Direct computation of characteristic temperatures and relaxation times for glass-forming polymer liquids

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Characteristic temperatures and structural relaxation times for different classes of glass-forming polymer liquids are computed using a revised entropy theory of glass formation that permits the chain backbone and the side groups to have different rigidities. The theory is applied to glass formation at constant pressure or constant temperature. Our calculations provide new insights into physical factors influencing the breadth of the glass transition and the associated growth of relaxation times. © 2005 American Institute of Physics. [DOI: 10.1063/1.2035087]

Numerous observations indicate a strong correlation between glass formation and a rapid drop of fluid entropy upon cooling.1–4 Gibbs and DiMarzio5 (GD) first formulated a thermodynamic theory of glass formation in polymer fluids, based on the identification of an “ideal” glass transition with the vanishing of the configurational entropy in a mean-field Flory-Huggins lattice model for a melt of semiflexible polymers. The configurational entropy $s(T)$ characterizes the number of distinct fluid conformational states and excludes the contributions from vibrational motions that are present in the experimentally measured fluid entropy. The lack of a clear relation between $s(T)$ and the measured entropy has led to persistent uncertainties in experimental tests of the entropy theory of glass formation (see below). Further progress in the entropy theory of glass formation emerged from the Adam–Gibbs (AG) relation between the rate of structural relaxation and the configurational entropy.6 Despite some idealizations, these theories still provide the foundation for many current ideas about glass formation.

Although the GD theory claims numerous successes in rationalizing trends in the glass transition temperature $T_g$ with molecular structure,5 its prediction of a vanishing $s(T)$ at a finite temperature $T_0$ has been questioned,6,7 casting doubt on the existence of an ideal glass transition. In our view, the question of whether $s(T)$ vanishes for $T_0 > 0 \, \text{K}$ is academic since it is impossible to equilibrate fluids at temperatures below $T_g$ where the fluid entropy and $s(T)$ extrapolate to zero. Thus, we have developed a new entropy theory that focuses on the temperature regime above $T_g$ where these conceptual difficulties do not arise and where a thermodynamic description of polymer melts is reliable. Our theory does not invoke the existence of an entropy catastrophe to define the glass transition, but still retains the notion of a temperature $T_0$ at which $s(T)$ extrapolates to zero as found experimentally for the total fluid entropy. Our entropy theory emphasizes the short-range correlations in the fluid that stem from chain connectivity, semi-flexibility of the chain backbone and side groups, and monomer structure. These variables are clearly relevant to describing how molecular structure affects the rate of structural relaxation in real polymer melts. This more realistic treatment of the thermodynamics of polymer melts is achieved through a lattice cluster (LCT) generalization of the Flory theory of semiflexible polymer melts.8

According to the Adam–Gibbs theory,3 the structural relaxation time of a polymer fluid is related to $s(T)$ through the well-known AG relation,

$$\tau = \tau_0 \exp(\beta \Delta \mu [s'/s(T)]),$$

where $\tau_0$ is the high-temperature limiting relaxation time in the fluid, $\Delta \mu$ is a (property and system dependent) activation energy at high temperatures, and $s'$ is the postulated high-temperature limit of $s(T)$. The AG equation for $\tau$ implies that the “fragility” of glass-forming liquids is related to the rate of change of $s(T)$ and to the strength of the van der Waals interactions and other microstructure effects through $\Delta \mu$.

A crucial modification of the classic entropy theory lies in our identification of $s$ in Eq. (1) with the configurational entropy $s_c$ per lattice site (an entropy density) rather than with the entropy $s_{c,n}$ per unit mass, as commonly assumed in analyzing experiments.9 This identification enables us to explain many aspects of the thermodynamics and dynamics of glass formation over the entire temperature range of this process and is consistent with the simulations of diffusion in lattice models of polymer melts by Binder et al.8 Since the complex changes in the dynamics of glass-forming liquids often initiate for $T > 2T_g$, it is important to determine the breadth of this transition by estimating the temperatures characterizing the beginning, middle, and end of this broad transition phenomenon. Thus, we not only distinguish between $T_g$ and the extrapolated temperature $T_0$, but also evaluate the onset temperature $T_0^*$ for the supercooled regime (below which $\tau$ no longer displays an Arrhenius temperature dependence) and the crossover temperature ($T_f$ in our notation) separating well-defined temperature regimes in which both $s_c$ and $\tau$ exhibit a rather distinct temperature depen-

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dence. The characteristic temperatures \( T_A, T_F \), and \( T_0 \) are determined from the maximum \( s ' \) of \( s_c \), the inflection point in \( s_c(T) \), and the extrapolated vanishing of \( s_c(T) \), respectively. The kinetic glass transition temperature \( T_g \) is calculated from a Lindemann-type relation \(^{10} \) for the instability of the solid (glass) to liquefaction when the mean interparticle separation increases by 12.5%-15% over the value for the “solid” at \( T_0 \),

\[
\frac{\nu(P, T = T_0) - \nu(P, T = T_g)}{\nu(P, T = T_0)} = \begin{cases} 
0.027 & \text{F-S class} \\
0.016 & \text{F-F class},
\end{cases}
\]

where \( \nu \) denotes the specific volume and the F-S and F-F polymer classes are defined below. Elsewhere, we discuss the application of this Lindemann criterion in detail.\(^{11} \)

Previous attempts at comparing the entropy theory to experiments are complicated by the difficulty of estimating \( s(T) \) for real fluids. For instance, Richert and Angell\(^{1} \) suggest that the AG model generally “breaks down” for temperatures 20-30 K above \( T_g \). On the other hand, molecular-dynamics simulations for model liquids\(^ {12} \) and Monte Carlo simulations of diffusion in lattice polymer fluids\(^ {8} \) both claim consistency with the AG model at temperatures far above \( T_g \). These conflicting conclusions are perhaps not surprising given that experiments and simulations invoke completely different measures of “configurational entropy.” The experimental studies identify \( s(T) \) of the AG theory with the molar fluid entropy \( S_{\text{exc}} \) relative to the crystalline or low-temperature glass state, while the simulations’ estimate of \( s(T) \) is obtained from the number of accessible configurational states. Since \( S_{\text{exc}} \) contains a substantial vibrational contribution, it is entirely unclear\(^ {13} \) if \( S_{\text{exc}} \) provides a good estimate of the \( s(T) \) that appears in Eq. (1). Below we suggest a simple logical alternative that establishes consistency between experimental and simulated estimates of the configurational entropy.

Experimental studies\(^ {14,15} \) of the structural origin of fragility in polymers suggest that polymers with simple side branch structures (e.g., polybutadienes and many polyolefins) are rather strong, while polymers with bulky, rigid side groups (e.g., polystyrene) are more fragile. Since the relative rigidity of the side groups and the chain backbone is the essential parameter governing the nature of glass formation in polymers, we assign different bending energies \( E_b \) and \( E_g \) for a pair of chain backbone and side group bonds, respectively, when two semiflexible bonds lie in orthogonal directions (gauche bonds). Calculations are performed for two generic categories of polymers: chains with flexible backbone and flexible side groups and chains with flexible backbone and rigid side branches, termed the F-F and F-S polymer classes, respectively. For simplicity, a common united atom monomer structure (shown in the inset to Fig. 1) is used in both classes. The F-F class is specified by \( E_h/k_B = 400 \text{ K} \) and \( E_g/k_B = 400 \text{ K} \) for \( \nu(P, T = T_0) \). The same \( E_h/k_B = 400 \text{ K} \) is assigned to the F-S chains, but a relatively large \( E_g/k_B = 4000 \text{ K} \) represents the stiff side groups. All computations refer to a pressure of 1 atm (0.101 325 MPa), unless otherwise specified, and are performed for the nearest-neighbor van der Waals interaction energy \( e/k_B = 200 \text{ K} \) [a typical value for poly (\( \alpha \)-olefins)] and the unit volume as \( v_{\text{cell}} = a_{\text{cell}}^3 = (2.7)^3 \text{ Å}^3 \). One trans and two gauche conformations are assumed for each backbone and side chain bond pair.\(^ {5} \)

![FIG. 1. Comparison of the LCT configuration entropies per site \( s_c / N \) and per united atom group \( s_{\text{u,u}} / (nM) \) for constant pressure \( P=1 \text{ atm polymer fluids} \ (M=40 \text{,001}) \). \( N_c, n, \) and \( M \) are the numbers of lattice sites, polymer chains, and united atom groups in a single chain, respectively. The molar mass is proportional to \( M \). The inset depicts the monomer structure used in our calculations.](Image 323x583 to 550x742)
former equation for \( \tau \) is just the well-known Vogel–Fulcher–Tammann–Hesse (VFTH) equation\(^{16}\) and was theoretically rationalized by Adams and Gibbs.\(^3\) A very different temperature dependence of \( s_\tau T \) emerges from our calculations for \( T > T_A \), however.

The ratio \( z^* = s_\tau / s_\nu(T) \) in Eq. (1) for \( \tau \) is generally interpreted as the average number of monomer elements in the dynamic cooperatively rearranging regions, structures that are hypothesized to form in cooled glass-forming liquids and that are associated with a growing activation energy barrier for transport. Figure 2 presents \( z^* \) as a function of the reduced temperature \( \delta T_A = |T - T_A| / T_A \). While \( z^* \) is unity at \( T_A \), it grows upon cooling, becoming about 2 near \( T_I \), and about 4 or 5 near \( T_g \). The fit to \( z^* \) as a function of \( \delta T_A \) in Fig. 2 is parabolic to a high degree for both polymer classes, i.e., \( z^* = -1 + C_s(\delta T_A)^2 \) for \( T_A - 100 K < T < T_A \), where \( C_s \) depends on polymer mass and polymer class. A similar scaling of \( z^* \) for \( T = T_A \) emerges from the theory of Schweizer and Saltzman.\(^{17}\) Remarkably, the LCT estimates of \( z^* \) are also compatible with recent experimental estimates of the reduced activation energy barrier \( \Delta E(T > T_A) \) for diverse fluids by Kivelson \textit{et al.} \(^{18}\) although with a somewhat larger exponent (8/3). Figure 2 shows that \( C_s \) is larger for F-S polymers, which in combination with Eq. (1) implies that \( \tau \) has a stronger temperature variation for the more fragile F-S polymers. The parameter \( C_s \) provides a measure of fragility in the high-temperature regime of glass formation, complementing the fragility parameter \( K_s \) appropriate to the low-temperature regime of glass formation.

Our extension of the entropy theory is combined with an empirically motivated relation between \( \Delta \mu \) and \( T_H \), namely, \( \Delta \mu / k_B \approx 6 T_H \), which enables explicit computation of \( \tau \) without adjustable parameters beyond the molecular parameters inherent in the LCT model. The resultant empirical connection between dynamic quantities and microscopic parameters of the LCT also permits us to explore the structural origins of fragility in glass-forming liquids, as will be described elsewhere. The approximate relation \( \Delta \mu / k_B \approx 6 T_H \) is based on the molecular-dynamics simulations for both binary Lennard-Jones glass-forming liquids\(^19\) and a Lennard-Jones bead model of polymer melts\(^20\) for which \( T_H \) is identified with the fitted mode-coupling temperature \( T_{mc} \). Comparisons of direct LCT computations for \( T_H / T_g \) and \( \tau (T = T_H) \) with literature estimates\(^{21,22}\) of \( T_{mc}/T_A \) and \( \tau (T = T_{mc}) \), respectively, confirm this identification of \( T_H \) with \( T_{mc} \). The relation is also supported by viscosity data for a wide range of glass-forming salts,\(^{23}\) where the high-temperature regime above \( T_H \) is experimentally accessible.

The revised entropy theory also provides detailed predictions for the dependence of \( \tau \) on temperature, pressure, molar mass, and monomer structure over the entire glass-formation temperature region from \( T_H \) to \( T_A \). Figure 3 illustrates the computed \( \tau \) as a function of the reduced inverse temperature \( T_{sc} / T \) for F-S and F-F polymer class fluids at \( P = 1 \) atm. We predict that \( \tau (T = T_H) \) at the onset of glass formation is on the order of a few picoseconds for both polymer classes, while \( \tau (T = T_I) \) is generally a few orders of magnitude larger, i.e., \( O(10^{-9} \text{ s}) \). The predictions in Fig. 3 agree reasonably well with recent tabulated estimates\(^{22}\) of \( \tau \) at the nominal mode-coupling temperature (the analog of \( T_H \)) for a wide variety of glass-forming liquids where \( \tau \) is \( O(10^{-8} \text{ s}) \).\(^{24}\) Figure 3 further exhibits \( \tau \) as increasing rapidly for \( T < T_H \), with \( \tau (T = T_g) \) becoming as large as \( 10^3 \text{ s} \), as is typical for glass-forming liquids.\(^{25}\) [Alternatively, \( T_g \) could be defined by \( \tau (T_g) = 10^3 \text{ s} \), and the resulting \( T_g \) could be used to derive the Lindemann criterion.] For both F-F and F-S polymer classes, \( \tau \) varies similarly with temperature, although the steepness of the rise in \( \tau \) at low temperatures is less pronounced for F-F polymers, reflecting the “stronger” nature of this class of fluids.

Glass formation can also be induced by increasing pressure at constant temperature.\(^{25,26}\) Specifically, an empirical pressure analog of the VFTH equation has been used to describe data for \( \tau (P = \text{const}) \) at variable pressures.\(^{25,26}\) This pressure analog, \( \tau (P) \approx \pi \exp[\alpha P/(P_0 - P)] \), where \( \alpha = \alpha (T) \) is a constant, exhibits an apparent singularity at a critical pressure \( P_0 \) which is the counterpart of the “Vogel temperature” \( T_{mc} = T_0 \) of the original VFTH equation. We represent \( \tau \) at fixed \( T \) and variable \( P \) as a generalization of Eq. (1) by \( \tau (P) = \tau_{sc} \exp[\beta \mathcal{E}_{AG}(P)] \), with \( \mathcal{E}_{AG}(P) \) written equivalently as

\[
\mathcal{E}_{AG}(P) = \Delta \mu [s_{\nu,0} / s_{sc,0}] [s_{\nu,0} / s_{\nu}(T, P)],
\]

where \( s_{sc,0} = s_{sc,0}(T) \) is the site configurational entropy at \( P = 1 \) atm and where a weak pressure dependence of \( \Delta \mu \) and \( s_{\nu} \)
is neglected.27 The equation for $\tau(P)$ can be rearranged as

$$\tau(P) = \tau(P = 1 \text{ atm}) \exp[\beta \mathcal{E}_{AG}(P = 1 \text{ atm}) \delta_s],$$

where $\delta_s = [s_{c,e} / s_e (T,P)] - 1$. The consistency of Eq. (3) with the empirical correlation for $\tau(P)$ requires that $\delta_s$ is inversely proportional to the reduced pressure $\tilde{P} = (P - P_0) / P$ as shown in Fig. 4 for an isothermal $F$-$S$ polymer melt. Thus, the origin of the pressure analog of the VFTH equation25 naturally follows from the entropy theory. The inset to Fig. 4 presents the critical pressure $P_0$ as scaling linearly with temperature, in agreement with experiments.28

Generally $P_0$ is a function of $T, e, E_b, E_s$, and monomer structure.

In summary, our analytic theoretical framework for both equilibrium and relaxation properties of glass-forming polymers provides a recipe for calculating the multiple characteristic temperatures of glass formation in polymer fluids and generates an understanding of the regularities observed in the magnitude of $\tau$ at these temperatures. This is the first analytical theory describing these aspects of glass formations in polymer fluids. Moreover, the theory is the first to explain the impact of different side group and backbone chain rigidities on glass formation and provides a theoretical basis for the pressure analog of the VFTH equation for $\tau$.

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