

Fragility of Glass-Forming Polymer Liquids[†]

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The fragility of polymeric glass-forming liquids is calculated as a function of molecular structural parameters from a generalized entropy theory of polymer glass-formation that combines the Adam–Gibbs (AG) model for the rate of structural relaxation with the lattice cluster theory (LCT) for polymer melt thermodynamics. Our generalized entropy theory predicts the existence of distinct high and low temperature regimes of glass-formation that are separated by a thermodynamically well-defined crossover temperature T_I at which the product of the configurational entropy and the temperature has an inflection point. Since the predicted temperature dependence of the configurational entropy and structural relaxation time are quite different in these temperature regimes, we introduce separate definitions of fragility for each regime. Experimentally established trends in the fragility of polymer melts with respect to variations in polymer microstructure and pressure are interpreted within our theory in terms of the accompanying changes in the chain packing efficiency.

I. Introduction

Many fluids exhibiting complex molecular structure or interactions solidify by glass formation rather than by crystallization, and this type of solidification is naturally prevalent in polymeric materials. The “plastic” nature of glass-forming polymeric materials is associated with the enormous variation of the viscosity η that is exhibited by these fluids when decreasing temperature over a moderate range. (For instance, a temperature change on the order of a couple of hundred degrees can cause alterations in η by as much as 14 orders of magnitude.) The rate at which η (and the corresponding molecular friction coefficient ζ) change with temperature governs the transport properties of these liquids which are crucial in their applications.^{1,2} Angell^{3–5} has introduced the concept of “fragility” to quantify the strength⁶ of this temperature dependence of η , and we investigate the molecular structural origins of fragility variations in polymer liquids (and glass-forming oligomeric liquids) by employing a generalized entropy theory of polymer glass formation.^{7,8} Our study is broadly motivated by the importance of predicting fragility for engineering the properties of synthetic polymer materials^{3,4,9,10} and for designing processes for preserving biological substances.^{11,12}

Substantial physical evidence^{13,14} supports the theoretical arguments of Gibbs and DiMarzio¹⁵ that glass formation is at least *qualitatively* associated with a reduction of the fluid's entropy to relatively small values in cooled liquids. Moreover, subsequent computational studies^{16–18} of glass-forming liquids confirm the existence of a *quantitative* relation between the rate of structural relaxation and the configurational entropy s (fluid entropy without the vibrational component) as proposed by Adam and Gibbs¹⁹ and elaborated by Mohanty and Oppenheim.²⁰ Experimental attempts to test the AG description of structural relaxation in glass-forming fluids have been incon-

clusive since s must be approximately estimated from specific heat data. Specifically, s is normally identified with the excess molar entropy S_{exc} (the fluid entropy relative to that of the crystal or glass). Unfortunately, S_{exc} and s are not equivalent^{21–23} because S_{exc} contains residual vibrational contributions that are absent in s . As discussed below, an additional issue regarding the difference between S_{exc} and s lies in the choice of normalization (per unit mass or volume, respectively). The particular choice qualitatively affects the temperature variation of these quantities and the predictions of the AG model.⁸ For example, careful experimental studies^{24,25} that simply approximate s by S_{exc} suggest a breakdown of AG theory at temperatures 20–30 K above the calorimetric glass transition temperature T_g , and other studies^{26,27} conclude that polymer fragility cannot be determined reliably from specific heat data. On the other hand, simulations^{16–18} that directly estimate s at temperatures much higher than T_g are claimed to be in good agreement with AG theory. As discussed in the next section, our LCT calculations⁸ of the configurational entropy offer a resolution to these contradictory conclusions.

The intrinsic difficulty in experimentally determining s is admittedly a significant limitation of the AG model for structural relaxation times, although considerable effort^{22,28} is being devoted to remedying this problem. One approach is to express the configurational entropy s in the AG relation for the structural relaxation time in terms of physically more accessible thermodynamic properties, as has been done, for instance, within the lattice cluster theory (LCT) for polymer melt thermodynamics. Specifically, we consider elsewhere²⁹ the interrelation between s and the specific volume, compressibility, and, of course, temperature and pressure, which leads to corresponding predictions for the structural relaxation rate in terms of these variables. This transformation of the entropy theory allows us to make contact with the phenomenology of glass-forming liquids and provides alternative perspectives concerning the thermodynamic conditions associated with glass formation. However, the present paper restricts attention to the configurational entropy and its

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impact on fragility, given the unique success of the AG framework in describing relaxation in computational studies of glass-forming liquids.⁸

No theoretical guidance currently exists for directly calculating fragility as a function of molecular structure or even for understanding qualitative trends in the variations of fragility between different classes of fluid structure. Roland and co-workers^{30,31} and Colucci and McKenna³² have made an important first step by classifying polymers into low, intermediate, and high fragility categories and by noting the structural characteristics of the polymer chains within these classes. These empirical studies^{30–32} indicate that polymers with simple backbone and side group structures are the strongest glass formers (e.g., polyisobutylene and many polyolefins), while flexible chains with bulky, stiff side groups, such as polystyrene (PS), are relatively fragile. Finally, polymers with bulky, stiff backbones (typified by polycarbonate) are highly fragile.

These qualitative observations relating fragility and molecular structure motivate the introduction of a general schematic model of polymer glass formation that 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. We term these broad categories of polymers as flexible–flexible (F–F), flexible–stiff (F–S), and stiff–flexible (S–F) polymer classes, respectively.^{7,8}

Section II briefly sketches those basic concepts invoked from Gibbs–DiMarzio and Adam–Gibbs theories, along with the main features of the lattice cluster theory (LCT) for the thermodynamics of polymer melts. The underlying schematic model for polymer glass formation is then specified. Section III summarizes LCT calculations of the combinatorial entropy s_c and provides an analysis of its relation to glass fragility. In particular, we examine the dependence of the computed fragility on the relative rigidities of the backbone and side groups of the polymer chains, as well as on the pressure. The general trends emerging from these calculations are compared with experimental observations. Section IV reiterates the main findings of our thermodynamic analysis, including the conditions for the internal consistency between the Adam–Gibbs theory of the structural relaxation rates and the entropy theory of glass formation.

II. Lattice Cluster Theory for Polymer Melt Glasses

Our approach is based on the lattice cluster theory (LCT) generalization^{33,34} of the Flory approximation for semiflexible polymer fluids. The LCT includes a perturbative treatment of short-range correlations arising from chain connectivity, chain semiflexibility, and monomer structure. These three factors govern chain packing which, in turn, controls glass formation in real polymer fluids. Importantly, the chain backbone and the side groups are allowed to have different rigidities since this stiffness disparity is expected to influence the strength of the temperature dependence of the configurational entropy $s(T)$ and since this factor is suggested to be a relevant variable affecting the fragility of glass-forming polymers based on previous experimental studies.^{30–32} The relative rigidity of the side groups and the chain backbone directly affects the structural relaxation times τ through the AG relation

$$\tau = \tau_0 \exp\{\beta \Delta\mu[s^*/s(T)]\} \quad (1)$$

where τ_0 is the high-temperature limiting relaxation time in the fluid, $\Delta\mu$ is a (property and system dependent) activation energy

at high enough temperatures (where τ has an Arrhenius temperature dependence, $\tau = \tau_0 \exp[\beta \Delta\mu]$), and s^* is the postulated high-temperature limit of $s(T)$. Equation 1 implies that glass fragility is directly related to the rate of change of $s(T)$, as well as to the strength of van der Waals interactions and other microstructure effects through the kinetic parameter $\Delta\mu$.

An essential 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 $s_{c,m}$ per unit mass, as is commonly assumed in analyzing experiments.^{24,25} This modification is consistent with the analysis of simulation data for diffusion in lattice models of polymer melts by Binder et al.,¹⁸ although the authors do not mention the significant departure of this identification from the use of S_{exc} in experimental tests of the AG model. The distinction between s_c and $s_{c,m}$ is important in connection with calculating structural relaxation times from the AG eq 1, since the entropy density s_c generally does not vary monotonically with temperature.^{8,35} In contrast, the entropy per unit mass, $s_{c,m}$, must change monotonically with T . Hence, the temperature dependence of $s_{c,m}$ is simply inconsistent with the assumption of AG concerning the existence of a high-temperature limit s^* for the configurational entropy. In particular, insertion of experimental data for $s_{c,m}$ into eq 1 does not lead to the prediction of a return to an Arrhenius temperature dependence of τ at a temperature, T_A , as postulated by AG. Our recent communication⁸ presents illustrative computations for both s_c and $s_{c,m}$ as functions of T for model polymer chains with various relative rigidities of the chain backbone and the side groups. We note also that the computed temperature dependence of the entropy density s_c from our theory is qualitatively consistent with estimates of the configurational entropy by Richert and Angel²⁴ that are obtained by fitting relaxation data to eq 1.

The new entropy theory predicts⁸ a series of characteristic temperatures of glass formation. Three of these temperatures have well defined thermodynamic signatures: the Arrhenius temperature T_A , the crossover temperature T_I , and the ideal glass transition temperature T_0 describing, respectively, the onset of a drop in $s_c(T)$ [taken at 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 (see below). The remaining characteristic temperature, the kinetic glass transition temperature T_g , is defined by merging a Lindemann localization–delocalization instability criterion^{36–40} with the LCT estimates for the excess free volume in the melt.⁸ The present paper discusses the implications of this LCT–AG theory for understanding variations of fragility in polymer and small molecule (oligomeric) liquids.⁴¹

Our model⁸ considers monodisperse chains (each containing 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 of 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 $E_i \rightarrow \infty$. Calculations are illustrated for the F–F and F–S generic polymer classes, that are assumed, for simplicity, to have the same monomer structure (see inset to Figure 1) in which the side group is a short linear chain with three united atom units, a structure inspired by many synthetic macromolecules. The focus here, therefore, is on the influence

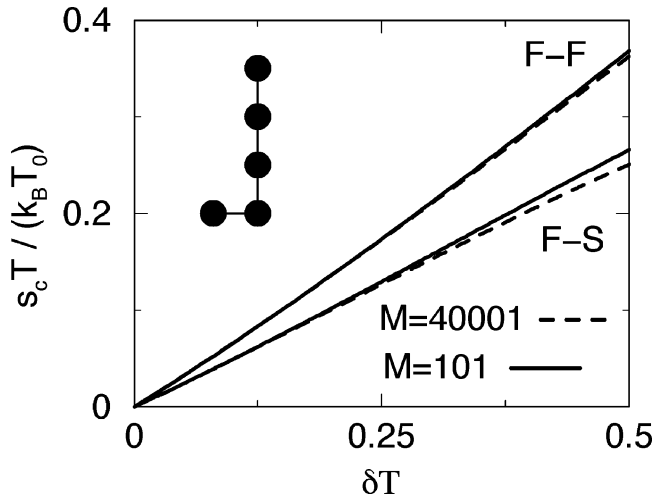


Figure 1. LCT configurational energy $s_c T$ as a function of the reduced temperature $\delta T \equiv (T - T_0)/T_0$ for low and high molar mass F–F and F–S polymer fluids at a constant pressure of $P = 1$ atm. The product $s_c T$ is normalized by the thermal energy $k_B T_0$ at the ideal glass transition temperature T_0 where $s_c(T) = 0$. Inset depicts the monomer structure (with three united atom groups in the side group) used in our calculations for F–F and F–S polymers.

of differing side group and backbone rigidities, while the dependence of glass formation on the length of the side groups is examined elsewhere.⁷ We choose the bending energies for the backbone (E_b) and side groups (E_s) to reproduce typical orders of magnitude of T_g for these classes of polymers. 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 for the stiff side groups. All computations refer to a pressure of $P = 1$ atm (0.101325 MPa), unless otherwise stated, and are performed for $\epsilon/k_B = 200$ K [a typical value⁴² 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. Our schematic model of glass formation, however, neglects some details of monomer microstructure (e.g., the variability of the van der Waals energies ϵ_{ij} and the bending energies E_b and E_s with the different chemical groups) and tacticity.

III. Dependence of Fragility on Chain Microstructure and Thermodynamic State

Since the temperature dependence of s_c largely governs variations of fragility within the entropy theory of glass formation, we begin with a discussion of the temperature dependence of s_c . Figure 1 illustrates the relation between $s_c T$ and $\delta T \equiv (T - T_0)/T_0$ over a broad temperature range (up to at least 100 K above T_0) for both the F–F and F–S classes and for small and large molar masses M_{mol} (where $M_{\text{mol}} \propto M$, the number of united atom groups per chain). The configurational energy $s_c T$ for both polymer classes varies approximately linearly with δT over the limited temperature range indicated, and the slopes are quite insensitive to molar mass. The proportionality of $s_c T$ to δT fails to hold to a good approximation at higher temperatures, and we refer to the temperature range $T_g < T < T_1$ as the low-temperature regime of glass formation.

The proportionality of $s_c T$ to δT implies that the AG eq 1 for τ reduces exactly to the Vogel–Fulcher–Tammann–Hesse (VFTH) equation,⁴³

$$\tau = \tau_{\text{VFTH}} \exp[DT_\infty/(T - T_\infty)], \quad T_g < T < T_1 \quad (2)$$

TABLE 1: Fragility Parameters (K_s, C_s) and Ratios of Characteristic Temperatures for F–F and F–S Polymer Fluids at a Pressure of $P = 1$ atm

property	F–F polymer fluid		F–S polymer fluid	
	$M = 101$	$M = 40001$	$M = 101$	$M = 40001$
K_s	0.181	0.200	0.308	0.361
C_s	2.79	2.87	6.53	7.10
$z^* = s_c^*/s_c(T_i)$	1.48	1.55	1.76	2.02
T_i/T_g	1.39	1.35	1.20	1.15
T_i/T_0	1.65	1.56	1.32	1.23
T_A/T_1	1.56	1.58	1.41	1.43
T_A/T_g	2.16	2.12	1.70	1.64
T_A/T_0	2.56	2.45	1.86	1.76

where T_∞ (coinciding with T_0) is the ‘‘Vogel temperature’’ at which τ extrapolates to infinity, D is a fragility constant describing the strength of the temperature dependence of τ , and τ_{VFTH} is an adjustable prefactor corresponding to τ_0 of eq 1. The identity between eqs 1 and 2 in the linear regime, where $s_c T \propto \delta T$, uniquely establishes a relation between the kinetic fragility parameter $D \equiv 1/K_s$ and the thermodynamic fragility $s_c T/\delta T$,

$$K_s = (s_c T/\delta T)/(\Delta\mu s_c^*/k_B) \quad (3)$$

The evaluation of K_s from eq 3 requires the determination of $\Delta\mu$ (which generally depends on M_{mol}) for polymers.⁴⁴ Observations based on experimental and simulation data suggest a means for estimating $\Delta\mu$. For example, simulations of both binary Lennard-Jones mixtures (the Kob–Anderson model)⁴⁵ and simple models of Lennard-Jones particle chains⁴⁶ indicate that $\Delta\mu/k_B$ is approximately six times the experimental ‘mode-coupling temperature’ $T_{\text{mc}}^{\text{exp}}$. A large body of data for the viscosity of glass-forming ionic^{47,48} and metallic^{49,50} melts also supports this approximation, although only a rough correlation with $T_{\text{mc}}^{\text{exp}}$ is specifically indicated.

While the theoretical interpretation of the phenomenological temperature $T_{\text{mc}}^{\text{exp}}$ is uncertain,⁵¹ it has the well-defined physical significance as a crossover temperature^{52,53} separating the high and low-temperature regimes of glass formation, where τ exhibits a qualitatively different (and non-Arrhenius) temperature dependence in each regime. (An additional high-temperature regime for $T > T_A$ exists where τ exhibits an Arrhenius temperature dependence to a good approximation.) The crossover temperature T_1 of the entropy theory is evidently a direct counterpart of $T_{\text{mc}}^{\text{exp}}$, since it likewise separates two distinct regimes of glass formation, with a qualitatively different temperature dependence of s_c and τ . Moreover, a direct comparison of LCT computations for T_i/T_g (see Table 1) with literature estimates^{54–56} of the ratio $T_{\text{mc}}^{\text{exp}}/T_g$ supports the identification of T_1 with $T_{\text{mc}}^{\text{exp}}$. Specifically, T_i/T_g equals 1.15 and 1.20 for high and low molar mass F–S chains, respectively, while $T_{\text{mc}}^{\text{exp}}/T_g$ is 1.14 for the high molar mass PS and 1.18 for the model fragile small molecule liquid, *o*-terphenyl.^{55,56} The larger values of T_i/T_g predicted for F–F chains (1.35–1.39) are qualitatively consistent with the ratios of $T_{\text{mc}}^{\text{exp}}/T_g$ for stronger fluids, but available data are largely restricted to ionic and hydrogen bond fluids or to F–F polymer melts whose glass formation is complicated by crystallization. Experimental estimates of $\Delta\mu$ are limited for polymer fluids, and our estimates of typical values of $\Delta\mu$ for F–F and F–S high molar mass polymers ($\Delta\mu/k_B \approx 2000$ and 2600 K, respectively) are comparable in magnitude with the $\Delta\mu$ obtained for high molar mass alkanes by Tabor ($\Delta\mu/k_B \approx 2700$ K).⁴⁴ Molecular dynamics simulations provide a potential alternative method for determin-

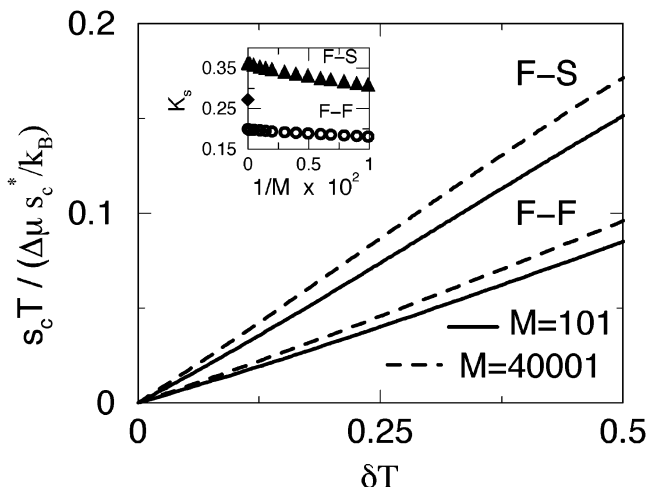


Figure 2. Same as Figure 1, but the configurational energy $s_c T$ is normalized by the product of the critical entropy s_c^* and the activation energy $\Delta\mu$. According to eq 3, the slope defines the fragility parameter K_s . The inset presents K_s as a function of the inverse number $1/M$ of united atom groups in single chains for constant-pressure ($P = 1$ atm) F–F and F–S polymer fluids. The single data point \blacklozenge refers to high molar mass F–S polymers at $P = 240$ atm.

ing $\Delta\mu$ and, thus, for testing our proposed relation between $\Delta\mu$ and T_1 or, alternatively, for determining $\Delta\mu$ for a specific polymer fluid treated by our theory. Based on the identification of T_{mc}^{exp} and T_1 and the empirical relation $\Delta\mu/k_B \approx 6T_{mc}^{exp}$, we can directly compute the fragility parameter K_s as a function of fluid structural parameters for the first time. Note that the dependence of T_1 on polymer microstructure, molar mass, and pressure implies a similar dependence of $\Delta\mu$ on these parameters.

The interrelation between $\Delta\mu$ and T_{mc}^{exp} has implications regarding the magnitude of the structural relaxation time τ at the crossover temperature T_{mc}^{exp} . Recent investigations^{55,57} indicate that τ at the crossover temperature T_{mc}^{exp} is nearly universal for a large number of polymer glass formers, i.e., $\tau(T_{mc}^{exp}) \sim \mathcal{O}(10^{-7\pm 1}$ s). A similar regularity has been reported^{25,58} for the enhancement of the apparent activation energy, $z^* = s_c^*/s_c(T)$, at T_{mc}^{exp} , namely, $z^*(T_{mc}^{exp}) \approx 2$. These observed regularities constrain the relation between $\Delta\mu$ and T_1 in our theory. Inserting the above two values into the AG relation of eq 1 and taking the typical magnitude⁵⁵ for the high-temperature limit of τ as $\tau_0 \sim \mathcal{O}(10^{-13}$ s) lead to the conclusion that $\Delta\mu/k_B$ should lie in the range

$$\Delta\mu/k_B = (7 \pm 1) T_{mc}^{exp}$$

which is consistent with the empirical relation adopted above. As another indication of consistency with experiment, we note that the value of $z^*(T_1)$ computed from the LCT (see Table 1) accords reasonably with the empirical universal value^{25,58} $z^* \approx 2$.

Figure 2 analyzes the variation of the fragility K_s with polymer class and with molar mass and departs from Figure 1 only by the use of a different normalizing factor for $s_c T$ as prescribed by eq 3. The slope defining K_s in Figure 2 is definitely larger for the F–S polymer class than for the F–F class and depends somewhat on the molar mass. The M -dependence is quantified in the inset to Figure 2, which shows that K_s first grows with M and then saturates for large M . (An increase in the fragility of polystyrene with increasing M has been noted by Santangelo and Roland.³¹) A similar behavior emerges⁷ from the LCT for the variation of T_g and other characteristic temperatures of glass-

forming fluids with M . (The high molar mass limit of K_s is summarized in Table 1.) Although recent measurements⁵⁹ indicate that the fragility of PIB decreases weakly with M , the observed dependence of fragility on M is indeed small, as would be expected for a F–F class polymer. This small deviation between the computed and observed M -dependence may be explained by a number of secondary effects that are neglected in our schematic model of glass formation (e.g., monomer shape, tacticity, variability of interaction and bending energies with chemically different united atom groups, etc.).

Our entropy theory estimates for K_s in Figure 2 compare quite reasonably with experimental values. For instance, the high molar mass limit of K_s for F–S polymers, $K_s^\infty = 0.36$, accords well with the value of 0.35 extracted by us from the data of Plazek and O'Rourke⁶⁰ for PS, which is a typical F–S class polymer. Some variability in the calculated K_s for PS appears, however, when the evaluation is based on the data tabulation of Ngai and Plazek.⁶¹ An average of $K_s = 0.42 \pm 0.1$ is determined from four different data sets⁶¹ for the stress-relaxation shift factor ($a_{T,\eta}$) for high molar mass glassy PS (where the uncertainty reflects the data range rather than measurement uncertainty). The rather large disparity in K_s for PS emerges from variations in methodology (e.g., the assumption of time–temperature superposition, temperature interval investigated, molar mass, polydispersity, tacticity, impurities, etc.)

Similar comparisons of our computations of K_s for F–F polymers ($K_s^\infty = 0.20$) are not straightforward because reliable data for K_s are sparse since many F–F polymers tend to crystallize. Partial crystallization renders both thermodynamic and transport properties highly sensitive to the cooling history and to other processing variables, and values of K_s as large as 1 are sometimes found for systems that crystallize.^{62,63} Literature data for T_g (or VFTH parameters) are notoriously disparate and controversial for simple polymer fluids, such as polyethylene or polypropylene.⁶¹ Polyisobutylene (PIB) is a well-known strong polymer fluid that does not crystallize, and experimental estimates^{61–63} of K_s for PIB are normally much smaller than for PS, typically in the broad range 0.06–0.13.

Glass formation is evidently not restricted to high molar mass polymers. *o*-Terphenyl, for example, can be considered as akin to a single monomer with aromatic side groups, and, indeed, the entropy theory fragility parameter for low molar mass F–S polymers ($K_s = 0.31$) is consistent with the experimental value $K_s = 0.29$ reported by Richert and Angell.²⁴ Comparisons of the current LCT predictions for low molar mass polymers with the literature values of K_s for small molecule glass formers should, however, be taken with some caution because the shortest polymer chains considered by us ($M = 100$) are still long relative to small molecules consisting of several united atom groups. (In principle, our theory can describe glass formation in small molecule fluids, but the mean-field approximation inherent to the LCT becomes less accurate for small M .) Similarly, viewing *n*-propanol as a representative member of the F–F class of monomers, the agreement between the experimental²⁴ $K_s = 0.18$ and the corresponding theoretical $K_s = 0.18$ from Figure 2 seems even better. The fragility of glycerol,⁵⁴ another strong liquid with rather simple structure, is somewhat lower ($K_s = 0.05$), however. Smaller values of K_s are characteristic of numerous sugars and other fluids exhibiting hydrogen bonding.⁶⁴ This trend is understandable from eq 3, which indicates that K_s varies inversely to $\Delta\mu$, which in turn depends on the cohesive energy density or the strength ϵ of van der Waals interactions.

The overall breadth of the temperature range over which glass-formation occurs and the rapidity with which the configurational entropy s_c varies with temperature are intimately related. Thus, ratios of the characteristic temperatures of glass formation provide model independent information about fragility (i.e., larger temperature ratios imply broader glass transition and stronger glasses). As summarized in Table 1, all the characteristic temperature ratios T_A/T_0 , T_A/T_g , T_A/T_I , T_I/T_g , and T_I/T_0 are found to be larger for F–F class than for F–S class polymers, while the M-dependence of these ratios is weak for both classes. The relatively large ratios for the F–F polymers indicate that they are stronger glass formers than the F–S chains. At the structural level, these results confirm the experimental finding^{30–32} that polymer chains with bulky, stiff side groups have higher fragility than polymers with side groups whose molecular structure and rigidity resemble the chain backbone segments. We trace the greater relative fragility of the F–S class to their lower packing efficiency in the melt, as quantified by the excess free volume concentration ϕ_v in the lattice model. The bulkiness and high rigidity of the side groups evidently lead to frustration in the packing of these polymers, i.e., to an inherently lower density or a larger ϕ_v . The packing structure is apparently more sensitive to temperature for the F–S class than for the more densely packed F–F class, and this is the molecular origin of the greater fragility of F–S polymers in our theory.

Increasing pressure is expected normally to reduce ϕ_v and, thus, to diminish fragility. This effect is more dramatic for the F–S polymers at high temperatures where a separate definition of fragility is introduced (see below) for the high-temperature regime of glass formation. Generally, all our computations point to variations in fragility as arising from the relative efficiency of packing complex shaped molecules. In simpler terms, more deformable molecules fill space better than hard molecules, leading to stronger fluids that are less sensitive to the structural changes induced by temperature variation.

We next consider how the predicted changes in fragility from the entropy theory compare to recent measurements for the variation of fragility with pressure. McKenna and co-workers²⁷ find that PS (a F–S class polymer) becomes less fragile at elevated pressures, and the same trend emerges for a wide range of non-associating glass formers from more recent studies^{65,66} by Roland and co-workers. Figure 3 presents the calculated s_c for high molar mass F–S polymers as a function of the reduced temperature $\delta T = (T - T_0)/T_0$ for two different pressures. Figure 3 demonstrates that a higher pressure leads to a weaker temperature dependence of $s_c(T)$, especially in the high-temperature regime of glass formation, $T_I < T < T_A$. This reduced temperature dependence of $s_c(T)$ at elevated pressures should affect fragility, and, indeed, the computed fragility K_s of high molar mass F–S polymers equals 0.27 for $P = 240$ atm, compared to 0.36 for $P = 1$ atm (see Figure 2).

The fragility parameter K_s defined by eq 3 applies in a limited temperature range above T_g where the effects of pressure on s_c are relatively small compared to the higher temperature regime of glass formation where the influence of pressure becomes appreciable (see Figure 3). It is evidently desirable to introduce separate definitions of fragility in the non-overlapping high ($T_I < T < T_A$) and low ($T_g < T < T_I$) temperature regimes of glass formation. Specifically, the parameter C_s , defined as the coefficient in the parabolic dependence of $z^* = s_c^*/s_c(T)$ on the reduced temperature δT_A ,

$$z^* - 1 = C_s [|T - T_A|/T_A]^2, \quad T_I < T_A - 100 \text{ K} < T < T_A \quad (4)$$

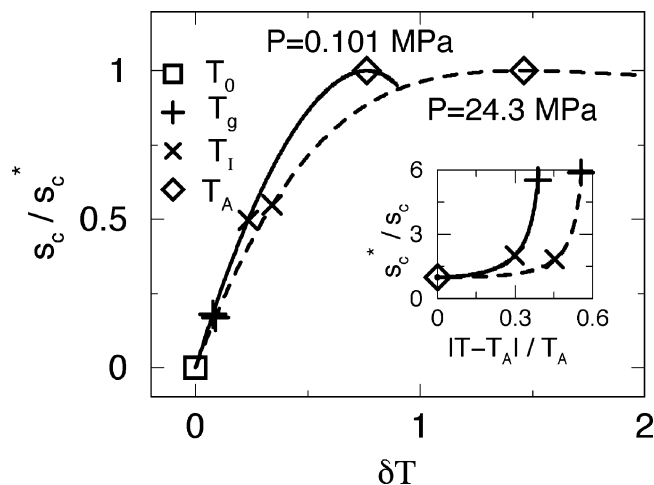


Figure 3. LCT calculations for the configurational entropy s_c per lattice site of a constant pressure, high molar mass ($M = 40001$) F–S polymer melt as a function of the reduced temperature $\delta T \equiv (T - T_0)/T_0$. The entropy s_c is normalized by its maximum value $s_c^* \equiv s_c(T = T_A)$. Solid and dashed curves refer to pressures of $P = 1$ atm and $P = 240$ atm, respectively. The ideal glass transition temperature T_0 , the glass transition temperature T_g , the crossover temperature T_I , and the Arrhenius temperature T_A are indicated in the figure. The inset presents the LCT estimates for $z^* = s_c^*/s_c(T)$ in the same system as a function of the reduced temperature $\delta T_A \equiv |T - T_A|/T_A$. Solid and dashed curves in the inset correspond to $P = 1$ atm and $P = 240$ atm, respectively.

serves as a useful measure of fragility in the high-temperature regime, complementing K_s in the low-temperature regime of glass formation. (The restriction to a temperature range of 100 K below T_A is dictated by the quality of the fit of z^* to eq 4, which is generally better than 1% over this temperature range.) The fragility changes in the high-temperature regime are quantified in the inset to Figure 3. Table 1 indicates that $C_s = 7.10$ for high molar mass F–S polymers at $P = 1$ atm, while a significantly smaller $C_s = 0.69$ is obtained for $P = 240$ atm. (The constant of proportionality in a relation like eq 4 has been advocated as a measure of fragility in spin models exhibiting glass formation,⁶⁷ where the power in the reduced temperature $|T - T_A|/T_A$ is found to be somewhat larger than 2, however.) Equation 4 is compatible with recent experimental correlations for the enhancement of the apparent activation energy z^* of diverse fluids by Kivelson et al.,⁶⁸ and Schweizer and Salzman⁶⁹ have derived a similar relationship for z^* of cooled liquids, i.e., $z^* - 1 = C[|T - T_A|/T_A]^2$, where the constants C and T_A are prescribed by their theory. Note that insertion of eq 4 into eq 1 implies a qualitatively different temperature dependence for τ in the high temperature regime of glass formation than the VFTH expression.

IV. Summary and Discussion

Recently we have proposed⁸ a general entropy theory of structural relaxation in glass forming polymer liquids based on three essential elements: the Adam–Gibbs (AG) model for structural relaxation, the lattice cluster theory (LCT) for polymer melt thermodynamics, and an empirical relation between the high-temperature activation energy $\Delta\mu$ of the AG model and a precisely defined characteristic temperature T_I that separates the high and low temperature regimes of glass formation and that is determined from the inflection point in the product of the LCT configurational entropy density and the temperature. Specifically, we tentatively use the phenomenological relation $\Delta\mu/k_B \approx 6T_I$ arising from simulations, experimental observations, and the identification of the experimental mode coupling

temperature T_{mc}^{exp} with the crossover temperature T_1 of our generalized entropy theory of glass formation in polymer fluids. Hence, $\Delta\mu$ varies with polymer microstructure, molar mass, and pressure through the dependence of T_1 on these parameters.

The present paper demonstrates the capacity of the generalized entropy theory to rationalize observed trends in the variations of polymer fragility with changes in polymer microstructural parameters and pressure. The calculations of polymer fragility have been performed for the schematic model of glass-formation which distinguishes different rigidities in the chain backbone and the side groups. This distinction is motivated by experimental studies^{30–32} of the molecular structural origins of polymer fragility, indicating that the relative rigidity of the side groups and the chain backbone is an essential parameter governing the nature of glass formation. The generalized entropy theory is thus the first molecular-based theory that allows the prediction of the influence of monomer structure, chain backbone and side branch rigidities, pressure, and polymer molar mass on fragility, and our calculations broadly accord with established trends. Our theoretical framework also suggests the existence of different measures of fragility for the low and high-temperature regimes of glass formation. In addition to the fragility parameters K_s and C_s , the ratios of the characteristic temperatures convey important information about polymer fragility over different temperature ranges.

A direct quantitative comparison between AG theory and measurements requires the resolution of two issues. First, the excess entropy S_{exc} must be normalized by the molar volume. We suggest that the lack of this normalization is partly responsible for previous claims^{24,25} that AG theory breaks down for small molecule fluids. Second, the vibrational contribution to S_{exc} , which is absent in s , must be subtracted reliably. While the first correction can be readily introduced, the inclusion of the second correction requires further investigation.^{21,22}

Another important limitation of our LCT–AG entropy theory of glass formation arises because the AG model implicitly focuses on large scale structural relaxation processes and cannot currently describe relaxation processes in the nonzero wave-vector q limit. This restriction to long wavelengths precludes treating many aspects of glass formation, such as the q -dependence of the structural relaxation time, bifurcation of relaxation times, etc. Thus, an important direction for the future extension of the entropy theory involves adding a square gradient contribution to the free energy (modeling the energetic cost of density fluctuations in the polymer melt) in order to describe the rate of structural relaxation at finite length scales.

Some critics have questioned the philosophical basis of the AG theory, which relates dynamical information, such as the structural relaxation time, to thermodynamic information, such as the configurational entropy. In response to these comments, we note that AG theory is derived from a dynamical model and involves overtly dynamical quantities, such as τ_0 (linked to the inverse collision frequency in the fluid) and the high-temperature activation energy $\Delta\mu$. There have been numerous attempts^{49,50,70–74} to correlate $\Delta\mu$ with thermodynamic properties (e.g., melting temperature, heat of vaporization, etc.), but these correlations can be properly understood only within the framework of a fully dynamical theory. We avoid this important but extremely difficult issue by invoking a phenomenological relation between $\Delta\mu$ and T_1 , thereby reducing the computation of the relative change in the structural relaxation time τ/τ_0 for polymer fluids to a purely thermodynamic description.

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