

The Glass Transition Temperature of Polymer Melts[†]

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We develop an analytic theory to estimate the glass transition temperature T_g of polymer melts as a function of the relative rigidities of the chain backbone and side groups, the monomer structure, pressure, and polymer mass. Our computations are based on an extension of the semiempirical Lindemann criterion of melting to locate T_g and on the use of the advanced mean field lattice cluster theory (LCT) for treating the thermodynamics of systems containing structured monomer, semiflexible polymer chains. The Lindemann criterion is translated into a condition for T_g by expressing this relation in terms of the specific volume, and this free volume condition is used to calculate T_g from our thermodynamic theory. The mass dependence of T_g is compared to that of other characteristic temperatures of glass-formation. These additional characteristic temperatures are determined from the temperature variation of the LCT configurational entropy, in conjunction with the Adam–Gibbs model for long wavelength structural relaxation. Our theory explains generally observed trends in the variation of T_g with polymer microstructure, and we find that T_g can be tuned either upward or downward by increasing the length of the side chains, depending on the relative rigidities of the side groups and the chain backbone. The elucidation of the molecular origins of T_g in polymer liquids should be useful in designing and processing new synthetic materials and for understanding the dynamics and controlling the preservation of biological substances.

I. Introduction

Although we still lack a truly predictive molecular theory of glass-formation, the thermodynamic theory of Gibbs and DiMarzio^{1–3} (GD) has achieved substantial success in rationalizing observed trends for the variation of the glass transition temperature T_g of polymeric materials with molecular parameters. In particular, GD theory provides definite predictions for how the “ideal glass transition temperature” T_0 (defined by the vanishing of the configurational entropy s_c) varies with chain molar mass, chain topology (rings vs linear polymers), cross-linking, the addition of plasticizers, etc., and these predictions generally follow experimental trends for the glass transition temperature T_g (determined from the maximum in the specific heat or from a change in the slope of the density as a function of temperature^{4–6}). Despite these phenomenological successes and the corresponding attractive view of glass-formation as arising from the vanishing number of configurational states accessible to the fluid at low temperatures, the precise link between T_0 and T_g remains obscure in GD theory. In reality, the measured T_g lies^{7–11} about 30–50 K above the experimentally determined T_0 , so that T_g is often estimated roughly from GD theory according to the “rule of thumb” as $T_g = T_0 + 50$ K. The uncertainty in locating T_g is certainly one drawback of the GD approach. In addition, difficulties of performing equilibrium measurements at temperatures below T_g and of estimating the *configurational entropy* from specific heat measurements¹² preclude the determination of whether s_c vanishes at a nonzero temperature below T_g and thus prevent a direct test of GD theory. On the positive side, the phenomenological success of

GD theory supports the qualitative physical picture of glass-formation as a dynamical transition occurring due to the sparseness of accessible configurational states at low temperatures.

Our goal lies in developing a version of the entropy theory of glass-formation that self-consistently explains the relation between T_g and T_0 within a predictive molecular framework. A theory of this kind should also provide a recipe for evaluating other characteristic temperatures of glass-formation that have been identified in recent years, namely the onset temperature T_A for glass-formation, where the configurational entropy begins to drop from its high-temperature value,^{13,14} and a “crossover temperature”^{7,8,15} T_I (often denoted as T_B or T_c in the literature) separating high and low temperature regimes with significantly different characters of structural relaxation and with structural relaxation times τ exhibiting different temperature dependences. The crossover temperature T_I typically occurs^{7,8,15} at about $1.2T_g$ in fragile glass-forming liquids, and T_A is nearly proportional to T_g to a rough approximation.¹⁶ Hence, these other characteristic temperatures of glass-formation are apparently linked to T_g in ways that we would like to understand as well. Moreover, the link between T_g and these other temperatures provides an opportunity to further test the validity of our estimates of T_g .

In addition to explaining the experimental aspects of glass-formation discussed above, several theoretical issues must also be confronted by a sound entropy theory of glass-formation. The GD theory is a highly approximate mean field theory that implicitly involves a high-temperature expansion,¹⁷ and the lattice cluster theory is an extension of this high temperature expansion to include higher order terms arising from chain connectivity and monomer structure. The perturbative nature of these approaches frankly renders both unreliable at very low

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temperatures. Indeed, Gujrati and Goldstein¹⁸ note that GD theory violates rigorous bounds for the fluid entropy at low temperatures, and simulations of (lattice) polymer fluids by Binder and co-workers^{19,20} strongly suggest that the configurational entropy does not vanish at low temperatures, but instead approaches a low-temperature plateau. Although these observations cast doubt on the very existence of an “ideal” glass transition, the validity of the entropy theory remains intact if the theory is viewed more qualitatively as implying that the glass transition (T_g) occurs when the particle motion becomes “sufficiently congested” at low temperatures due to the sparseness of accessible configurational states. Of course, this vague idea requires quantification, as we address below.

A competing “free volume” model of glass-formation in polymer fluids by Fox and Flory²¹ has been developed into a successful and highly utilized phenomenological approach for the rate of structural relaxation in polymer fluids by Ferry,⁹ Simha,²² and their respective co-workers. The free volume model of polymer relaxation has its antecedent in Doolittle’s free volume model of transport in low molar mass fluids.^{23,24} This class of models describes glass-formation as ensuing when the free volume (defined below in terms of the specific volume v), rather than the configurational entropy, becomes critically small. Substantial data support¹⁰ the approximate validity of this estimate for a calorimetrically determined glass transition temperature T_g at constant pressure, but the value of the free volume at T_g is only inferred empirically. Moreover, glass-formation is known also to occur at constant volume, a situation that evidently cannot be analyzed by this simple free volume theory. Nevertheless, some qualitative truth certainly underlies the free volume description of polymer glass-formation.

In the present paper, we combine and extend these former approaches to modeling glass-formation by using the lattice cluster theory (LCT) for the thermodynamics of polymer melts in conjunction with the Lindemann criterion. In this revised entropy theory of glass-formation, both T_0 and T_g retain their former meanings as in the classical entropy and free volume theories of glass-formation,^{1–3,9,21,22} namely, the temperatures at which the configurational entropy *extrapolates* to zero and at which the free volume assumes a critical value, respectively. The *extrapolated* vanishing of the configurational entropy in our generalized entropy theory corresponds to the experimental procedure of extrapolating the excess fluid entropy to a vanishing value at low temperatures.^{4,25} Neither of these procedures implies that the fluid entropy (or configurational entropy) *actually vanishes* at a nonzero temperature below T_g . The question of whether the configurational entropy vanishes at $T_0 > 0$ is ill-posed, given that equilibrium measurements cannot be performed at temperatures well below T_g where the entropy catastrophe is predicted to occur. Thus, T_0 is defined within this restricted sense of an extrapolation and should not be taken as a literal condition for the vanishing of the configurational entropy.

Of course, other aspects of glass-formation must be explained besides the conceptual interpretation of T_g and its explicit computation in terms of molecular parameters. Ideally, a generalized entropy theory should predict the rate of long wavelength structural relaxation at *all* temperatures above T_g where the fluid can be equilibrated and where a thermodynamic description is reliable. We formally obtain such a theoretical tool by combining our LCT thermodynamic theory with the Adam–Gibbs (AG) model²⁶ of structural relaxation, which explicitly links the rate of structural relaxation to the configurational entropy s_c .²⁷ Although the Adam–Gibbs (AG) model

is not rigorously established, recent studies by Oppenheim and co-workers,²⁸ Lubchenko and Wolynes,²⁹ and Bouchaud and Biroli³⁰ have placed the AG model on a sounder theoretical foundation. Nevertheless, the combination of the LCT and AG theories enables us to provide quantitative predictions³¹ for the rate of structural relaxation over the entire temperature range of glass-formation, and these predictions are subject to clear experimental test. Moreover, by focusing on temperatures *above* T_g , we avoid conceptual pitfalls regarding whether the configurational entropy vanishes at $T_0 > 0$ and focus instead on testing the resulting entropy theory of glass-formation based on a reasonably accurate thermodynamic description of semiflexible polymer melts at higher temperatures than T_g .

Section II defines the Lindemann criterion and its application to glass-formation. Section III sketches the basic features of the LCT and the underlying model used to describe the thermodynamics of polymer melts. These two sections provide the theoretical foundation for our analytical calculations for the dependence of T_g and the other characteristic temperatures of glass-forming polymer liquids on monomer structure, relative backbone and side group rigidities, and molar mass. The calculations are summarized in section IV. Section V discusses correlations between T_g , specific volume, and fragility, while section VI briefly reviews the role of the isothermal compressibility and high-frequency shear modulus in characterizing the nature of the glass transition. Examples of LCT calculations for the influence of side group length and flexibility on T_g are illustrated in section VII.

II. Glass Transition as an Iso-Free Volume State

Once the dynamical “glass transition” occurs, equilibration of the fluid becomes extremely difficult, and a thermodynamic theory no longer applies at lower temperatures. On a molecular level, T_g corresponds to the temperature at which particles become spatially localized about well-defined average positions and exhibit constrained local dynamics similar to that within a crystal. However, this particle localization in a glass at T_g only remains for time scales up to a structural relaxation time. Very slow residual structural relaxation and molecular motions (other than vibrations) occur in supercooled liquids due to rare collective fluctuation events that provide the only remaining channel for molecular motion in the jammed fluid.³² This physical picture implies that the glass transition can be characterized on the molecular scale by a particle localization–delocalization transition, as in melting. In both cases, the transition arises from the rapid growth of elastic constants that emerge upon cooling due to the confining influence of ever more restrictive interparticle interactions. This viewpoint motivates us to extend the Lindemann localization–delocalization criterion^{33,34} for melting to glass formation, in accord with the prior suggestion by Xia and Wolynes,³⁵ who summarize physical evidence and independent theoretical arguments supporting the applicability of the Lindemann criterion to real structural glasses. We note that the Lindemann criterion has also been applied successfully to describe changes in the local dynamics of proteins³⁶ and atomic clusters,³⁷ so that its use has already extended far beyond its the original formulation in terms of crystal melting.

The calculation of the temperature variation of the reduced specific volume $\delta v(T)$ at constant pressure is an essential ingredient in the extension of the Lindemann criterion^{33–35,38–40} to the “softening transformation” in glass-forming liquids. The

reduced specific volume δv relative to its value at the limiting temperature T_0 (where s_c extrapolates to zero)^{1,31}

$$\delta v(T) = [\nu(T) - \nu(T = T_0)]/\nu(T) \quad (1)$$

is a well-defined macroscopic fluid property^{22,41} that quantifies how much “free space” exists, on average, for atomic motion in the polymer material. The definition of δv does not include the residual unoccupied space that is frozen in at temperatures lower than T_0 . The vanishing of $\delta v(T)$ at T_0 is consistent with a molecular scale definition of free volume based on Debye–Waller factors.⁴² The temperature T_0 is identified in our entropy theory with the Vogel temperature T_∞ at which the structural relaxation time extrapolates to infinity, rather than with the Kauzmann temperature T_K at which the molar excess entropy vanishes. The difference between T_∞ and T_K , which is apparently small for many fluids,⁷ may emerge because the configurational entropy is generally *not equivalent*^{43,44} to the excess entropy estimated from specific heat measurements.

According to the Lindemann melting criterion,^{33–35,38–40} the root-mean-square amplitude of particle displacements $\langle u^2 \rangle$ at the glass softening or crystal melting temperature is on the order of 0.1 times the interparticle separation $2R$.⁴⁵ The particular value depends on the type of ordering and on the nature of the intermolecular potential.³⁵ At one end of this range, the value ≈ 0.125 is characteristic of the melting of hard spheres^{46,47} (a reasonable model for molecules having simple symmetric geometrical structures), while values closer to 0.15 or even larger (0.17–0.185) are cited for particles having longer range interactions.^{38,39} When applied to a spherical particle of radius R in spherical cavity, this criterion implies that the ratio between the excess volume available for the particle’s center of mass motion and the particle’s own limiting low-temperature volume ranges from about $(0.25)^3 = 0.016$ to $(0.3)^3 = 0.027$. Correspondingly, we tentatively define the glass transition temperature T_g by the condition that the relative free volume $\delta v(T)$ at constant pressure achieves the high end of this range [i.e., $\delta v(T = T_g) = 0.027$] for relatively fragile polymers and a value $\delta v(T = T_g) = (0.25)^3 \approx 0.016$ for relatively strong polymers.⁴⁸ This choice is also heuristically motivated by the observation that the excess free volume ϕ_v is generally significantly smaller for strong polymer fluids. These definitions of T_g lead to the computed relaxation times $\tau(T = T_g) \sim \mathcal{O}(10^2 \text{ s} - 10^3 \text{ s})$ for both classes of fluids within our LCT-AG computational framework,³¹ and the estimates are consistent with the standard phenomenological definition^{49,50} of T_g in terms of the order of magnitude of τ . Of course, the Lindemann criterion only provides rough estimates of the experimental T_g (at which fluid properties abruptly change in cooling measurements) because the experimental T_g is an inherently uncertain quantity that depends somewhat on cooling rate, cooling history, etc.⁶ Essentially the same iso-free volume glass transition criterion as ours for fragile polymers [$\delta v(T = T_g) \equiv 0.025$] has been suggested empirically long ago by Ferry and co-workers.⁹ Our theory thus provides a theoretical basis for understanding these phenomenological observations that have previously been obtained by fitting free volume model parameters to experimental data.

III. Lattice Cluster Theory of Polymer Melt Glasses

We describe the thermodynamics of polymer liquids using the lattice cluster theory (LCT) generalization¹⁷ of the Flory approximation for semiflexible polymer fluids. This generalized lattice theory includes a perturbative treatment of *short-range*

correlations arising from chain connectivity, chain semiflexibility, and monomer structure. These three factors govern chain packing and thereby control glass-formation in real polymer fluids. Importantly, *different rigidities* are assigned to the chain backbone and the side groups since this stiffness disparity can be expected⁵¹ to influence the strength of the temperature dependence of the configurational entropy $s(T)$ and thus the rate of structural relaxation within the AG model. Another essential modification³¹ of the classic entropy theory¹ lies in our consideration of the configurational entropy s_c *per lattice site* (an entropy density) as the quantity to be used in the AG model rather than the entropy $s_{c,m}$ per unit mass as is commonly assumed^{52,53} in analyzing experiments. This modification enables the entropy theory to generate predictions for several characteristic temperatures of glass-formation, the magnitudes of τ at these temperatures,³¹ and the fragility of polymer fluids as a function of monomer structure, molar mass, and pressure.¹² (It is again emphasized that the configurational entropy cannot be reliably estimated from specific heat measurements.^{43,44})

Our new entropy theory^{12,31} predicts a series of characteristic temperatures T_A, T_I, T_0 describing, respectively, the onset of a drop in $s_c(T)$ [taken as the maximum $s_{c,*}$ of s_c], an inflection point in $s_c(T)$ T , and the extrapolated vanishing of s_c with T . The inflection point temperature T_I separates regimes of glass-formation that are characterized by a *qualitatively different* temperature dependence for s_c and τ . The above temperatures and the *kinetic* glass transition temperature T_g are identified as the basic characteristic temperatures of glass-formation³¹ and are determined from the conditions,

$$s_c(P, T = T_0) = 0 \quad (2)$$

$$\delta v \equiv \frac{\nu(P, T = T_g) - \nu(P, T = T_0)}{\nu(P, T = T_g)} = \begin{cases} 0.027 \text{ F-S and S-F classes} \\ 0.016 \text{ F-F class} \end{cases} \quad (3)$$

$$\left. \frac{\partial^2 [s_c(P, T) T]}{\partial T^2} \right|_{P, T = T_I} = 0 \quad (4)$$

$$\left. \frac{\partial s_c(P, T)}{\partial T} \right|_{P, T = T_A} = 0 \quad (5)$$

where $s_c(T)$ is the configurational entropy per unit volume³¹ and where the notation F–S, S–F, and F–F is explained below. Roughly speaking, T_A demarks the beginning of the glass transformation regime, and T_0 is the end. Hence, these temperatures together provide a measure of temperature breadth of glass-formation. The intermediate temperature T_I has a well-defined thermodynamic meaning, while T_g denotes a rough kinetic condition associating with fluid jamming. A comparative description of the molar mass dependence of these characteristic temperatures is presented in the next section.

Our model^{12,31} considers monodisperse structured monomer chains (i.e., each with M united atom groups) that interact with a common monomer averaged nearest neighbor van der Waals energy ϵ . Gauche energy penalties E_b and E_s are ascribed to sequential pairs of chain backbone and side group semiflexible bonds, respectively, when they lie along orthogonal directions. If $E_i = 0$ ($i \equiv b, s$), the bonds are fully flexible, whereas the bonds are completely rigid when $E_i \rightarrow \infty$. The model distinguishes three general classes of polymer fluids: chains with a flexible backbone and flexible side groups, chains with a

relatively flexible backbone and stiff side groups, and chains with a relatively stiff backbone and flexible side groups. These broad categories are termed the flexible–flexible (F–F), flexible–stiff (F–S), and stiff–flexible (S–F) classes of polymers, respectively.³¹ The side groups in all classes are short linear chains with three united atom groups attached to every other backbone unit. The F–F class of polymers is modeled by taking $E_b/k_B = E_s/k_B = 400$ K. The same E_b/k_B is ascribed to the F–S chains, but a relatively large $E_s/k_B = 4000$ K is chosen to represent the stiff side groups. The S–F class is specified by $E_b/k_B = 700$ K and $E_s/k_B = 200$ K and is only briefly analyzed. The choice of E_b and E_s for the S–F class is designed to reproduce observed values for T_g in a series of poly(*n*-alkyl methacrylates).⁵⁴ All computations refer to the pressure $P = 1$ atm (0.101325 MPa) and are performed for the nearest neighbor van der Waals interaction energy $\epsilon/k_B = 200$ K [a typical value⁵⁵ for poly(α -olefins)] and the unit cell volume $v_{\text{cell}} = (2.7)^3 \text{ \AA}^3$. Each backbone and side chain bond pair may adopt one trans and two gauche conformations, and the lattice coordination number z is chosen as $z = 6$, appropriate to a simple cubic lattice.

Calculations of δv from the LCT are straightforward. Equation 1, in combination with the LCT equation of state,^{17,56} enables expressing δv in terms of the polymer volume fraction $\phi(T)$,

$$\delta v(T) = [\phi(T) - \phi(T = T_0)]/\phi(T) \quad (6)$$

where $\phi(T) = 1 - \phi_v$ is computed from the LCT as a function of temperature T and pressure P (for the specified lattice cell volume v_{cell} , monomer structure, energies, etc.).

IV. Molar Mass Dependence of T_g

Parts a and b of Figure 1 display the polymer mass dependence of T_A , T_I , T_g , and T_0 for the F–F and F–S classes of polymers, respectively, following the semilog format presentation employed in analyzing⁵⁷ experimental data for T_g . The characteristic temperatures T_α in Figure 1a and 1b are normalized with the corresponding high molar mass limits $T_\alpha(M \rightarrow \infty) \equiv T_\alpha^\infty$, while the variable M ($M \propto M_{\text{mol}}$) is divided by the value M_g at which the ratio T_g/T_g^∞ nearly saturates, i.e., where $T_g(M \equiv M_g)/T_g^\infty \equiv 0.95$. (A separate paper¹² focuses on the relative magnitude of $T_\alpha^\infty/T_g^\infty$ as measures of glass fragility.⁵⁸) A stronger mass dependence of T_g for F–S polymers implies a larger value of M_g . All four characteristic temperatures exhibit the same physical trend, i.e., growing with increasing M and saturating to constants in the high molar mass limit $M \rightarrow \infty$. Comparison of Figure 1, parts a and b, reveals that these characteristic temperatures generally vary more strongly with M for the F–S polymers. All four characteristic temperatures T_α ($\alpha \equiv 0, g, I, A$) of glass-formation for F–S polymers exceed their counterparts for F–F polymers. The molar mass dependence differs among the various characteristic temperatures T_α , a feature that can be checked experimentally. Figure 1a and 1b show that T_0 and T_I have the strongest and the weakest dependence on M , respectively. This latter trend is also noticeable from the insets to Figure 1a and 1b, which display the inverse ratios T_α^∞/T_α as functions of $1/M$. The ratios T_α^∞/T_α *universally* scale in a linear fashion with $1/M$, but their slopes vary between the different T_α . (The linearity of the scaling is less accurate for the inverse ratio T_α/T_α^∞).

V. Fragility and Free Volume

One recognized and striking observation for glass-forming polymer liquids is that their density ρ at T_g tends to *decrease*

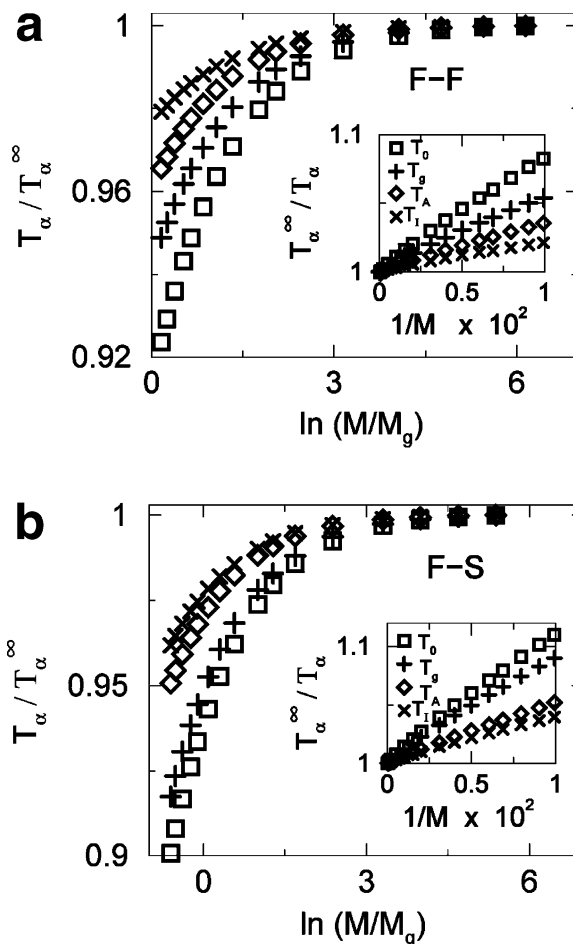


Figure 1. (a) Molar mass dependence of the characteristic temperatures $\{T_\alpha\}$ in semilog format for constant pressure ($P = 1$ atm) F–F model monodisperse polymer fluids whose monomer structure is obtained from that depicted in Figure 4b when $n = 3$. The temperatures T_0 , T_g , T_I , and T_A are normalized by their corresponding high molar mass limits $T_\alpha(M \rightarrow \infty) \equiv T_\alpha^\infty$, while the number M of united atom groups in a single chain is divided by M_g , the molar mass at which the ratio T_g/T_g^∞ nearly saturates, i.e., where $T_g(M \equiv M_g)/T_g^\infty \equiv 0.95$ ($M_g = 86$ for F–F polymers). The inset emphasizes a universal linear scaling for the inverse ratios T_α^∞/T_α with $1/M$. (b) Same as part a, but for F–S polymer fluids ($M_g = 184$).

with increasing molar mass.⁵⁹ This trend is *opposite* to that observed at temperatures much higher than T_g where ρ increases monotonically with molar mass.⁵⁷ More specifically, measurements indicate⁵⁹ that the reciprocal of the density (specific volume) at T_g is nearly proportional to T_g itself, suggesting the existence of a correlation between ρ_g and T_g . Figure 2 demonstrates that this empirical correlation between $v(T = T_g)$ and T_g emerges from LCT calculations for both F–S and F–F polymers and that the slope is substantially larger for the F–S class of polymers.

Our considerations elsewhere¹² of the fragility of glass-forming liquids indicate a general trend that F–S class polymers are more fragile than F–F polymers. This trend has been traced¹² to the larger excess free volume ($\phi_v = 1 - \phi$) in the F–S polymer fluids that physically reflects the difficulty in packing those complex-shape molecules due to the stiffness of the side groups. The packing of F–F polymers is more efficient, and little excess free volume ϕ_v is present at the glass transition for this class. Thus, ϕ_v changes slowly with temperature for the F–F class, in contrast to the relatively large excess free volume for the F–S polymers that is more susceptible to changes with temperature.

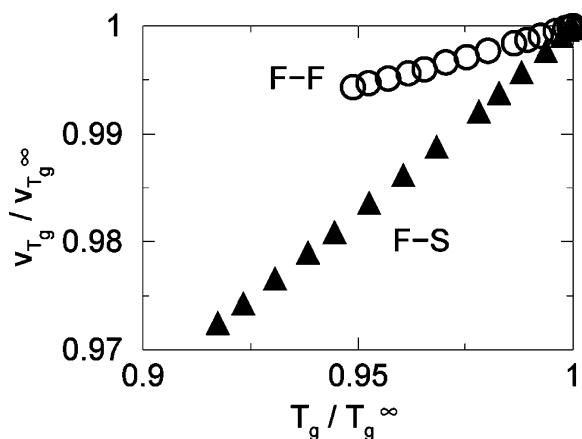


Figure 2. Variation of the specific volume v_{T_g} at the glass transition temperature T_g with the glass transition temperature T_g as calculated from the LCT for constant pressure ($P = 1$ atm) F–F and F–S polymer fluids ($n = 3$). Both v_{T_g} and T_g are normalized by the corresponding high molar mass limits ($v_{T_g^\infty}$ or T_g^∞).

The results of Figure 2 provide further evidence that a higher T_g (for fixed van der Waals interaction energy ϵ) can be associated with higher excess free volume ϕ_v in the glassy state, which in turn is ultimately related to the frustration in packing more complex shaped or extended molecules. The stronger dependence of $v(T = T_g)$ on T_g for the F–S class reflects the relative fragility of polymers in this class compared to the F–F class, as well as the significant change in fragility and rate of change in T_g as M is varied.

VI. Structural Arrest and the Isothermal Compressibility κ_T

Experiments reveal that the smooth variations of thermodynamic properties (e.g., v , κ_T , and the specific heat C_p at constant pressure) with temperature are interrupted by cooling rate dependent “kinks”. In our view, these features cannot be described by an equilibrium statistical mechanical theory, but rather represent a challenge for nonequilibrium theories of glass-formation. In particular, our theory indicates that no overt feature is present in the temperature dependence of the specific volume or other thermodynamic properties at the glass transition *for a fluid at equilibrium*. Nonetheless, some insight into the origin of these observed “kinks” in quasi-thermodynamic properties and the qualitative meaning of the fluid becoming “stuck” can be gleaned from considering the magnitude of the isothermal compressibility κ_T at T_g is approached.

The high-frequency shear modulus G_∞ is an equilibrium fluid property that is closely related⁶⁰ to κ_T since G_∞ describes the mean square amplitude of particle displacements about their quasi-equilibrium positions in the dense fluid, while κ_T reflects the mean square amplitude of density fluctuations. The reciprocal of κ_T is normally termed the “bulk elasticity modulus” because it can be viewed as the fluid analogue of the bulk modulus of an elastic material.⁶¹ The rough proportionality between the shear modulus and the bulk modulus implies the approximate scaling relation $G_\infty \sim 1/\kappa_T$ in the glassy regime $T_g < T < T_l$. [Indeed, computed values of $1/\kappa_T$ at T_g are on the order of 1 GPa, which is a typical order of magnitude for G_∞ and $1/\kappa_T$ near the glass transition for both F–S (polystyrene) and F–F (polypropylene, poly(dimethyl sulfoxide)) classes of polymers.^{62–64}]

Cooling a liquid to near T_g leads to a relatively abrupt reduction in the fluid compressibility κ_T and specific volume v (see Figure 3) and correspondingly to a rise in the high-

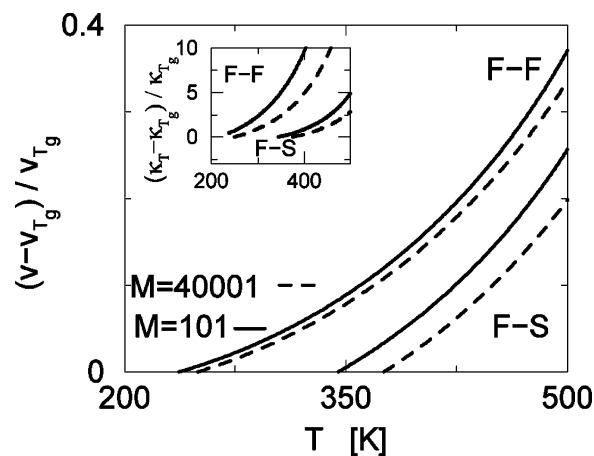


Figure 3. Reduced specific volume $(v - v_{T_g})/v_{T_g}$ and reduced isothermal compressibility $(\kappa_T - \kappa_{T_g})/\kappa_{T_g}$, defined relative to the glass transition temperature T_g and calculated from the LCT as functions of temperature for constant pressure ($P = 1$ atm) polymer fluids ($n = 3$). The normalization of v and κ_T emphasizes that equilibrium measurements are not possible below T_g . Different curves refer to F–F and F–S classes of polymers and to different numbers M of united atom groups in single chains.

frequency shear modulus^{61,65,66} G_∞ . This increase in the “stiffness” of glass-forming liquids ultimately becomes so large that it causes the molecular motions associated with thermal fluctuations to become “frozen” at the glass transition.⁶¹ (This “inertial catastrophe” viewpoint of glass-formation is briefly discussed by Starr et al.⁴²) Because of this structural instability, the high-frequency shear modulus G_∞ and the specific volume vary more slowly with temperature below T_g , while κ_T decreases more sharply.^{61,65,66} The latter important changes in *apparent* thermodynamic properties are not captured by the thermodynamic theory since they arise from the extremely congested nature of the molecular motions (i.e., dynamics) and reflect the rate of cooling in the measurements. The relatively rapid reduction in κ_T near T_g is a signal that the fluid has entered a “jammed” nonequilibrium state with solidlike characteristics. We view this process anthropomorphically as a kind of “death rattle” for the liquid state.

VII. Influence of Side Group Length and Flexibility on T_g

Our discussion so far has focused on the impact of the relative flexibility of the chain backbone and side groups on the glass transition of glass-forming polymers, a consideration that has heretofore not been possible within an analytic theory nor has been probed with simulations. The side groups in the F–F and F–S model polymers used for the calculations presented in Figures 1–3 are short linear chains with three united atom units, a structure inspired by many synthetic polymers in which the size of the side groups is on the order of a few carbon–carbon bonds. Within this idealized model of polymer glass-formation, the computed T_g (and other characteristic temperatures) generally increase with either E_s or E_b , in accord with physical intuition and experimental observations indicating that greater chain rigidity leads to a higher T_g . However, the rate of this increase in T_g depends on the *relative magnitude* of E_b and E_s (i.e., on the polymer class) and on the side group length n . We next examine the dependence of T_g on n when all other characteristic parameters (ϵ , E_b , E_s , and M) of the model are held *constant*. Because a description of the contrasting influences of rigidity in the side groups and the chain backbone requires considering chains with at least a pair of bonds in the side groups, Figure 4a presents LCT calculations of T_g as a function of the side

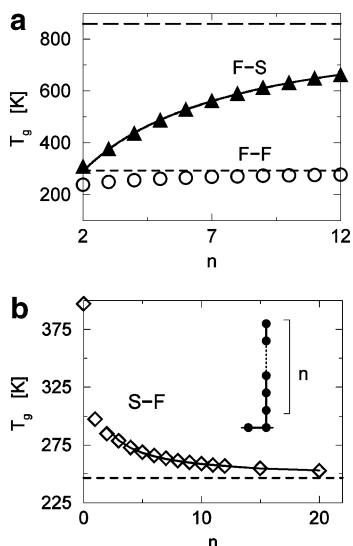


Figure 4. (a) Glass transition temperature T_g (symbols) as a function of the number n of united atom units in the side group as calculated from the LCT for constant pressure ($P = 1$ atm) F–F and F–S polymer fluids having fixed molar mass ($M = 40\,001$). Dashed lines indicate $T_g(n)$ for a melt composed of linear chains ($M = 40\,001$) whose bending energy E_b is the same as the bending energy E_s in F–F or F–S polymers. Solid line is a least-squares fit $T_g = an/(1 + bn)$ (with $a = 215.8$ K and $b = 0.2422$) for F–S polymers. (b) Same as part a, but for S–F polymer fluids. The solid line represents a least-squares fit $T_g = (a + bn)/(1 + n)$ ($n = 3$ – 20) with $a = 375.3$ K and $b = 246.9$ K. The dashed line denotes the glass transition temperature for a melt of linear chains whose bending energy E_b is the same as the bending energy E_s in the S–F polymers. The inset depicts the monomer topology for the S–F, F–S, and F–F class polymers.

group length n for polymer chains having a fixed number $M = 40\,001$ of united atom groups and $n \geq 2$. An increase of n for F–S polymers leads to a sharp rise in T_g in Figure 4a. This trend of increasing T_g with more extended, rigid side groups seems to be quite general from our calculations and is consistent with recent measurements^{67,68} for poly(2-vinyl naphthalene), a system with a fairly rigid and extended side group. Specifically, the measurements reveal that T_g of high molar mass poly(2-vinyl naphthalene) is 50 K larger than the T_g of polystyrene ($T_g^\infty = 373$ K),⁶⁹ which has a smaller phenyl side group. The calculated n dependence of T_g is significantly weaker for the F–F polymer class, where the backbone and side group rigidities are similar by definition. In both F–F and F–S cases, T_g grows monotonically with n and approaches the T_g of the purely linear chain whose bending energy E_b is the same as E_s for the side groups of the structured monomer chains. These asymptotic large n limits are indicated in Figure 4a by dashed lines. Inspection of Figure 4a suggests that the appearance of additional “chain ends” as n is reduced (at fixed M) leads to a decrease of T_g (relative to the T_g of the asymptotic linear chain), in accord with the simple free volume arguments of Fox and Loshaek.⁴¹ Specifically, the free ends comprise (at constant M) a smaller fraction of the total chain segments as n grows, and T_g correspondingly rises toward its large n asymptote. The increase in T_g with n is accompanied by a decrease of the excess free volume concentration ϕ_v with n for a given $T > T_g$. A similar decrease in ϕ_v and increase in T_g arise in our calculations when ϵ is raised at constant n . In *real* polymer systems, on the other hand, the van der Waals energies ϵ_{ij} vary with the different chemical groups and other effects (e.g., microstructure, tacticity, etc.). Since these effects are not included in the calculations presented in Figure 4a, deviations may appear from the trends

in Figure 4a, especially for F–F class polymers where the computed T_g shifts depend weakly on n .

The predicted growth of $T_g(M = \text{constant})$ with n is *not universal* for all polymer classes. If flexible side groups are attached to a relatively stiff backbone, T_g drops with increased n since the longer side groups “plasticize” the stiff backbone. This trend for S–F polymers is illustrated in Figure 4b, which exhibits a sharp decrease of $T_g(M = 40\,001)$ with n ; T_g levels off for $n \sim \mathcal{O}(10)$; and finally T_g saturates to the T_g of the model linear chain for which $E_b = 200$ K and $M = 40\,001$. A very similar behavior is observed in numerous studies^{54,70–72} for an experimental counterpart of S–F polymers—a homologous series of poly(*n*-alkyl methacrylates). Increasing the side group length n (i.e., decreasing the fraction of “free ends” at constant M) again leads to a diminished excess free volume concentration ϕ_v at a given $T > T_g$. However, this trend does not produce an increase of T_g for the S–F polymers, as the free volume arguments of Fox and Loshaek⁴¹ would imply. Apparently, the manner in which “free ends” affect the glass transition temperature depends on the relative flexibility of the chain backbone and side groups. Nevertheless, when n becomes large in each of the three polymer classes (F–F, F–S, and S–F), the glass transition temperature generally approaches that of a melt of linear chains having a bending energy E_b equal to the E_s of the long chain side groups.

Our separate discussion¹² of the fragility of glass-forming liquids indicates that fragility tends to decrease with improved packing efficiency in the melt, as quantified by the excess free volume concentration ϕ_v in the LCT. The general decrease in the calculated ϕ_v with growing n suggests that there is a common tendency toward reduced fragility as n becomes larger than three. This suggestion is supported by experimental studies of poly(2-vinyl naphthalene)⁶⁷ and poly(*n*-alkyl methacrylate)^{54,70–73} polymers which exhibit stronger glass-formation with increasing side group size.

VIII. Discussion

By extending the lattice cluster theory (LCT) to describe glass-formation in polymer melts and by adopting venerable concepts from the Gibbs–DiMarzio (GD) and Adam–Gibbs (AG) theories of glass-formation and the Lindemann criterion to determine T_g , we self-consistently explain the relation between the kinetic glass transition temperature T_g and the “ideal” glass transition temperature T_0 (at which the fluid configurational entropy s_c extrapolates to zero), as well as between T_g and other characteristic temperatures of glass-formation, such as the onset temperature T_A for the supercooled regime (below which the structural relaxation time τ no longer displays an Arrhenius temperature dependence), and the crossover temperature T_1 (separating well-defined high and low-temperature regimes of glass-formation in which both s_c and τ exhibit a rather distinct temperature dependence). While the concepts of the configurational entropy s_c and the “ideal” transition temperature T_0 intrinsically follow from GD theory, the AG postulate of a specific relation between τ and s_c allows the self-consistent definition of both T_A and T_1 in terms of the s_c that is computed from the LCT. This progress in the predictive capacities of the entropy theory of glass-formation arises, in part, because the LCT generates analytical expressions for thermodynamic properties that include effects of short range correlations stemming from chain connectivity, different flexibilities of chain backbone and side groups, and monomer structure, molecular factors that cannot be described by classic GD theory. Notably, GD theory exclusively focuses on computing T_0 which occurs well below

the kinetic T_g , so the scope of GD theory is much more limited than the present entropy theory.

Merging our statistical mechanical theory of polymer melts with the AG model for structural relaxation also provides an analytical theoretical framework for predicting the variation with monomer structure of both equilibrium and relaxation properties of glass-forming polymer liquids, including their fragility.¹² GD theory does not permit the description of these important monomer structural effects. Finally, the quantitative relation between the configurational entropy s_c and the rate of structural relaxation had not been explored by GD theory and has only recently been probed in Monte Carlo studies by Binder and co-workers.²⁰

The present paper is devoted to the particularly difficult problem of estimating the kinetic glass transition temperature T_g within the entropy theory. It is well-known that the glass transition is characterized by relatively small values of both the configurational entropy (number of accessible conformations) and the excess free volume δv available for molecular motion. These thermodynamic changes in the liquid are associated with relatively sharp reductions in the fluid isothermal compressibility and with a corresponding increase in the high-frequency shear modulus (material "stiffness"). The glass transition temperature T_g is viewed here as a kinetic event that occurs when thermal particle motions can no longer overcome the confining forces induced by the growing rigidity of the surrounding medium, thereby leading to particle localization as in a crystal.³⁵ This viewpoint motivates us to introduce a definition of the glass transition based on a kinetic instability (Lindemann) criterion that identifies the *thermodynamic conditions* under which this *kinetic event* takes place. Specifically, we translate the microscopic Lindemann "softening" criterion into an iso-free volume condition involving the specific volume (at constant pressure) which, in turn, is determined from the lattice cluster theory. Of course, the use of a Lindemann criterion for determining T_g is not new conceptually,²⁹ but this criterion has never been used before to construct a specific analytic recipe for computing T_g as a function of molar mass, monomer structure, and pressure.

Our illustrative calculations of T_g at constant pressure for three homologous series of model polymers demonstrate that T_g can increase or decrease with the length of the polymer side branch, depending on the relative rigidities of the side groups and the chain backbone. For polymers with a flexible backbone and flexible or stiff side groups, T_g is found to grow monotonically with the side group length n , and greater growth occurs for species containing stiff side groups. The computed T_g , however, decreases with n when flexible side groups are attached to a relatively stiff backbone, and this trend accords with existing experimental data^{54,70–73} for a homologous series of poly(n -alkyl methacrylates). This agreement with experiment represents a stringest test for the theory and is encouraging in the view of predictions summarized in Figure 4 for F–F and F–S polymer classes. When n becomes large, T_g for all three polymer classes generally approaches that of a melt of linear chains whose stiffness coincides with the rigidity of side group chains in a given class. Our calculations in parts a and b of Figure 4 indicate that controlling side group structure provides a means to regulate the glass transition in synthetic and biological glass-forming polymers.

The other characteristic temperatures of glass-formation,³¹ the temperature T_0 where the configurational entropy extrapolates to zero, the crossover temperature T_I between high and low temperatures regimes of glass-formation, and the Arrhenius temperature T_A signaling the onset of glass-formation are

calculated from the temperature variation of the LCT configurational entropy s_c (using eqs 2, 4, and 5, respectively). All four characteristic temperatures T_α of glass-formation for F–S polymers exceed their counterparts for F–F polymers. The ratios T_α^∞/T_α for all characteristic temperatures (see Figure 1, parts a and b) exhibit linear scaling with the reciprocal of the molar mass, but the strength of this dependence differs between the various characteristic temperatures T_α . These predictions should be subject to experimental tests.

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