Fragility of Glass-Forming Polymer Liquids†

Jacek Dudowicz,‡ Karl F. Freed,*‡ and Jack F. Douglas§

The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, and Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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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 $T_c$ 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 $\eta$ 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 $\eta$ by as much as 14 orders of magnitude.) The rate at which $\eta$ (and the corresponding molecular friction coefficient $\zeta$) change with temperature governs the transport properties of these liquids which are crucial in their applications.1,2 Angell3–5 has introduced the concept of “fragility” to quantify the strength6 of this temperature dependence of $\eta$, 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 materials3,4,9,10 and for designing processes for preserving biological substances.11,12

Substantial physical evidence13,14 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 studies16–18 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 inconclusive since $s$ must be approximately estimated from specific heat data. Specifically, $s$ is normally identified with the excess molar entropy $S_{\text{exc}}$ (the fluid entropy relative to that of the crystal or glass). Unfortunately, $S_{\text{exc}}$ and $s$ are not equivalent 21–23 because $S_{\text{exc}}$ contains residual vibrational contributions that are absent in $s$. As discussed below, an additional issue regarding the difference between $S_{\text{exc}}$ 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 studies24,25 that simply approximate $s$ by $S_{\text{exc}}$ suggest a breakdown of AG theory at temperatures $20–30$ K above the calorimetric glass transition temperature $T_g$, and other studies26,27 conclude that polymer fragility cannot be determined reliably from specific heat data. On the other hand, simulations16–18 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 effort22,28 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
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 coworkers3031 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 studies303132 indicate that polymers with simple backbone and side group structures are the strongest glass formers (e.g., polysisobutylene 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.78

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) generalization3334 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.303132 The relative rigidity of the side groups and the chain backbone directly affects the structural relaxation times $\tau$ through the 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 enough temperatures (where $\tau$ 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.2425 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 $s_{c,m}$ 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.835 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 $\tau$ at a temperature, $T_\lambda$, 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 $s_c(T)$, an inflection point in $s_c(T)$, 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 $\tau$ (see below). The remaining characteristic temperature, the kinetic glass transition temperature $T_g$, is defined by merging a Lindemann localization—delocalization instability criterion1640 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 $\epsilon$. Gauche energy penalties $E_\beta$ 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 $E_i = 0$ ($i = \beta, s$), 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
of differing side group and backbone rigidities, while the dependence of glass formation on the length of the side groups is examined elsewhere. 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 \(E_s/k_B\) is ascribed to the \(F-S\) chains, but a relatively large \(E_b/k_B = 4000\) 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 \(E/k_B = 200\) K [a typical value for poly(\(\alpha\)-olefins)] and the unit cell volume \(v_{\text{cell}} = (2.7)^3\) \(\text{Å}^3\). 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 \(e_j\) 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 \(M_{\text{mol}}\) (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 \(\delta T\) over the limited temperature range indicated, and the slopes are quite insensitive to molar mass. The proportionality of \(s_c/T\) to \(\delta T\) 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 \(\delta T\) implies that the AG eq 1 for \(\tau\) reduces exactly to the Vogel–Fulcher–Tammann–Hesse (VFTH) equation:

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

where \(T_{\omega}\) (coinciding with \(T_0\)) is the “Vogel temperature” at which \(\tau\) extrapolates to infinity, \(D\) is a fragility constant describing the strength of the temperature dependence of \(\tau\), and \(\tau_{\text{VFTH}}\) is an adjustable prefactor corresponding to \(\tau_0\) 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 \(D = 1/K_s\) and the thermodynamic fragility \(s_c/T \delta T\):

\[
K_s = \frac{(s_c/T \delta T)}{(\Delta \mu s_c^2/k_B)} \tag{3}
\]

The evaluation of \(K_s\) from eq 3 requires the determination of \(\Delta \mu\) (which generally depends on \(M_{\text{mol}}\)) for polymers. 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) and simple models of Lennard-Jones particle chains indicate that \(\Delta \mu/k_B\) is approximately six times the experimental ‘modelling temperature’ \(T_{\exp}\). A large body of data for the viscosity of glass-forming ionic and metallic melts also supports this approximation, although only a rough correlation with \(T_{\exp}\) is specifically indicated.

While the theoretical interpretation of the phenomenological temperature \(T_{\exp}\) is uncertain, it has the well-defined physical significance as a crossover temperature separating the high and low-temperature regimes of glass formation, where \(\tau\) exhibits a qualitatively different (and non-Arrhenius) temperature dependence in each regime. (An additional high-temperature regime for \(T > T_A\) exists where \(\tau\) exhibits an Arrhenius temperature dependence to a good approximation.) The crossover temperature \(T_1\) of the entropy theory is evidently a direct counterpart of \(T_{\exp}\), since it likewise separates two distinct regimes of glass formation, with a qualitatively different temperature dependence of \(s_c\) and \(\tau\). Moreover, a direct comparison of LCT computations for \(T_1/T_0\) (see Table 1) with literature estimates of the ratio \(T_{\text{exp}}/T_0\) supports the identification of \(T_1\) with \(T_{\exp}\). Specifically, \(T_1/T_0\) equals 1.15 and 1.20 for high and low molar mass \(F-S\) chains, respectively, while \(T_{\text{exp}}/T_0\) is 1.14 for the high molar mass PS and 1.18 for the model fragile small molecule liquid, \(\alpha\)-terphenyl. The larger values of \(T_1/T_0\) predicted for \(F-F\) chains (1.35–1.39) are qualitatively consistent with the ratios of \(T_{\text{exp}}/T_0\) 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 Tabo (\(\Delta \mu/k_B \approx 2700\) K). Molecular dynamics simulations provide a potential alternative method for determin-

<table>
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<th>Property</th>
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<th>(F-S) polymer fluid</th>
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<td>(T_p/T_0)</td>
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### 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
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 $\Delta \mu/k_B \approx 67T_{mc}^{exp}$, 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 $\tau$ at the crossover temperature $T_{mc}^{exp}$. Recent investigations\textsuperscript{55,57} indicate that $\tau$ at the crossover temperature $T_{mc}^{exp}$ is nearly universal for a large number of polymer glass formers, i.e., $\tau(T_{mc}^{exp}) \sim \mathcal{O}(10^{-7.41})$. A similar regularity has been reported\textsuperscript{25,58} for the enhancement of the apparent activation energy, $z^a = s^2/\tau(T)$, at $T_{mc}^{exp}$, namely, $z^a(T_{mc}^{exp}) \approx 2$. 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 magnitude\textsuperscript{55} for the high-temperature limit of $\tau$ 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 $z^a(T_1)$ computed from the LCT (see Table 1) accords reasonably with the empirical universal value\textsuperscript{25,58} $z^a \approx 2$.

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 $s/T$ 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.\textsuperscript{31}) A similar behavior emerges\textsuperscript{7} 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 measurements\textsuperscript{59} indicate that the fragility of PB 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, tactility, 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’Rourke\textsuperscript{60} 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.\textsuperscript{61} An average of $K_s = 0.42 \pm 0.1$ is determined from four different data sets\textsuperscript{61} for the stress-relaxation shift factor $(\alpha T_\beta)$ 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, tactility, 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.\textsuperscript{62,63} Literature data for $T_g$ (or $VFTH$ parameters) are notoriously disparate and controversial for simple polymer fluids, such as polyethylene or polypropylene.\textsuperscript{64} Polysobutylene (PIB) is a well-known strong polymer fluid that does not crystallize, and experimental estimates\textsuperscript{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. $\alpha$-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.\textsuperscript{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 experimental\textsuperscript{24} $K_s = 0.18$ and the corresponding theoretical $K_s = 0.18$ from Figure 2 seems even better. The fragility of glycerol,\textsuperscript{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.\textsuperscript{54} 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 $\epsilon$ 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 \( T_A/T_g \), \( T_g/T_c \), \( T_A/T_c \), and \( T_c/T_0 \) 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 \( \phi_v \) 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 \( \phi_v \). 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 \( \phi_v \) 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-workers\(^{27} \) 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 \( K_f \) 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 \( K_f \) 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 \( \delta T_A \),

\[
\frac{z^*}{C_s} - 1 = \frac{C_s}{T - T_A}/|T_A|^2, \quad T_i < T_A - 100 K < T < T_A
\]

IV. Summary and Discussion

Recently we have proposed\(^{8} \) 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, $\Delta S$ 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 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 $K$ and $C_v$, 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 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.

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 wavenumber $q$ 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 $t_\alpha$ (linked to the inverse collision frequency in the fluid) and the high-temperature activation energy $\Delta u$. There have been numerous attempts to correlate $\Delta u$ 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 $\Delta u$ and $T_1$, thereby reducing the computation of the relative change in the structural relaxation time $t/t_\alpha$ for polymer fluids to a purely thermodynamic description.

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References and Notes

(6) The simple interpretation of fragility as a measure of the rate at which $J$ changes with temperature applies only to substances that have similar activation energies.
(13) Simon, F. E. Naturwissenschaften 1930, 9, 244.
(23) Although the Kauzmann temperature $T_K$ at which the excess molar entropy $S_{exc}$ extrapolates to zero is often very close to the VFT temperature $T_v$ (see, for instance, Cangialosi, D.; Alegria, A.; Colmenero, J. Europhys. Lett. 2005, 70, 614), these findings imply that $s$ and $S_{exc}$ are inequivalent in the latter cases, even when normalized in the same way.
(41) We avoid analyzing estimates of fragility based on specific heat data since the large vibrational contribution and a dependence of the measurements on cooling rates leads to inherently uncertain estimates of $s(T)$.
(57) Sokolov, A. P., personal communication.
(59) Ding, Y.; Novikov V. N.; Sokolov, A. P.; Cuilliaux, A.; Dalle-Ferrier, C.; Alba-Simionesco, C. Macromolecules 2004, 37, 9264.