulations. Upon super-cooling the bead-spring melts below its crystallization temperature (which is $T = 0.76$, see the section on thermodynamic properties), and a large decrease in the self-diffusion coefficient is observed (see Figure 9). The temperature dependence below $T = 1$ is compatible with a Vogel–Fulcher law with a seemingly vanishing self-diffusion coefficient at $T_0 = 0.32 \pm 0.02$. Note, however, that even for this coarse-grained model, which is much easier to simulate than chemically realistic models, the information on the chain center of mass diffusion derived from the simulation in a (meta-)stable equilibrium is limited to temperatures above approximately $1.44 T_0$, which makes the deduction of $T_0$ from these data a risky extrapolation. We will comment on the MCT fits in this figure later in this chapter.

No crystalline order is visible for the bead-spring model upon cooling to the frozen-in phase at $T = 0.3$. The break in the volume-temperature curve (described in the section on thermodynamic information) occurring between $T = 0.4$ and $T = 0.45$ leads us to expect that the two-step decay described by MCT should be observable at simulation temperatures above (and close to) this region. This expectation is borne out in Figure 10, which shows the

![Figure 9](image_url)  
**Figure 9** Chain center of mass self-diffusion coefficient for the bead-spring model as a function of temperature (open circles). The full line is a fit with the Vogel–Fulcher law in Eq. [3]. The dashed and dotted lines are two fits with a power-law divergence at the mode-coupling critical temperature.
intermediate incoherent scattering function in the bead-spring model for several values of momentum transfer at $T = 0.48$. The basic length scale of MCT is the intermolecular distance as given by the position of the amorphous halo, which is $q = 6.9$ for the bead-spring model. For $q \geq 6.9$, we see a well-developed plateau regime in the figure. The amount of decorrelation on the microscopic time scale increases with $q$. Also indicated in the figure is the time scale $t_\sigma$ derived from an application of the MCT predictions (Eq. [51]) for the $\beta$-relaxation regime.

The time scale $t_\sigma$ and the amplitudes $h_q$ from Eq. [56] are predicted by MCT to show a power law dependence on $T - T_c$. When one plots $t_\sigma$ and the amplitudes $h_q$ taken to the inverse of the predicted exponent versus temperature, one can directly find the critical temperature of MCT, $T = 0.45$, as shown in Figure 11. From the MCT analysis in the $\beta$-regime, one also obtains the von Schweidler exponent, $b = 0.75$, and therefore all other exponents through Eqs. [52], [55], and [57]. Another test of MCT, which is suggested by the form of Eq. (56), is to plot the ratio

$$R(t) = \frac{\phi_q(t) - \phi_q(t')}{\phi_q(t'') - \phi_q(t')}$$

where all times $t, t', t''$ are within the plateau region ($\beta$-regime, see Figure 12). It follows from Eq. [56] that the function $R(t)$ defined in this way has to be independent of the correlation function that one studies. This so-called factorization theorem, i.e., Eq. [68], has been tested in detail for the
bead-spring model\textsuperscript{132,133} and shown to be valid for many correlators, including coherent as well as incoherent scattering and the Rouse modes.

The von Schweidler exponent, $b = 0.75$, obtained from the $\beta$-relaxation determines the exponent for the $\alpha$-relaxation to be $\gamma = 2.09$. This exponent should be observable in the temperature dependence of the self-diffusion coefficient shown in Figure 9. The dashed line in this figure is a fit with fixed values of $T_c = 0.45$ and $\gamma = 2.09$ as determined from the $\beta$-relaxation analysis; the dotted line is the best fit at fixed $T_c$. The quality of the fit can be improved if one allows the exponent to differ from the prediction based on the $\beta$-relaxation behavior. Actually, a systematic decrease of the best-fit value for the exponent in the $\alpha$-relaxation temperature dependence with increasing length scale was observed.\textsuperscript{134} The $\alpha$ time scale is also the time scale of the final decay in the scattering functions $S(q, t)$, be it coherent or incoherent scattering. This time scale is typically obtained by fitting a KWW (Eq. [9]) time dependence to the final decay of the correlators. In a finite temperature regime above $T_c$, the stretching exponent $\beta$ of the KWW functions is independent of temperature. In this temperature range, $\beta$ is momentum transfer dependent with values between 0.65 and 0.75 and approaching the value of the von Schweidler exponent for $q \to \infty$. In the temperature window with constant $\beta$, the time-temperature superposition principle, which is often used to reconstruct complete time-dependent curves from experimental measurements at different temperatures, is valid. The physical interpretation of the time-temperature superposition is that molecular

Figure 11 MCT $\beta$-scaling for the amplitudes of the von Schweidler laws fitting the plateau decay in the incoherent intermediate scattering function for a $q$-value smaller than the position of the amorphous halo, $q = 3.0$, at the amorphous halo, $q = 6.9$, and at the first minimum, $q = 9.5$. Also shown with filled squares is the $\beta$ time scale. All quantities are taken to the inverse power of their predicted temperature dependence such that linear laws intersecting the abscissa at $T_c$ should result.
relaxation mechanisms are the same within this temperature window. This is generally valid only over limited temperature ranges.

The structural relaxation time scale, however, also determines relaxation processes on large length scales like, for example, the decay of the Rouse modes.\textsuperscript{135,136} In Figure 13 we can see that the time scales of the first five Rouse modes follow the predicted $\alpha$-scaling of relaxation times over a certain temperature window above $T_c$. When one comes too close to $T_c$, the system does not actually freeze. Instead, other relaxation processes not considered in the idealized MCT take over. The glassy freezing therefore enters into the Rouse picture only through the temperature dependence of the segmental friction $\zeta(T)$, following the temperature dependence of the $\alpha$-relaxation time scale.

One also finds that the value of the $\alpha$-exponent (and consequently all other exponents) does not depend on the thermodynamic path one follows to reach the state-point given by $(T_c, \rho_c)$,\textsuperscript{134} which conforms to another prediction by MCT. In summary, MCT has been found to be consistently applicable to the glassy slowdown in the bead-spring polymer model over a narrow range of temperature above $T_c$. What is the reason underlying the applicability of MCT, considering the fact that the theory was developed for simple liquids and has no connectivity built in? The physics behind the success of MCT in describing the slowdown in bead-spring melts becomes clear when we look at the mean-square displacement master curve. This curve is obtained

\textbf{Figure 12} Test of the factorization theorem of MCT for the intermediate coherent scattering function for the bead-spring model and a range of $q$-values indicated in the Figure. Data taken from Ref. 132 with permission.
by plotting the displacements at all simulated temperatures against $D(T)t$, where $D(T)$ is the chain center of a mass diffusion coefficient at a given temperature, as shown in Figure 14. Also shown in the figure is the same master curve constructed for a binary Lennard–Jones fluid. For $t \to \infty$, the data for

Figure 13 Temperature dependence of the time scales for the first five Rouse modes in the bead-spring model in the vicinity of the MCT $T_c$.

Figure 14 Master curve generated from mean-square displacements at different temperatures, plotting them against the diffusion coefficient at that temperature times time. Shown are only the envelopes of this procedure for the monomer displacement in the bead-spring model and for the atom displacement in a binary Lennard–Jones mixture. Also indicated are the long-time Fickian diffusion limit, the Rouse-like subdiffusive regime for the bead-spring model ($\sim t^{0.63}$), the MCT von Schweidler description of the plateau regime, and typical length scales $R_g^2$ and $R_e^2$ of the bead-spring model.
the two models must agree by construction. At very early times, the particles move freely, and both models exhibit ballistic motion, followed by the slow displacement characteristic for the $\beta$-process of MCT. However, where the Lennard–Jones fluid directly crosses over from the cage effect to the free diffusion, the polymer exhibits an intervening connectivity-dominated regime for length scales between the bond length, $l = 1$, and the end-to-end distance. In this regime, the observed mean-square displacement increases less quickly ($\sim t^{0.63}$) than it does in the MCT description, which is here displayed as the effective von Schweidler law

$$g_1(t) = 6r_{sc}^2 + A_1(Dt)^{0.75}, \quad (r_{sc} = 0.087, A_1 = 11.86)$$

before free diffusion sets in. This difference from simple liquids, i.e., the crossover to Rouse-like motion, has recently been included in mode coupling theory.\(^ {138,139}\)

Furthermore, it is important to note that the values of the plateau displacement in the bead-spring model as well as in the Lennard–Jones liquid model are well below one. For the Lennard–Jones liquid, this is the scale of the intermolecular packing $\sigma = 1$, but for the bead-spring polymer, this is also the scale of the bond-length $l \sim \sigma = 1$. The packing constraints thus act on a length scale much smaller than the bond length in this polymer model; i.e., the monomers are caged before they actually feel that they are bonded along the chain. This might also explain why both models have very similar critical temperatures ($T_c = 0.45$ for the bead-spring model vs. $T_c = 0.435$ for the LJ mixture).

As we discussed in the section on the structural properties of amorphous polymers, the relative size of the bond length and the Lennard–Jones scale is very different when comparing coarse-grained models with real polymers or chemically realistic models, which leads to observable differences in the packing. Furthermore, the dynamics in real polymer melts is, to a large extent, determined by the presence of dihedral angle barriers that inhibit free rotation. We will examine the consequences of these differences for the glass transition in the next section.

**DYNAMICS IN 1,4-POLYBUTADIENE**

Structural relaxation in glass-forming polymers has been studied for many years using chemically realistic simulations. Most of the early work that examined incoherent, as well as coherent scattering functions, is more of a qualitative nature because of the unsatisfactory quality of the force fields employed and the severe limitations on the length of the MD simulations performed. Roe studied the slowdown of structural relaxation in a PE-like model\(^ {140,141}\) as well as for polystyrene.\(^ {142}\) More recently Okada et al.\(^ {143,144}\)
performed MD simulations of cis-1,4-polybutadiene\textsuperscript{143,144} to identify candidates for jump motions in asymmetric double-well potentials. The idea of jumps in double-well potentials had been used earlier to explain quasi-elastic neutron scattering (QENS) data\textsuperscript{145,146} on PB. A detailed analysis of mode-coupling predictions was performed by van Zon and de Leeuw for a PB-like model\textsuperscript{147} and a PE-like model\textsuperscript{148} and by Lyulin et al.\textsuperscript{149–151} for polystyrene. In the work by van Zon and de Leeuw, no quantitative comparison with experimental data was possible because of the limitations of the force field quality and the short runs performed. In the work of Lyulin et al., the simulations extended to several tens of nanoseconds, but there too no quantitative comparison was made with the experiment.

In the works of Lyulin et al. and of van Zon and de Leeuw, MCT was found to provide a consistent description of the coherent as well as incoherent intermediate scattering functions over a temperature range between $T_c$ and about $1.2T_c$. The value of the critical temperature van Zon and de Leeuw obtained for PB was $T_c \sim 162\,\text{K}$, which is about 50 K below the experimental value. Their conclusions mostly agreed with those derived for the bead-spring model with an important difference:\textsuperscript{148} The relaxation in real polymers is far more stretched than in the bead-spring model. This stretching results in a smaller value of the von Schweidler exponent ($b = 0.46$ for the PE-like model vs. $b = 0.75$ for the bead-spring model) as well as for the KWW stretching exponent ($\beta \sim 0.4$ for the PE-like model vs. $\beta \sim 0.7$ for the bead-spring model), which are interrelated by the MCT prediction $\beta_q \to b$ for $\lambda \to \infty$. The result for the KWW exponent for the chemically realistic simulation agrees well with typical values found in neutron scattering or dielectric experiments. In contrast, the result for the bead-spring model is much larger.

We can therefore conclude that differences in the structural relaxation between bead-spring and chemically realistic models can be attributed to either the differences in packing that we discussed above or the presence of barriers in the dihedral potential in atomistic models. To quantify the role of dihedral barriers in polymer melt dynamics, we now examine high-temperature relaxation in polymer melts.

There has been extensive effort in recent years to use coordinated experimental and simulation studies of polymer melts to better understand the connection between polymer motion and conformational dynamics. Although no experimental method directly measures conformational dynamics, several experimental probes of molecular motion are spatially local or are sensitive to local motions in polymers. Coordinated simulation and experimental studies of local motion in polymers have been conducted for dielectric relaxation,\textsuperscript{152–158} dynamic neutron scattering,\textsuperscript{157,159–164} and NMR spin-lattice relaxation.\textsuperscript{17,152,165–168} A particularly important outcome of these studies is the improved understanding of the relationship between the probed motions of the polymer chains and the underlying conformational dynamics that leads to observed motions. In the following discussion, we will focus on the
NMR experiments that have been used to probe local reorientational motion. NMR \(^{13}\)C spin-lattice relaxation times are sensitive to the reorientational dynamics of \(^{13}\)C–\(^1\)H vectors. The motion of the attached proton(s) causes fluctuations in the magnetic field at the \(^{13}\)C nuclei, which results in decay of their magnetization. Although the time scale for the experimentally measured decay of the magnetization of a \(^{13}\)C nucleus in a polymer melt is typically on the order of seconds, the corresponding decay of the \(^{13}\)C–\(^1\)H vector autocorrelation function is on the order of nanoseconds, and, hence, is amenable to simulation.

The spin-lattice relaxation time \(T_1\) can be determined from simulation by using the relationship\(^{169}\) of Eq. [70]

\[
\frac{1}{nT_1} = K[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)]
\]  

where \(J(\omega)\) is the spectral density as a function of angular frequency given by

\[
J(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} P_2(t) \exp\{i\omega t\} dt
\]  

Here \(n\) is the number of attached protons at a given carbon atom and \(\omega_H\) and \(\omega_C\) are the proton and \(^{13}\)C resonance frequencies. The constant \(K\) assumes a value of \(2.29 \times 10^9 \text{ s}^{-2}\) and \(2.42 \times 10^9 \text{ s}^{-2}\) for sp\(^3\) and sp\(^2\) nuclei, respectively. The orientational autocorrelation function is obtained from the simulation trajectory using the relationship

\[
P_2(t) = \frac{1}{2} [3(\langle|\hat{e}_{CH}(t) \cdot \hat{e}_{CH}(0)|^2\rangle - 1)]
\]  

where \(\hat{e}_{CH}(t)\) is the unit vector along a C–H bond at time \(t\). Equation [72] is an ensemble average over all carbon atoms with the same chemical environment. Experimentally, \(T_1\) values can be determined for \(^{13}\)C nuclei in various chemical (bonding) environments because of the different chemical shifts of these nuclei (the resonances one can distinguish in a cis-trans copolymer of polybutadiene are shown in Figure 15).

The chemically realistic simulations we are discussing have been performed using a united atom representation of PB, which leads to the question: How does one actually measure a CH vector reorientation for such a model? The answer to this question is to use the trick we discussed in the analysis of the pressure dependence of the melt structure factor of PB. Hydrogen atoms are placed on the backbone carbons at their mechanical equilibrium positions for each structure that has been sampled along the MD trajectory. The CH vector dynamics we are showing in Figure 16 is solely from the backbone reorientations of the chain.
We can see that the different positions along the chain show distinct temperature-dependent relaxation curves. To further analyze these relaxation functions, we must Fourier transform them to determine their spectral density, which is best done employing an analytic representation of the data that

![Figure 15](image1)

**Figure 15** Sketch of the local environment along a polybutadiene chain of cis-and trans-conformers. For sp$^3$-hybridized carbon atoms (indicated by the gray spheres), the chemical shift is different when they belong to a cis-monomer than when they belong to a trans-monomer. For sp$^2$-hybridized carbon atoms (shown by black spheres) in a cis-monomer, NMR shows a different chemical shift whether they have another cis-monomer as a neighbor or a trans-monomer as a neighbor, and it is similar for the sp$^2$-hybridized carbon atoms in the trans monomer.

We can see that the different positions along the chain show distinct temperature-dependent relaxation curves. To further analyze these relaxation functions, we must Fourier transform them to determine their spectral density, which is best done employing an analytic representation of the data that

![Figure 16](image2)

**Figure 16** Second Legendre polynomial of the CH vector autocorrelation function for the sp$^3$ cis-carbon (dashed lines) and the sp$^2$ carbon in a trans-group next to a trans-group (dashed-dotted lines) for two different temperatures. The fit curves to the cis-correlation functions are a superposition of exponential and stretched exponential discussed in the text.
enables us to extrapolate to “infinite” time. For this process, we fit the data to the following superposition of exponential and stretched exponential decay

\[
P_2(t) = Ae^{-t/\tau_1} + (1 - A)e^{-(t/\tau_2)^b}
\]

As one can see in Figure 16, where two fit functions are included, our ansatz for \(P_2(t)\) can describe the data very well, except for the sub-picosecond vibrationally dynamics, which, however, has a negligible contribution to the spin-lattice relaxation time. From this information, we can then calculate the \(T_1\) times for different positions along the chain.

For PB, comparison of \(^{13}\text{C}\) NMR spin-lattice relaxation times and nuclear overhauser enhancement (NOE) values from simulation and experiment over a wide range of melt temperatures revealed excellent agreement. 168 A comparison between simulation and experiment for two temperatures for six different resonances is shown in Figure 17. Comparing the variation in \(T_1\) for carbon atoms in different chemical environments with the variation in mean waiting time between conformational transitions for the different types of torsions present in PB (\(\beta\), cis-allyl and trans-allyl), one concludes that spin-lattice relaxation for a given nucleus in PB cannot be associated with the dynamics of any particular torsion. Instead, the \(^{13}\text{C}\) relaxation occurs as the result of multiple conformational events involving several neighboring torsions. 168 However, a close correspondence was found to torsional autocorrelation times \(\tau_{\text{TOR}}\). The torsional autocorrelation time is given by the time integral of the torsional autocorrelation function

\[
\Phi_{\text{tor}} = \frac{\langle \cos \phi(t) \cos \phi(0) \rangle - \langle \cos \phi(0) \rangle^2}{\langle \cos^2 \phi(0) \rangle - \langle \cos \phi(0) \rangle^2}
\]
where $\phi(t)$ is the dihedral angle for a particular torsion at time $t$ and the average is taken over all dihedrals of a given type. The C–H vector correlation time $\tau_{CH}$ is given as the time integral of $P_2(t)$ (see Eq. [73], upon which $T_1$ depends). This correspondence is illustrated in Figure 18.

The close correspondence between $\tau_{TOR}$ and $\tau_{CH}$ shown in Figure 18 has also been observed in simulations of other polymer melts.\textsuperscript{152,165} Interestingly, both the C–H vector and the torsional correlation times exhibit stronger than exponential slowing with decreasing temperature, whereas the rate of conformational transitions exhibits Arrhenius temperature dependence as shown in Figure 18. The divergence of time scales between the torsional correlation time and the rate of conformational transitions is a first indicator of increasing dynamic heterogeneity with decreasing temperature. We will come back to this point later on. The $T_1$ values themselves were found to correlate well with $\tau_{CH}$ at higher temperatures as expected for the extreme narrowing regime (NOE is approximately three). However, at lower temperatures, the temperature dependence of $T_1$ corresponds neither to that observed for $\tau_{CH}$ nor to that observed for the mean conformational transition times, which implies that the temperature dependence of the experimentally measurable $T_1$ values reveals no quantitative information about the dynamics of the underlying conformational motions that lead to spin-lattice relaxation.\textsuperscript{168}

A similar analysis in terms of conformational dynamics can be performed as well for the interpretation of neutron scattering data in the pico-second time window\textsuperscript{159} and dielectric data.\textsuperscript{156} How do these findings then
relate to the interpretation of translational motion and scattering functions in super-cooled liquids in terms of MCT that was presented above for the bead-spring model?

To separate the contributions of dihedral barriers and packing effects, Krushev and Paul\textsuperscript{111} compared simulations of PB using the chemically realistic force field (CRC) with identical calculations in which all torsion energies were set to zero (FRC = freely rotating chain). Because the different conformational states in PB are almost isoenergetic and the torsion potentials are highly symmetric, no discernible influence was detected on either the single chain structure factor or the liquid structure factor.\textsuperscript{111} Furthermore, the long-time dynamics was only rescaled by a change in diffusion coefficient.\textsuperscript{170} All simulations were performed at high temperatures using runs on the order of 100 ns, to ensure that the results were not influenced by quenching in non-equilibrium structures.

A comparison of the melt structure factor and the single-chain structure factor of these models shows complete agreement.\textsuperscript{111} According to mode-coupling theory, both models should then show the same dynamics. Figure 19 reveals that this is not the case: For the FRC model at 273 K, one observes a crossover from short time vibrational motion to Rouse-like motion, whereas the CRC model shows a well-defined plateau regime between the short-time and the long-time behavior at this temperature. This plateau regime is not present for the CRC model at high temperatures and extends in time as the temperature is lowered. The physical origin for this separation of time scales is not the packing as assumed in MCT but the presence of intramolecular barriers. The short-time vibrational motions are damped out on a time scale of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure19}
\caption{Mean square monomer displacements using the CRC model of PB at three temperatures compared with the monomer displacement in an FRC version of the polymer model. Also indicated is the Rouse-like regime with the subdiffusive $t^{0.61}$ power law entered after the caging regime (CRC at low $T$) or after the short time dynamics (FRC and CRC at 353 K).}
\end{figure}
about 1 ps for all temperatures. Local reorientation needs transitions over the barriers in the torsion potentials (as discussed in detail earlier). These thermally activated processes occur on an average time scale of several picoseconds at high temperatures. Upon lowering the temperature, the waiting time between torsional transitions increases in an Arrhenius fashion (see Figure 18), which leads to a separation of time scales between vibrational motions and structural relaxation. Thus, in polymers, we have a second mechanism for the time scale separation between short-time vibrational motion and α-relaxation besides the packing mechanism considered in MCT.

Packing effects can contribute to the increase in waiting times between torsional transitions that require enough thermal energy to overcome the intramolecular barrier as well as space to accommodate the change in local conformation. This may require neighboring chains to move out of the way, which in turn may require those neighbor chains to undergo a torsional transition. So an intricate interaction exists between the intramolecular energetics and the local packing. It is not yet understood how the influence of packing versus the influence of torsional barriers balances as a function of temperature. For the melt regime in PB, however, it has been established that the activation energy for the Arrhenius temperature dependence of the mean waiting time between torsional transitions is given by the intramolecular dihedral barriers alone\textsuperscript{168} (see Figure 18).

A quantitative assessment (by simulations) of the low-temperature dynamics in the super-cooled melt for a polymer like PB requires “well-equilibrated” starting configurations. For the PB model we discuss here these configurations have been generated using parallel tempering techniques\textsuperscript{171} combined with very long (several hundred nanoseconds) MD runs. We surround “well equilibrated” with quotation marks because, as discussed, one cannot propagate the chemically realistic model chains into the free diffusion limit at low temperatures (temperatures approaching $T_c$). However, the volume of the model systems can be equilibrated and the runs are more than long enough to equilibrate local conformational statistics. As we discussed, no relevant temperature dependence of the coil-structure exists in PB, which makes this polymer an ideal model system where one can expect to observe only small effects developing from the time-scale limitations of chemically realistic simulations.

In the discussion on the dynamics in the bead-spring model, we have observed that the position of the amorphous halo marks the relevant local length scale in the melt structure, and it is also central to the MCT treatment of the dynamics. The structural relaxation time in the super-cooled melt is best defined as the time it takes density correlations of this wave number (i.e., the coherent intermediate scattering function) to decay. In simulations one typically uses the time it takes $S(q,t)$ to decay to a value of 0.3 (or 0.1 for larger $q$-values). The temperature dependence of this relaxation time scale, which is shown in Figure 20, provides us with a first assessment of the glass transition.
in PB. The temperature dependence of the $\alpha$-relaxation time scale can be described over a large temperature interval by a VF law, as was found when computing the diffusion coefficient of the bead-spring model. The Vogel–Fulcher temperature used in Figure 20 is not an independent fitting parameter; it was obtained by determining from the simulation the dielectric process for temperatures above 253 K. $T_0$ determined in this way agrees with the results from dielectric experiments and dynamic mechanical measurements. This VF law, however, fails to describe the low-temperature behavior of the $\alpha$ time scale, which is purely Arrhenius as the dashed fit curve indicates that it is actually a superposition of two Arrhenius laws. The low-temperature Arrhenius behavior has an activation energy of 5650 K, which illustrates the general finding that the VF law is a crossover law that can interpolate successfully between a high- and a low-temperature behavior. Upon approaching the glass transition temperature, which for PB is 178 K, the relaxation time temperature dependence becomes Arrhenius-like and the VF law fails. The Vogel–Fulcher temperature $T_0$, therefore, is an extrapolation artifact similar to the Kauzmann temperature.

In the interval between 198 K and 253 K, the form of the structural relaxation does not change as is evidenced by the success of the time-temperature superposition shown in Figure 21. One can also see from this figure that an additional regime intervenes between the short-time dynamics (first 10% of the decay at the lowest temperatures) and the structural relaxation (last 80% of the decay). We will identify this regime as the MCT $\beta$-regime.

Figure 20 Temperature dependence of the $\alpha$-relaxation time scale for PB. The time is defined as the time it takes for the incoherent (circles) or coherent (squares) intermediate scattering function at a momentum transfer given by the position of the amorphous halo ($q = 1.4 \text{Å}^{-1}$) to decay to a value of 0.3. The full line is a fit using a VF law with the Vogel–Fulcher temperature $T_0$ fixed to a value obtained from the temperature dependence of the dielectric $\alpha$ relaxation in PB. The dashed line is a superposition of two Arrhenius laws (see text).
later. The duration of this additional regime increases with decreasing temperature, and its amplitude increases with decreasing temperature.

We can analyze this intervening time regime as we did for the bead-spring model by fitting it with an extended von Schweidler law

\[ S(q,t) = f_q c^{q/C_0} h_t b + h_t (2) t^{2b} \pm \ldots \]  

The von Schweidler law describes well the decay from the plateau in both the coherent and the incoherent scattering functions. All correlators for PB can be fitted with a von Schweidler exponent \( b = 0.3 \) (see Figure 22). Like the findings by van Zon and de Leeuw\(^{148}\) and by Lyulin and Michels,\(^{149}\) the decay is much more stretched for the chemically realistic PB model than for the bead-spring model. Typical values for the stretching exponent in the KWW fit to the \( \alpha \) relaxation (which should approach \( b \) for \( q \to \infty \)) are around 0.5, which agrees well with experimental values. Using the \( \beta \) fit parameters, we can determine the critical temperature in a manner that is similar to what we did for the bead-spring model. The value we obtain this way is \( T_c = 214 \pm 2 \) K,\(^{176}\) which agrees perfectly with experiment.\(^{177}\) It has so far not been possible to obtain a value for the von Schweidler exponent experimentally, which we can therefore predict by these chemically realistic simulations of PB.

Finding that the scattering functions at low temperature are amenable to an MCT description, we are faced with a dilemma. On the one hand, the high-temperature mean-square displacement curves lead us to conclude that dihedral barriers constitute a second mechanism for time scale separation in super-cooled polymer melts besides packing effects. On the other hand, the
plateau regime in the low-temperature scattering data is perfectly described by MCT. The resolution of this dilemma can be observed in the fact that for PB MCT does not correctly predict the temperature dependence of the \( \tau \) time scale in the vicinity of \( T_c \). The exponent \( \gamma \) governing the divergence of the \( \tau \) time scale on approaching \( T_c \) is much smaller than that calculated from the von Schweidler exponent using the exponent relations of MCT.\(^{176}\) The difference between successful description of the \( \beta \) regime and the failure in the \( \alpha \) regime can be an indication that the plateau regime is packing dominated and the structural relaxation is influenced by both mechanisms for time scale separation, but at this point in time, our arguments are only speculative. Additional studies of PB models with modified dihedral barriers are under way\(^ {178}\) to provide more insight into which mechanism dominates the relaxation processes in which time regime.

### Dynamic Heterogeneity

It has been clearly demonstrated by experiments as well as by simulations that the glass transition phenomenon is associated with an increase in dynamic heterogeneity in the motion of the glass-forming moieties. This heterogeneity is best observed experimentally at temperatures close to or below \( T_g \), where the heterogeneity is well developed.\(^ {179-181}\) The existence of domains of fast- and slow-moving molecules is closely connected with the existence of a characteristic length scale measuring correlated behavior and with the temperature dependence of this length scale.\(^ {182}\) As far as geometrical information can be inferred from the experiments (as, for example, in References 183–185), these regions

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**Figure 22** von Schweidler fits (dotted lines) to the plateau decay of the coherent intermediate scattering function in the temperature interval 198–253 K.
seem to be on the order of a few nanometers in size, even at and below $T_g$, and there is no indication that this length scale is becoming macroscopic.

Using computer simulations of simple liquids, it was suggested that the non-Gaussianity of the van-Hove correlation functions for tagged particle motion can identify fast-moving particles. Typically, the van Hove function $G_s(r, t)$ from the simulation develops a tail when compared with the Gaussian approximation $G_s^G(r, t)$ having the same second moment, i.e., having the same mean-square displacement of the molecules. Defining the fraction of molecules with displacements beyond the crossing point $r^*$ defined by $G_s(r^*, t) = G_s^G(r^*, t)$ as fast-moving particles yields around 6% of fast particles. This definition of fast-moving and variants thereof have been applied to identify such particles and an eventual clustering phenomenon from simulations of the bead-spring polymer model.

When one studies the clustering properties of these fast particles, one finds that the clusters are typically very ramified, string-like objects. The average mass of the clusters as a function of time lag from a starting configuration has a peak in the vicinity of the late $\beta$ regime, where the non-Gaussianity of the van Hove function is maximum. At this point in time, the particles break out of their cages. This peak in the average cluster size is a consequence of the identification of the fast particles as those being faster than predicted by the Gaussian behavior. A dynamic correlation length (defined as the weight average mean-squared size of the cluster) increases only from $\xi / \sigma^2$ to $\xi / \sigma^3$ on approaching $T_c$ from above, where $\sigma$ is the Lennard–Jones radius of the bead-spring monomers. This small increase is compatible with the experimental finding that the typical size of a domain of fast relaxing molecules at temperatures below $T_c$ is only a few nanometers, which translates into between 3 and 10 Lennard–Jones radii.

The new qualitative insight obtained from the cluster analysis is the string-like character of clusters of fast particles, which means that these particles tend to follow each other along their paths of movement. However, only very short scale correlation of this motion exists. There is also no observable tendency for the bead-spring monomers to move along their chain contour to take up the position of their bonded neighbor. In contrast, for PB, a clear tendency exists for a monomer to replace its bonded neighbor on the average time scale of a torsional transition.

Torsional transitions combined with the local packing in a melt of chemically realistic chains (see the discussion on structural properties) give rise to a distinct type of motion as shown in Figure 23. Here we show isosurfaces of the intrachain distinct part of the van Hove function, that is, the probability that one particle of a chain is at the origin at time zero and another particle is at position $r$ at time $t$. The structure along the $r$-axis for small $t$ gives the intrachain radial distribution function with distinct peaks created by the C–C bond length, the average C–C–C bond angle, and the torsional isomers. On the average time scale of a torsional transition (around 100 ps), the bonded neighbor moves into the space...
that had been occupied by the reference united atom at time zero. That is, the torsional transitions lead to a slithering motion of the chain along its contour. This motion is also observable in the van Hove self-functions for the attached hydrogen atoms, and it influences the scattering at lower temperatures.

As mentioned, the measures for dynamic heterogeneity typically applied to the bead-spring model are similar to those used for simple liquids. For chemically realistic polymer models, however, a much simpler measure of dynamic heterogeneity has been used for many years in this type of simulation. This heterogeneity is found in transition rates for different chemically identical dihedrals in the melt. This heterogeneity shows up most strikingly in the divergence in the rate of conformational transitions for dihedrals, which follow an Arrhenius temperature dependence with activation barriers resulting primarily from internal rotation barriers, and the relaxation time for the torsional autocorrelation function shown in Figure 18. Although at high temperatures the relaxation times for torsional autocorrelation functions closely follow the rate of conformational transitions, the former exhibit Vogel–Fulcher-like temperature dependence, whereas the latter stay Arrhenius-like. The torsional autocorrelation times are closely related to the rates of local relaxation, which give rise to experimentally measurable quantities like the NMR spin-lattice relaxation time, as discussed. The Vogel–Fulcher parameters that one typically finds for the relaxation time scales for the torsional autocorrelation function agree well with those parameters obtained for dielectric or magnetic relaxation from experiment.

The divergence between the rate of conformational transitions and the decay of the torsional autocorrelation functions (and hence local relaxations)
in amorphous polymers may lie in the increasingly heterogeneous nature of conformational transitions with decreasing temperature, which is an observation that has now been confirmed by computer simulations.$^{152,154,156,166,168,193–196}$ Heterogeneity here is defined as some dihedrals exhibiting much faster motion than average dynamics, whereas other (chemically equivalent) dihedrals exhibit much slower motion than average. The mean conformational transition time, which follows Arrhenius temperature dependence, is sensitive to fast events. For example, a few fast dihedrals may exist in a system, with the remaining being quiescent. This system can yield the same mean conformational transition time as a system in which all dihedrals have average dynamics. On the other hand, for the torsional autocorrelation function to decay, and hence for $^{13}$C-NMR relaxation and dielectric relaxation to occur, each dihedral in the polymer must visit its available conformational states with ensemble average probability.

Heterogeneity in conformational dynamics can be quantified by measuring the distribution of waiting times for a given number of transitions. For PB, as shown in Figure 24,$^{156}$ one observes an increase in probability for very short waiting times, which is from correlated transitions. Furthermore, a long time tail develops, indicating the existence of very slow dihedrals. These results are compared in the figure with the expected Poisson behavior of independent random events. At high temperatures, the distribution approaches the expected Poisson behavior. When reducing the temperature, the distribution becomes increasingly heterogeneous.

![Figure 24](image)

**Figure 24** Probability distributions for the waiting time for 10 dihedral transitions. Time is given in units of the average waiting time $10t^*$. The distributions are peaked around $10t^* = 1$ and are much broader than the Poisson distribution but approach it for high $T$. For low $T$, a high probability for short waiting times exists and a long time tail of the distribution develops.
The dispersion of this waiting time distribution, i.e., its second central moment, is a measure that we can use to define a “homogenization” time scale on which the dispersion is equal to that of a homogeneous (Poisson) system on a time scale given by the torsional autocorrelation time. The homogenization time scale shows a clear non-Arrhenius temperature dependence and is comparable with the time scale for dielectric relaxation at low temperatures.\cite{156}

The source of emerging heterogeneity (slow movers and fast movers) in the conformational dynamics of amorphous polymers when decreasing the system’s temperature remains unknown. In light of the packing arguments underlying MCT, it is reasonable to attempt to associate differences in transition rates with the local packing environment, i.e., a dense packing environment for slow dihedrals and a looser packing environment for faster dihedrals. The work by Jin and Boyd\textsuperscript{153} in this direction and efforts by de Pablo’s group\textsuperscript{197} trying to relate heterogeneous dynamics to inhomogeneous stress distributions have so far been inconclusive. Phenomenologically, it is clear from simulations that conformational transitions become increasingly self-correlated with decreasing temperature. (Here, correlation is defined in terms of the probability that, once a dihedral undergoes a transition, this dihedral will then undergo another transition (usually back to the original state) before a neighboring torsion undergoes a transition.) It has been observed for several polymer melts\textsuperscript{193,194} that the probability of self-correlation increases dramatically with decreasing temperature. Self-correlation may account for the ineffectiveness of conformational transitions to induce relaxation with decreasing temperature: A relatively few torsions jumping back-and-forth rapidly between two conformational states can contribute significantly to the rate of conformational transitions, but they will contribute little to the experimentally observable local polymer relaxations.

The homogenization (or equilibration) process of the torsional transitions can be examined in even more detail. For example, one can differentiate between a first regime where every dihedral becomes mobile and is able to visit other isomeric states, and a second regime where the frequency of these visits approaches its thermal equilibrium value. Bedrov and Smith\textsuperscript{198,199} have analyzed the time scales for these two regimes recently using modified PB-models and have shown that the first regime corresponds to the time scale of the dielectric $\beta$ relaxation, whereas the second regime follows the $\alpha$-relaxation time scale. This study is a first inroad into a mechanistic understanding of dielectric processes based on MD simulations.

**SUMMARY**

This chapter has the title “Determining the Glass Transition in Polymer Melts,” but we might ask: “Which glass transition?” Do we consider
the Vogel–Fulcher temperature $T_0$, the calorimetric (or viscosimetric) glass transition temperature $T_g$, or the mode-coupling critical temperature $T_c$ to mark the transition?

The calorimetric or viscosimetric definitions of the glass transition temperature are arbitrary because they single out a temperature where the intrinsic relaxation time of the glass forming system is approximately 100 s. When one performs either a calorimetric experiment or a volumetric experiment with suitable cooling rates, a smeared step in the corresponding thermodynamic response function (specific heat or isobaric expansion coefficient) is observed around $T_g$. When one is more patient in performing the experiment, as exemplified by the classic work by Kovacs, the temperature at which the step in the response function is observed shifts to lower temperatures. For the class of fragile glass formers, to which most polymers belong, this shift is small, which gives some validity to the arbitrary definition of $T_g$. For strong glass formers, however, the shift can be of the same order as $T_g$ itself (for example, for silica melts). Also, there is no qualitative change in any system-specific time scale near the viscosimetric $T_g$. From a basic physical point of view, the calorimetric or viscosimetric glass transition temperature is therefore an inadequate measure to use for defining the glass transition.

We have shown in the section on the thermodynamics of the glass transition that an extrapolation of $T_g(\Gamma)$, the cooling-rate dependent step temperatures in the thermal expansion coefficient, postulating the empirical Vogel–Fulcher law as a description of the temperature dependence of internal relaxation times extrapolates to $T(\Gamma \to 0) = T_0 = 0.35$ for the bead-spring model. This is in good agreement with what one obtains for $T_0$ from the temperature dependence of the chain center-of-mass self-diffusion coefficient for this model. Additionally, one generally finds that the so-called Kauzmann temperature (where the extrapolated excess entropy of the super-cooled liquid in comparison with the crystal seems to vanish) agrees closely with $T_0$. This agreement has led people to speculate about an underlying phase transition around the Kauzmann temperature, especially based on the Gibbs–Di Marzio theory for the excess configurational entropy of polymer melts, which also produced a Kauzmann paradox. We have shown, however, that, although the theory nicely reproduced the shape of the entropy curve as a function of temperature, the predicted absolute values were too small compared with the simulation data and the entropy catastrophe was just a consequence of inaccurate approximations. Furthermore, careful studies revealed that the Vogel–Fulcher law cannot describe the temperature dependence of the $\alpha$-relaxation time scale close to $T_g$. Instead, this temperature dependence can be described by a low-temperature Arrhenius law to which the high-temperature dependence crosses over. Thus, the Vogel–Fulcher temperature and the Kauzmann temperature are purely extrapolation artifacts having no underlying physical significance.
The only remaining candidate for the definition of the glass transition temperature is therefore the crossover temperature from the high-temperature behavior to the low-temperature behavior of the \( \alpha \)-relaxation time scale. A crossover that occurs around some temperature \( T_x \) that one also finds to be the merging temperature of dielectric \( \alpha \)- and \( \beta \)-relaxation and the critical temperature of mode-coupling theory. Physically, at \( T_x \), a crossover occurs from a high-temperature transport (or relaxation) mechanism to a low-temperature mechanism. For simple liquids, MCT identifies this crossover as originating from the cage effect. At high temperatures, the cage of neighboring particles opens up on the same time scale it takes the central particle to reach its boundary. Contrarily, at lower temperatures, the cage particles are themselves caged and an activated process is needed for the central particle to be able to leave its cage. This simple picture, and the theoretical predictions for the behavior of the density fluctuations as being the dominating slow variables within the theory, have been tested on diverse systems like hard-sphere colloids, \(^{200}\) Lennard–Jones mixtures, \(^{137}\) and silica melts. \(^{201}\) We have shown that MCT can also describe fairly well the glass transition in a bead-spring polymer melt and in a chemically realistic model of PB. Deviations between MCT predictions and simulation results from chain connectivity, which were found in the bead-spring chain simulations, have been incorporated into an extension of the theory. For a chemically realistic model, we have shown that a competition exists between two mechanisms, which leads to a time scale separation between vibrational motion and structural relaxation. One mechanism is related to the packing effects captured by MCT, and the other mechanism is from the presence of dihedral barriers. How these two mechanisms can be joined theoretically remains an open question.

The answer to our question at the beginning of this summary therefore has to be as follows. When you want to locate the glass transition of a polymer melt, find the temperature at which a change in dynamics occurs. You will be able to observe a developing time-scale separation between short-time, vibrational dynamics and structural relaxation in the vicinity of this temperature. Below this crossover temperature, one will find that the temperature dependence of relaxation times assumes an Arrhenius law. Whether MCT is the final answer to describe this process in complex liquids like polymers may be a point of debate, but this crossover temperature is the temperature at which the glass transition occurs.

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