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The glass transition in polymer melts: a review of recent Monte Carlo results

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Abstract. This paper briefly reviews recent results of extensive Monte Carlo simulations for the glass transition of polymer melts. The simulation used the bond-fluctuation model, a lattice model, which exhibits glassy behaviour due to the development of a competition between packing constraints and chain stiffening at low temperatures. For this model static and dynamic properties were analysed, such as the influence of the cooling rate and of the chain length on the glass transition temperature, physical aging effects, the time-dependences of various mean-square displacements and structural relaxation functions and the temperature-dependences of structural relaxation times and of the diffusion coefficient. Besides an outline of these results we discuss in some detail a quantitative comparison between the incoherent intermediate scattering function and the extended mode-coupling theory and between the entropy of the melt and the Gibbs–Di Marzio theory.

1. Introduction and description of the model

Glass-like freezing is a rather general phenomenon. It is observed not only for structurally complex materials, such as polymers, but also for ionic salts, low-molecular-mass organic liquids, colloidal suspensions and so on [1, 2]. Despite the differences in chemical structure and in interaction potential of these (fragile) glass formers, their vitrification process exhibits common features. Among them are, for instance, the great increase in the structural relaxation time, a phenomenon not observed during the crystallization process, and the pronounced stretching of the corresponding relaxation functions [1, 2].

The theoretical concepts to explain the microscopic origin of these phenomena are still rather controversial and lead to many questions. Is the glass transition the precursor of an underlying (second-order) phase transition, which would occur in the limit of infinitely slow cooling? Such a point of view is, for instance, suggested by the free-volume theory [3] or the Gibbs–Di Marzio theory [4]. If so, to what extent do non-equilibrium effects blur this transition and is there a corresponding order parameter, whose spatial correlations grow as the glass transition temperature T_g is approached? Or, can one perhaps interpret the glass transition as a percolation phenomenon in the sense that the molecules form clusters which percolate at the (thermodynamic) glass transition? This physical picture has recently been proposed again by analogy to the behaviour of spin glasses [5]. On the other hand, mode-coupling theory [6, 7] challenges the perception of an underlying static transition. It rather connects the glass transition to a change in the dynamic behaviour of the glass former, which occurs at a critical temperature $T_c > T_g$.

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In view of this stratified situation computer simulations may be helpful to complement the experimental and theoretical findings [8]. Although these simulations are restricted to small samples and short observation times compared to experiments, they have the advantage that many different static and dynamic properties can simultaneously be calculated for a suitably defined model. Such a model may either be atomistically detailed to study (short-time) properties of a specific material or highly simplified to investigate general features of the glassy behaviour and to contribute to answering some of the above-posed questions.

The present paper summarizes recent results for such a simplified model, the bond-fluctuation model, of a glassy polymer melt [9]. This model consists of linear monodisperse chains on a (simple cubic) lattice. The chain length is $N = 10$, which roughly corresponds to a degree of polymerization of 30–50 for simple polymers, such as polyethylene [10]. The simulation therefore deals with fairly short, oligomeric chains. These chains interact by a hard-core potential and possess an internal energy that increases their stiffness with decreasing temperature. During supercooling the tendency of a single chain to expand generates a competition with the associated enlarged volume requirement of all chains. In a dense melt these opposing forces greatly slow down the structural relaxation and induce the glassy behaviour of the model. This behaviour will be described in the next section.

2. The glassy behaviour of the bond-fluctuation model

The above-mentioned competition between the internal energy and the packing constraints of the polymers prevents the melt from crystallizing so that it may easily be supercooled. During the supercooling process the structural relaxation time of the melt increases in a non-Arrhenius fashion [9, 11, 12]. As soon as it has become comparable to the time scale of the simulation the melt freezes in an amorphous structure (as manifested by the static structure factor [9, 13]). The resulting (kinetic) glass transition temperature T_g depends both on the cooling rate [9, 11] and on the chain length [9, 14]. It varies inversely with the chain length in a linear fashion and with the cooling rate in a nonlinear fashion. Both of these results are also found in experiments [15, 16].

If one further equilibrates the melt in the temperature region close to the kinetic glass transition the model exhibits the phenomenon of physical aging [15, 17]. A first analysis of these effects [18] shows that the approach towards equilibrium is an extremely stretched process which obeys an aging-time–temperature superposition property. Similar observations have also been made in experiments [15, 17].

If one removes these non-equilibrium effects sufficiently the incoherent intermediate scattering function $\phi_q^s(t)$ decays in two steps [16, 19]. Such a two-step relaxation is predicted by the mode-coupling approach [6, 7] to the structural glass transition. It should occur within an intermediate time window (the β -relaxation regime), provided that the temperature is close to a critical temperature T_c (experimentally $T_c > T_g$) [6, 7]. For the β -relaxation regime $\phi_q^s(t)$ may be expressed as

$$\phi_q^s(t) = f_q^{sc} + h_q^s t_0^a \left(\frac{1}{t_\sigma^a} g(\hat{t}, \pm 1, \hat{\delta}) \right) \quad (1)$$

where f_q^{sc} (the non-ergodicity parameter) and h_q^s (the critical amplitude) are temperature-independent quantities. The temperature-dependence of $\phi_q^s(t)$ results from the microscopic time scale t_0 (not specified by mode-coupling theory at present) and the β -scaling function

g which depends on the scaled time

$$\hat{t} = \frac{t}{t_\sigma} \quad t_\sigma = t_0 |\sigma|^{-1/2a} \quad \sigma = C(T_c - T) \quad (2)$$

and on the scaled hopping parameter

$$\hat{\delta} = \delta \frac{t_\sigma^{1+2a}}{t_0^{2a}} \quad \delta \propto \exp\left(-\frac{A}{\kappa_T T}\right). \quad (3)$$

In equations (2) and (3) C and A are system-dependent constants, a is a temperature-independent (critical) exponent and κ_T is the isothermal compressibility. The last equations mathematically express the physical picture that, close to T_c , the neighbours of a fluid particle build up long-lived free-energy barriers (an ergodicity-breaking ‘cage effect’), which may be overcome by thermally activated processes (an ergodicity-restoring ‘hopping process’). Figure 1 presents a comparison of the theory with the simulation data. It shows that (the extended) mode-coupling theory can quantitatively describe the relaxation of $\phi_q^s(t)$ within an intermediate time window [19]. During the fit all quantities that do not vary critically with temperature could be replaced by their asymptotic values at T_c , namely $f_q^{sc} = 0.8$, $h_q^s = 0.406$, $a = 0.239$ and $\delta = 2.8 \times 10^{-8}$ [20]. The temperature-dependence of the simulation data may be related to that of the (polymer-specific) short-time scale t_0 (which is strongly temperature-dependent) and to that of σ , yielding $T_c \approx 0.15$ [19].

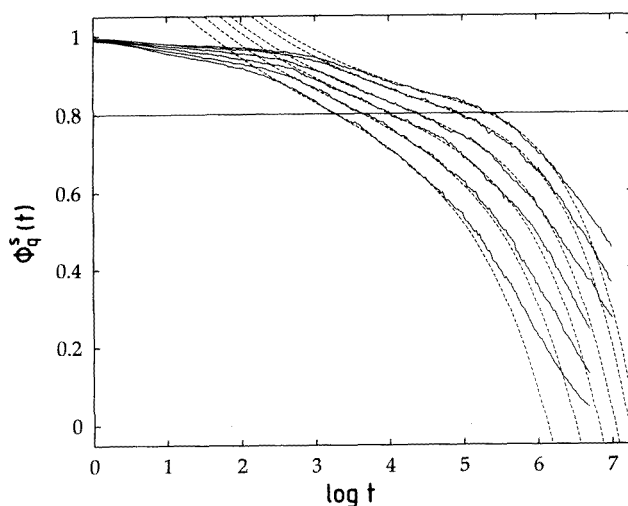


Figure 1. An extended mode-coupling analysis (broken lines) of the simulation data (full lines) for the temperatures $T = 0.16, 0.17, 0.18, 0.19, 0.20$ and 0.21 (the temperature decreases from left to right in the figure) [20]. The horizontal full line represents the value of the non-ergodicity parameter (see equation (1)). From [19].

Experimentally T_c is larger than the Vogel–Fulcher temperature T_0 , at which the structural relaxation times (seem to) diverge [21]. Similar results are also found for the present model. An extensive analysis of many different dynamic properties (the relaxation function of the bond vectors, of the radius of gyration and so on, mean-square displacements of the monomers and chains, Rouse-mode analysis), which were calculated from completely equilibrated configurations for a temperature regime slightly above T_c ($T \geq 0.21$), yields $T_0 \approx 0.12$ – 0.13 [12].

Using these completely equilibrated configurations the entropy of the melt was determined [22] and compared with various theoretical predictions: the Gibbs–Di Marzio theory, a theory by Flory for semi-flexible polymers and an extended theory by Wittmann considering Milchev’s criticism of Flory’s calculation [23]. Whereas the Gibbs–Di Marzio theory and the Flory theory predict that the entropy vanishes at a finite temperature T_K (experimentally there is evidence that $T_K \approx T_0$ [24]), Milchev’s approach yields $T_K = 0$. In order to apply the theories to the simulation data three theoretical input parameters, the bond angle flexibility, the number of ‘holes’ in the melt and the coordination number of a monomer, have to be determined. This was done in a separate simulation (after suitable generalization of the theoretical lattice model to the bond-fluctuation model [23]) so that the comparison contains no adjustable parameter. Figure 2 shows the result. The simulated entropy decreases with decreasing temperature, but exhibits no (clear) tendency to vanish at a finite temperature. Therefore Milchev’s theory lies closer to the simulation data than do the Gibbs–Di Marzio or Flory theories. Certainly, further simulation points at low temperature are needed to corroborate this analysis and to allow a significant test of the Adam–Gibbs relation [25] between the entropy and the structural relaxation times. Work in this direction is under way.

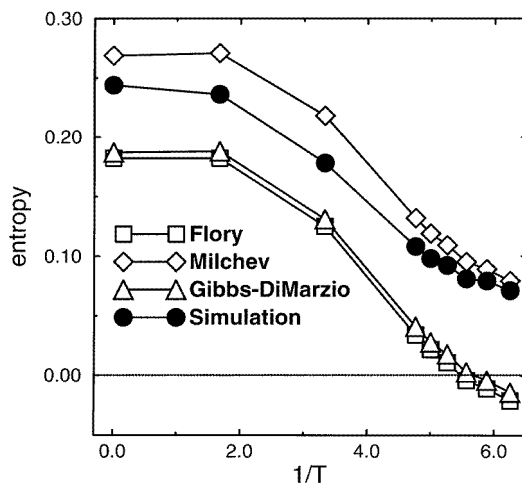


Figure 2. A comparison of the temperature-dependence of the entropy per lattice site s with three theoretical predictions. Whereas the Gibbs–Di Marzio and Flory theories predict that the entropy vanishes at a finite temperature T_K , Milchev’s theory yields $T_K = 0$ [20]. From [23].

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