

Glass Formation in Polymers: Theory of Glass Transition

Some theoretical concepts on the glass transition (entropy catastrophe, free volume, mode coupling theory, characteristic length of cooperative regions, ...) are briefly reviewed and corresponding evidence from experiments and simulations is critically evaluated. Similarities and differences with the glass transition in nonpolymeric materials is discussed. Evidence is given that the typical relaxation processes (α , β , ...) of glass-forming polymer melts are related to motions on smaller scales of space and time than the Rouse-like Brownian motion by which polymer chains reorganize their global configurations (see *Glass Formation and Sub-T_g Transitions in Polymers: Influence of Chain Chemistry*).

1. Basic Experimental Facts That the Theory Should Address

When one cools a polymer melt to low enough temperatures, the structural relaxation times steadily increase, until finally the material falls out of (metastable) equilibrium and freezes into an amorphous solid (McKenna 1990; Zarzycki 1991). The mechanism underlying this dramatic slowing down is not at all obvious, since typically the structure (as it shows up via the scattering of X-rays or neutrons) changes at the glass transition only very little. For example, in polybutadiene the scattering intensity (the static structure factor $S(q)$) at $T = 160$ K (about 20 K lower than the glass transition temperature T_g) hardly differs from that at $T = 260$ K (Richter *et al.* 1988).

These (as well as most other) characteristics are not at all unique to polymers but rather common to all glass-forming fluids (J ckle 1986): small-molecule liquids like orthoterphenyl, molten silicas, etc. all show similar behavior, despite the disparity in their chemistry. A typical feature is the increase of the relaxation time (measured, for instance, by the viscosity η of a simple fluid, or the friction coefficient ζ in a polymer melt), which can approximately be described by the Vogel–Fulcher law.

$$\tau \approx \tau_\infty \exp[E_{\text{act}}/(T - T_0)] \quad (1)$$

Here, τ_∞ is some prefactor, E_{act} is some effective activation energy, and the Vogel–Fulcher temperature T_0 typically is about 30 K lower than T_g . At least, this is true for the so-called “fragile glassformers” (Angell 1997), to which polymers belong, while in the so-called “strong glassformers” (such as molten SiO_2) $T_0 = 0$, and η follows a simple Arrhenius law. However, it is not clear how fundamental this distinction is; intermediate cases between “strong” and “fragile” exist, and in some materials Eqn. (1) fits only over some

intermediate range, and closer to T_g a simple Arrhenius behavior applies.

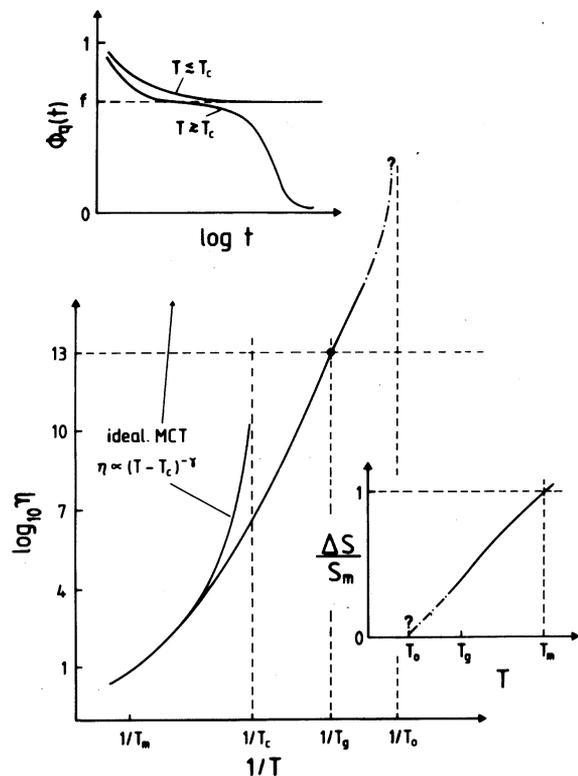
A further characteristic feature is that relaxation functions $\varphi(t)$, accessible via mechanical or dielectric relaxation, multidimensional NMR, or neutron-spin-echo scattering, e.g., Richter *et al.* (1988), exhibit the Kohlrausch–Williams–Watts stretched exponential relaxation (J ckle 1986)

$$\varphi(t) \propto \exp[-(t/\tau_0)^\beta], \quad 0 < \beta < 1 \quad (2)$$

The exponent β typically is close to 1/2 but is not universal but at least for one material often temperature-independent: if so, $\varphi(t)$ exhibits the “time-temperature-superposition principle.”

Thermal properties (such as enthalpy, specific volume, etc.) of a fluid that is cooled through T_g typically show a (rounded) kink, and corresponding derivatives (thermal expansion coefficient $\alpha(T)$, specific heat $C_p(T)$, ...) show a (rounded) step. Both the position $T_g(\gamma)$ of this kink (or step respectively) and the extent of the rounding depend on the cooling rate (e.g., Gutzow and Dobrev 1992): the slower the cooling, the sharper these features become, and there is a systematic decrease of $T_g(\gamma)$ with decreasing cooling rate γ . Thus, often it is speculated that in the limit $\gamma \rightarrow 0$, a thermodynamic transition occurs from a supercooled fluid to an “ideal glass”; however, the limit is not well defined (it can be reached only when crystallization does not occur). Practically, the extrapolation to $\gamma \rightarrow 0$ is not possible since $T_g(\gamma)$ depends on γ only logarithmically (or even slower). If there were a line $T_k = T_k(p)$ in the pressure–temperature plane (p, T) of a thermodynamic transition with discontinuities in second derivatives of the thermodynamic potential, Ehrenfest relations should hold between these discontinuities, and the Prigogine–Defay (1954) ratio should be unity. These relations seem all to be violated (J ckle 1986). The interpretation of these findings has been questioned (Nieuwenhuizen 1997), emphasizing the role of the “configurational entropy” (related to the number of equivalent glassy states in which the system can freeze into at T_g) which is “lost” at the glass transition.

Experimentally, the configurational entropy of the supercooled fluid is linked to the entropy difference ΔS of the fluid relative to the crystal of the same material. Typically (J ckle 1986, Gutzow and Dobrev 1992), $\Delta S(T)$ decreases almost linearly with T between the melting temperature T_m and T_g (see Fig. 1); with $\Delta S/S_m \approx 1/3[S_m \equiv \Delta S(T_m)]$. Interestingly, a linear extrapolation of $\Delta S(T)$ to lower temperatures indicates a vanishing of $\Delta S(T)$ at a temperature close to the temperature T_0 . Since $\Delta S(T)$ should not become negative (the disordered fluid should have a larger configurational entropy than the ordered crystal: “Kauzmann’s paradox”), this behavior of $\Delta S(T)$ also is used to infer a phase transition from supercooled fluid to the (ideal) glass, thus avoiding this “entropy catastrophe” that $\Delta S(T) < 0$ at low temperatures.


Figure 1

Schematic plot of the logarithm of the viscosity of a supercooled glass-forming fluid (of small molecules) vs. inverse temperature. From the melting temperature T_m to the glass transition temperature T_g , $\eta(T)$ rises by many decades, and T_g here is taken by the empirical choice $\eta(T = T_g) = 10^{13}$ P. The upper insert qualitatively illustrates the main prediction of idealized MCT for the relaxation function $\Phi_q(t)$ of density fluctuations at wave number q corresponding to the peak (“amorphous halo”) of the static structure factor $S(q)$. While $\Phi_q(t)$ for $T > T_c$ decays with time to zero in two steps, for $T \leq T_c$ it decays only towards nonergodicity parameter f . The lower insert shows the excess configurational entropy ΔS (relative to the crystal) normalized by its value S_m at the melting temperature T_m vs. temperature. T_o is either found by a linear extrapolation of ΔS vs. T or by a fit of $\eta(T)$ to Eqn. (1). But both extrapolations are questionable, as emphasized by the question marks in the figure, since below T_g , there is a substantial interval where no data are available, and T_o depends on the temperature region used for the fit.

2. The Mode Coupling Theory of the Glass Transition

It is most natural to base a theory of the glass transition on a microscopic theory of the dynamics of fluids, and this is precisely what the mode coupling theory (MCT) attempts (Götze 1991). So far, this theory has only been worked out for simple (monatomic) liquids and

for diatomic molecules (Schilling and Scheidsteger 1997) but not for polymers; nevertheless it has been applied to interpret both experiments (e.g., Frick *et al.* 1990) and simulations (e.g., Baschnagel and Fuchs 1995, Bennemann *et al.* 1998, 1999a).

Starting from the projection operator approach to nonequilibrium statistical mechanics, MCT derives (via uncontrolled decoupling approximations) a closed nonlinear equation for the correlation function of density fluctuations,

$$\phi_q(t) \equiv \langle \delta \rho_q^*(t) \rho_q \rangle / \langle \delta \rho_q \delta \rho_q \rangle \quad (3)$$

$\delta \rho_q$ being the (complex) Fourier component of a density deviation from the average density ρ at wavevector \vec{q} . In its idealized version, MCT predicts the existence of a dynamical transition at a critical temperature T_c (or a critical density ρ_c , respectively) from an ergodic to a nonergodic state.

In the ergodic state ($T > T_c$ or $\rho < \rho_c$) $\phi_q(t \rightarrow \infty) \rightarrow 0$ while in the nonergodic state the decay of $\phi_q(t)$ stops at the nonergodicity parameter f , $\phi_q(t \rightarrow \infty) \rightarrow f$, cf. upper insert of Fig. 1. This transition implies a simple power law divergence of relaxation times and the viscosity, $\eta(t) \propto [T - T_c]^{-\gamma}$, with an exponent γ typically close to $\gamma \approx 2$. As is emphasized in Fig. 1, this transition occurs at a temperature typically 50 K higher than T_g (in fragile liquids), where (for small molecules) in reality $\eta(T_c) \approx 10^3$ P, 10 orders of magnitude lower than $\eta(T_g)$. For polymers η depends on degree of polymerization N , of course, and hence the ordinate scale in Fig. 1 is the time constant associated with the friction coefficient $\zeta(T)$ of the monomers (for nonentangled chains in a melt, the dynamics is described by the Rouse model, i.e. the relaxation time $\tau = \zeta(T)b^2N^2/[3\pi^2k_B T]$, b being the size of an effective monomer).

Now the singular behavior predicted by idealized MCT at T_c does not occur in reality, and an extended version of MCT (Fuchs *et al.* 1992) shows indeed that this singularity is rounded off, and a crossover to a simple Arrhenius-type behavior occurs. The physical picture behind MCT is the “cage effect”: in a dense fluid, every atom sits in a “cage” formed by its neighbors, and as $T \rightarrow T_c$ the lifetime of these cages strongly increases. For $T \sim < T_c$, thermally activated hopping (qualitatively similar to self diffusion of atoms in crystals) is needed to restore ergodicity—these processes were neglected by the idealized MCT. Unfortunately, MCT needs a variety of phenomenological parameters which cannot be easily predicted on a molecular level, and explicit predictions on the behavior in the region $T \leq T_c$ are scarce.

3. Entropy Theory

MCT emphasizes the similarity of the glass transition of many different systems. Since it is formulated for simple fluids, it is not clear to what extent it holds for polymer melts. In contrast, the entropy theory of Gibbs and DiMarzio (1958) focuses on the con-

figurational entropy of polymers. Thus, it cannot explain why small-molecule fluids behave in a similar fashion. We summarize here only the main steps, following Baschnagel *et al.* (1997).

One considers a lattice with M sites and K polymers of length N . Each monomer occupies a single lattice site, and the polymers are modeled by self-avoiding walks. The total number of configurations Ω of the melt yielding the entropy density as $s = (\ln \Omega)/M$ is approximated by an intrachain (Ω_{intra}) and an interchain (Ω_{inter}) contribution, $\Omega \approx \Omega_{\text{intra}} \Omega_{\text{inter}}$. Ω_{intra} accounts for the increase of the chain stiffness when the temperature is lowered. Associating an energy with the bond angle, this energy being 0 if two successive bonds are colinear and ε otherwise. The probability p that two successive bonds are not colinear then is $p = (z-2) \exp(-\varepsilon/k_B T) / [1 + (z-2) \exp(-\varepsilon/k_B T)]$, z being the coordination number of the lattice. One then finds

$$\Omega_{\text{intra}} = \binom{K(N-2)}{pK(N-2)} \left(\frac{1}{z-1} \right)^{(1-p)K(N-2)} \times \left(\frac{z-2}{z-1} \right)^{pK(N-2)} \quad (4)$$

(Ω_{inter}) describes the number of ways the K chains can be put on the lattice,

$$\Omega_{\text{inter}} = \frac{1}{2^K} \frac{1}{K!} \prod_{k=0}^{K-1} v_{k+1} \quad (5)$$

v_{k+1} being the total number of configurations of the $(k+1)$ th chain if there are already k chains on the lattice. Approximately

$$v_{k+1} \approx (M - kN) N_{\text{empty}}^{N-1} z(z-1)^{N-2} \quad (6)$$

where $M - kN$ is the number of empty lattice sites after k chains have been put on, and $z(z-1)^{N-2}$ represents the number of possibilities to place the remaining $N-1$ monomers of the $(k+1)$ th chains after the first one has been put, forbidding only the immediate backfolding of the random walk.

The factor N_{empty}^{N-1} approximately accounts for the self- and mutual avoidance of the walks. Flory (1956) simply used $N_{\text{empty}} = 1 - kN/M$, while Gibbs and DiMarzio (1958) corrected this as $N_{\text{empty}} = (1 - kN/M) / [1 - k(N-1)(Mz/2)]$ and Milchev (1983) as $N_{\text{empty}} = (1 - kN/M) / (1 - k/K)$. The idea behind these corrections is that not all empty lattice sites can serve as starting points for the new polymer but only those which lie outside of the volume already consumed by the other k chains. Unfortunately, neither Eqn. (6) nor the expressions for N_{empty} can be justified with mathematical rigor. The validity of these theories *a priori* is rather questionable. While for the approximations of Flory (1956) and Gibbs and DiMarzio (1958), the entropy at low temperatures is negative

$\{s(T \rightarrow 0, N \rightarrow \infty) = -1 \quad \text{or} \quad s(T \rightarrow 0, N \rightarrow \infty) \rightarrow (\frac{z}{2} - 1) \ln(1 - \frac{2}{z})\}$, Milchev's entropy stays non-negative.

When one studies this model by Monte Carlo simulation, avoiding thus the above questionable approximations, one finds the polymers to form (liquid)-crystalline clusters of stretched-out chains at low temperatures (Baumgärtner 1984); thus the model does not at all describe the coil structure near T_g . In fact, Flory (1956) proposed this model rather for polymer crystallization!

However, this latter problem can be cured by considering the bond fluctuation model (Paul and Baschnagel 1995). In this model, each effective monomer blocks a whole elementary cube of the lattice from further occupation, and the length of effective bonds varies from 2 to $\sqrt{10}$ lattice spacings. One now chooses an energy depending on the bond length, namely, for a length $b = 3$ this energy is 0, for all other bonds it is ε . This choice does not lead to any significant stretching of the chains. Monte Carlo simulations (Paul and Baschnagel 1995) show a glass transition, $T_c \approx 0.150$ and $T_0 \approx 0.125$ if units are $\varepsilon = 1$ and $k_B = 1$. The physical interpretation of glassy freezing is a “geometric frustration” effect: whenever a bond takes its ground state length, four sites between its adjacent effective monomers become unavailable for occupation by any other monomers, too much “free volume” is wasted: efficient dense packing of monomers is in conflict with the tendency of bonds to reach their ground state.

For this model the analog of the parameters p, z in Eqns. (4)–(6) can be evaluated from the simulation as function of T (Baschnagel *et al.* 1997), as well as the approximate formulas for the entropy due to Flory (1956), Gibbs and DiMarzio (1958) and Milchev (1983). Again, both Flory's and Gibbs' and DiMarzio's formulas predict an “entropy catastrophe,” i.e. $s(T)$ becomes negative for $T \leq 0.18$. This result clearly is an artifact of the approximations made: the actual T_g is much lower, and furthermore the actual entropy—which derives from the simulation exactly, apart from statistical errors—is severely underestimated by these theories over the entire temperature range (unlike Milchev's (1983) theory, which overestimates the entropy).

If $S(T) = S(T = \infty) - \Delta S(T)$, the main error concerns the entropy of the melt at very high temperatures [$S(T = \infty)$], while all theories describe $\Delta S(T)$ rather accurately. Thus, the theory of Gibbs and DiMarzio (1958) and its extensions describes many experimental trends, e.g., the variation of T_g with pressure, molecular weight, influence of plasticizer, crosslinks, etc. (Baschnagel *et al.* 1997). Finally, very different theories motivated by spin glasses (Franz and Parisi 1998) also describe the glass transition by the vanishing of the configurational entropy or “complexity,” which is related to the number of “global” free energy minima \mathbb{N} as $\mathbb{N} = \exp(NS_{\text{conf}}(T))$.

4. Free Volume Theory

The concept that local rearrangement motions in dense systems require some empty space which can be taken by atoms involved in this motion clearly is intuitively appealing. Free volume theory (Cohen and Grest 1979) implies that, in the liquid, the free volume accessible to the atoms forms a percolating structure, and as temperature is lowered (and/or the density gets higher), less and less free volume is available, until in the glass, free volume occurs only in small localized regions, and hence global rearrangement of the structure is arrested.

While this theory exists in many variations (e.g., Robertson 1992), the notion of free volume is somewhat ill-defined. It has a precise meaning for lattice models (occupancy of lattice sites) or for particles in the continuum with hard core potentials—but for realistic situations there always remain ambiguities of definition. This also applies to attempts to “measure” free volume experimentally (analyzing the diffuse scattering experiments, positron annihilation studies, photoisomerization of probe molecules, etc. (Robertson 1992). As Robertson has put it, “a difficulty with using any of the above measures of free volume is their general lack of internal consistency.” So, to a large extent, the free volume approach is phenomenological, and is most plausible for van der Waal liquids of small molecules.

The salient features can be summarized as follows (Grest and Cohen 1981, Jäckle 1986): The average free volume \bar{v}_f per molecule is the total average molecular volume $\bar{v} = V/N$ minus a volume v_o occupied by the molecule itself, $\bar{v}_f(T) = \bar{v}(T) - v_o$. For a constant thermal expansion coefficient $\bar{v}_f(T) = v\alpha_p(T - T_o)$, T_o being the temperature at which no free volume is left. Assuming that the distribution $p(v_f)$ of v_f in the liquid is uncorrelated between different molecules, one obtains $p(v_f) = (1/\bar{v}_f)\exp(-v_f/\bar{v}_f)$. Assuming the rate of transport is given by the probability of finding a free volume exceeding a critical value v_c , i.e.

$$1/\eta(T) \propto \exp(-v_c/\bar{v}_f) = \exp[-v_c/(\bar{v}(T) - v_o)] \quad (7)$$

which is Doolittle’s (1951) formula. For a constant α_p it is equivalent to Eqn. (1). Clearly, parameters such as v_c and v_o are adjustable constants. Rather than fitting the viscosity, one also can invoke equation-of-state descriptions based on free volume concepts, and fit those to data. Using this approach for the description of kinetic processes, one obtains impressive fits of data such as volume recovery (Robertson 1992). However, even if free volume may be a useful framework for the experimentalist, this author does not consider this approach as a well-founded theory.

5. Characteristic Length at the Glass Transition

In “spin glasses” (randomly diluted magnets with competing exchange interactions, where spin orienta-

tions freeze in random directions instead of ferro- or antiferromagnetic alignments), the relaxation time also can be described by Eqn. (1) (Binder and Young 1986). However, a more accurate analysis of the experiment (and simulations) revealed that the behavior is a power law divergence with a large dynamic exponent z ,

$$\tau \propto \xi^z \propto (T - T_f)^{-zv} \quad (8)$$

$\xi \propto (T - T_f)^{-\nu}$ being a static correlation length that diverges at the freezing temperature T_f with critical exponent ν . Equation (8) is standard “critical slowing down,” an unusual aspect being only the large value of z .

In view of the success of Eqn. (8) for spin glasses, it is occasionally tried for structural glasses (Souletie 1990, Colby 1999) and there has been a search for a characteristic length (e.g., Donth 1992, Kokshenev 1998). But all estimations (values of a few nm at T_g) are very indirect and hence doubtful, and simulations—where one should be able to extract a length ξ from finite size effects (Binder *et al.* 1999)—have so far failed to give evidence for such a length.

It must be envisaged that glass-forming fluids may have large correlation lengths that are not directly related to the glass transition. For example, a melt of semiflexible polymers (Weber *et al.* 1997) exhibits evidence for a growing ξ due to nematic clusters (and for long enough chains, liquid–crystalline order occurs before glassy freezing). The increase of $S(q)$ for small q observed here resembles the excess scattering due to the so-called “Fischer clusters” (Fischer 1993). However, the scale of the latter is orders of magnitude larger than the clusters in this simulation, and it is controversial to what extent the “Fischer clusters” are intrinsic to the glass transition.

Kivelson *et al.* (1995) argue that the glass transition occurs because another ordering phenomenon (of a more conventional type) is avoided due to frustration: then a correlation length ξ associated with this conventional order grows but stays finite as one approaches T_g . The dramatic increase of $\eta(T)$ can also phenomenologically be fitted by this model. Unfortunately, such fits cannot discriminate between theories—the Adam-Gibbs entropy approach, the free volume approach, Eqn. (8), and formulas based on an “energy landscape” model (Schulz 1998) also provide good fits of $\eta(T)$.

Even if one takes the analogy between structural and spin glasses seriously, one must note that the structural glass is not similar to the Ising spin glass, where each spin can be in two states related by a spin reversal symmetry, rather the Potts glass where each “spin” can be in a large number of states, and no symmetry exists. In the mean field limit, this model has a first-order glass transition temperature T_g where the spin glass susceptibility stays finite, but at a temperature $T_c > T_g$, a dynamical transition (similar to MCT) occurs. If short-range versions of this model

also have such a transition, the associate glass correlation length would stay finite at T_g . Potts spin glasses may be a reasonable model for quadrupolar glasses (i.e., strongly diluted molecular crystals, Binder (1998)).

A very interesting idea suggests that a characteristic length should not be defined from any purely static correlation function, but rather one has to consider the dynamics. This is implicit in the “cooperatively rearranging regions” of Adam and Gibbs (1965), and can be demonstrated in lattice gas models with two-vacancy assisted hopping (Donati and Jäckle 1996). While this model is rather abstract, recently a growing length has been extracted from displacement–displacement correlation functions separated in time by the relaxation time of α -relaxation (Bennemann *et al.* 1999b). A detailed theory of these observations is still lacking.

6. Rouse Model vs. Cage Effect

Polymers in a melt far above T_g undergo a Brownian motion, described by the Rouse model (for short chains) or reptation model (for entangled long chains), respectively (Doi and Edwards 1986). These aspects have played no role in the concepts described so far. However, as $T \rightarrow T_g$, this description of polymer dynamics and the glassy dynamics must become parts of a common framework! This problem has recently been elucidated by simulations (Bennemann *et al.* 1999c), for short nonentangled polymers modeled by bead–spring chains, presenting an analysis of the Rouse modes. These “normal coordinates” are defined in terms of the monomer positions $\vec{r}_n(t)$ as

$$\vec{X}_p(t) = N^{-1} \sum_{n=1}^N \vec{r}_n(t) \cos \left[\left(n - \frac{1}{2} \right) \pi p / N \right];$$

$$p = 0, 1, \dots, N-1 \quad (9)$$

If the Rouse model holds, these modes are orthogonal to each other and decay with a single exponential,

$$\phi_{pq}(t) = \langle \vec{X}_p(t) \cdot \vec{X}_q(0) \rangle / \langle \vec{X}_p(0) \cdot \vec{X}_q(0) \rangle$$

$$= \delta_{pq} \exp[-t/\tau_p(T)] \quad (10)$$

where

$$\tau_p(T) = \zeta(T)b^2 / \{12k_b T [\sin(p\pi/2N)]^2\}$$

$$\rightarrow \zeta(T)N^2 b^2 / [3\pi^2 k_b T p^2] \quad (11)$$

the last result being true for $p/N \ll 1$. The simulations showed that near the glass transition, the orthogonality property remains true and although Eqn. (10) does not hold—rather the Rouse modes are described by stretched exponentials {Eqn. (2)}, with an exponent β that decreases with increasing p from $\beta \approx 1$ for $p = 1$ to $\beta \approx 0.7$ for large p —Eqn. (11) still is an excellent approximation. All the glassy dynamics hence is

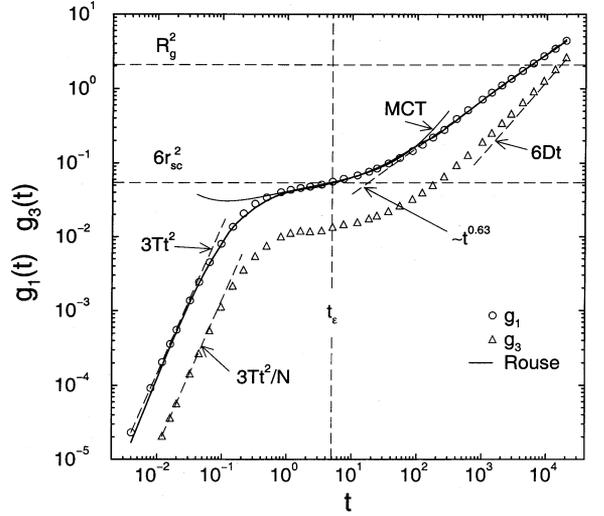


Figure 2

Log-log plot of the mean-square displacements of an inner monomer, $g_1(t)$ and of the chain’s center of mass, $g_3(t)$, vs. time for $T = 0.48$ (Note that nonbonded monomers interact through a Lennard-Jones potential, $U_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, and units $\epsilon = 1$, $\sigma = 1$ are chosen the chain length being $N = 10$). The initial ballistic behavior ($g_1(t) = 3Tt^2$, $g_3(t) = 3Tt^2/N$) is followed by the regime where the monomers are confined in cages formed by their neighbors. This is described here by the MCT theory in the β -relaxation regime, where the characteristic length $r_{sc} \approx 0.03$ which is reached at $t_\epsilon = 4.933$ (time being measured in standard molecular dynamics units, $\tau_0 = \sigma(m/\epsilon)^{1/2}$, m being the mass of the effective monomers). For $t \gg t_\epsilon$ MCT becomes the von Schweidler law, $g_1(t) \propto t^{0.75}$. However, this law holds only for $g_1(t) \sim < 1$, while then a crossover to Rouse-like relaxation occurs. Due to the shortness of the chains, $g_1(t) \propto t^{0.63}$ instead of the theoretical $t^{1/2}$ law is observed. Finally (beyond the range of the figure), a crossover to ordinary diffusion ($g_1(t) = g_3(t) = 6Dt$) occurs (if $g_1(t) \gg R_g^2$, the mean square gyration radius of the chain). From Bennemann *et al.* (1999c).

subsumed in the friction coefficient $\zeta(T)$ in Eqn. (11), which follows approximately Eqn. (1) [or a power law near the critical temperature of MCT, respectively].

It is instructive to consider the time-dependence of mean-square displacements near the glass transition (Fig. 2). MCT describes motions on very small scale—where chain connectivity plays practically no role—while the Rouse-like dynamics only sets in on time—and length scales where monomers have “escaped” from their cages.

7. Discussion

It should be evident now that an accepted theory of the glass transition does not yet exist! We have discussed various concepts—MCT describing the onset of the

cage effect, the decrease of configurational entropy and its consequences, the decrease of free volume near T_g , the idea of a growing characteristic length. There is some evidence for all these concepts, but what is lacking is a unified theory which puts all these concepts in place in a coherent picture. Many experimental properties of polymer melts can be qualitatively reproduced nicely by simplified, coarse-grained models suitable for simulation studies.

Such models are the bond fluctuation model (where the tendency to form a glass results from the geometric frustration induced by the energetic preference of long bonds that eliminate free volume) or the bead-spring model, where the intermonomer distance along the chains (preferred by the spring potential) and between nonbonded monomers are incommensurate, preventing crystallization. These models have shown that MCT is useful for a description of small-scale motions, where monomers are essentially confined in the cages formed by their neighbors, so chain connectivity is not much felt. So, the slowing down near the glass transition can, on the level of the Rouse/reptation models, simply be incorporated in the friction coefficient. Thus, the glass transition in polymer melts is not essentially different from small molecule materials, and it makes sense to apply “universal” theories of the glass transition to polymers, too.

There are many important topics that we have not touched upon, such as “dynamic heterogeneity” (e.g., Sillescu 1999), theories of aging phenomena (e.g., Sollich 1998), violation of fluctuation–dissipation relations (Barrat and Kob 1999), etc.

Also, the above discussion of the “main” concepts is by no means complete—for alternative ideas see Hunt (1994), Vilgis (1994), Phillips and Thorpe (1985) and Phillips (1982), for instance.

See also: Structure of Polymer Glasses: Short Range Order; Glass Transition

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