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The meaning of the “universal” WLF parameters of glass-forming polymer liquids

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Although the Williams-Landell-Ferry (WLF) equation for the segmental relaxation time $\tau(T)$ of glass-forming materials is one of the most commonly encountered relations in polymer physics, its molecular basis is not well understood. The WLF equation is often claimed to be equivalent to the Vogel-Fulcher-Tammann (VFT) equation, even though the WLF expression for $\tau(T)$ contains no explicit dependence on the fragility parameter D of the VFT equation, while the VFT equation lacks any explicit reference to the glass transition temperature T_g , the traditionally chosen reference temperature in the WLF equation. The observed approximate universality of the WLF parameters $C_1^{(g)}$ and $C_2^{(g)}$ implies that $\tau(T)$ depends only on $T - T_g$, a conclusion that seems difficult to reconcile with the VFT equation where the fragility parameter D largely governs the magnitude of $\tau(T)$. The current paper addresses these apparent inconsistencies by first evaluating the macroscopic WLF parameters $C_1^{(g)}$ and $C_2^{(g)}$ from the generalized entropy theory of glass-formation and then by determining the dependence of $C_1^{(g)}$ and $C_2^{(g)}$ on the microscopic molecular parameters (including the strength of the cohesive molecular interactions and the degree of chain stiffness) and on the molar mass of the polymer. Attention in these calculations is restricted to the temperature range ($T_g < T < T_g + 100$ K), where both the WLF and VFT equations apply. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905216>]

I. INTRODUCTION

It is rather standard practice in the analysis of viscoelastic and dielectric properties of polymeric materials to rescale temperature dependent data for the segmental relaxation function, by using the principle of time temperature superposition and exploiting the near invariance of the relaxation functional form as temperature is varied.¹ This conventional mode of data reduction provides a single master curve for the segmental relaxation time relative to its value at some conveniently chosen reference temperature, normally taken to be the glass transition temperature T_g .^{1,2}

Williams, Landel, and Ferry (WLF) have found^{1,2} that the reduced relaxation time $\tau(T)/\tau(T_g)$, estimated from data for a wide variety of polymeric glass-forming liquids, can be described by a remarkably simple universal representation. Formally, the WLF relation follows from the Vogel-Fulcher-Tammann (VFT)³ expression for $\tau(T)$, if $\tau(T)$ is assumed to have the VFT form,

$$\tau(T) = \tau_0 \exp[DT_{VFT}/(T - T_{VFT})], \quad (1)$$

where τ_0 is the high temperature limiting segmental relaxation time which is on the order of a vibrational time scale,^{1,2} i.e., 10^{-13} s to 10^{-14} s, D is the fragility parameter quantifying the degree to which relaxation is non-Arrhenius, and T_{VFT} designates the VFT temperature at which τ extrapolates to

infinity. Equation (1) implies the WLF equation,

$$\log[\tau(T)/\tau(T_g)] = -C_1^{(g)}(T - T_g)/(C_2^{(g)} + T - T_g), \quad (2)$$

where $C_1^{(g)} \equiv DT_{VFT}/[(T_g - T_{VFT}) \ln 10]$ and $C_2^{(g)} \equiv T_g - T_{VFT}$, the WLF parameters, are nearly “universal” constants (i.e., $C_1^{(g)} = 17.44$ and $C_2^{(g)} = 51.6$ K) for the first set of polymer materials investigated, a behavior rationalized by free volume arguments.^{2,4} The superscript (g) on $C_1^{(g)}$ and $C_2^{(g)}$ indicates the choice of the glass transition temperature T_g as the reference temperature in the WLF equation, although other possible choices of a reference temperature are possible.⁵ Since T_g is normally defined as the temperature at which $\tau(T)$ is about 100 s, the WLF equation combined with universal $C_1^{(g)}$ and $C_2^{(g)}$ would imply that the segmental relaxation time τ for glass-forming polymer liquids follows a remarkably universal pattern because the determination of $\tau(T)$ then only requires specification of a single parameter, T_g , as can be seen from Eq. (2), where τ depends only on $T - T_g$. However, the suggested universality of the WLF equation, even as an approximation, is odd for a number of reasons. For instance, T_g depends on the recipe for its determination, such as cooling rate; so how can such a parameter be used in an equation of state type data reduction as if this parameter was somehow a fundamental thermodynamic variable? What on earth is the significance of $C_1^{(g)}$ and $C_2^{(g)}$ parameters and how can these quantities be universal?

Due to the practical importance of the WLF equation in the characterization of materials,⁶ a large body of data has been accumulated for $C_1^{(g)}$ and $C_2^{(g)}$, thereby better enabling the assessment of the original claims of universality. Values of $C_1^{(g)}$ are often found⁶ to lie within a range of 16–17, but $C_2^{(g)}$ for common polymers^{4,6} can vary from 24 K (e.g., for polypropylene oxide) to 104 K (e.g., for polyisobutylene), so the proposed universality of the WLF parameters is clearly incorrect.

Angell⁶ has reviewed the experimental data for the WLF parameters for polymers and non-polymeric glass-forming liquids and has emphasized that the parameter $C_1^{(g)}$ has a direct physical interpretation within the frame of the original WLF arguments. In particular, $C_1^{(g)}$ describes the *dynamic* range of the glass transition, the number of decades of change in the segmental relaxation time upon passing from the high temperature “simple fluid” limit (where $\tau(T)$ exhibits an Arrhenius type dependence) to a fluid at its glass transition,

$$C_1^{(g)} = \log[\tau(T_g)/\tau_0]. \quad (3)$$

Taking a vibrational time scale τ_0 on the order of 10^{-13} s to 10^{-14} s and $\tau(T_g) \approx 100$ s implies that $C_1^{(g)}$ should lie between 15 and 16. Of course, this estimate of $C_1^{(g)}$ assumes that the VFT equation holds over the entire range of glass-formation, while, in fact, the VFT relation only describes⁴ experimental data for temperatures up to about $T_g + 100$ K, a limitation actually deduced⁵ from the generalized entropy theory (GET). Experimental data, on the other hand, often cover a wider range, a feature consistent with somewhat larger values of $C_1^{(g)}$. At any rate, the general magnitude of $C_1^{(g)}$ is quite understandable.

Angell⁶ has also provided important insights into the physical meaning of $C_2^{(g)}$ by showing that the quantity $1 - C_2^{(g)}/T_g = T_{VFT}/T_g$ provides a measure⁶ of the fragility of glass-formation, an important parameter characterizing the relative steepness of the temperature dependence of $\tau(T)$. (Poorly understood correlations of fragility with the non-linearity of relaxation, physical aging,⁷ and with the non-exponentiality⁸ of segmental relaxation in glassy materials indicate that fragility has widespread interest for practical applications of glassy materials.) An average value of $C_2^{(g)}$ around 50 K implies that polymers tend to be relatively fragile compared to many small molecule liquids. Even though $C_2^{(g)}$ is not really constant, the observation of a “typical” value of $C_2^{(g)}$ for many polymers deserves some consideration since a rough constancy of $C_2^{(g)}$ could serve as a rule of thumb approximation for materials design.

The current paper examines the reduced segmental relaxation time τ of glass-forming polymer liquids based on the GET, with a view to answering the questions stated above and to elucidating the conditions under which the WLF parameters might be universal. After briefly reviewing necessary concepts underlying the GET in Sec. II and the beginning of Sec. III, we directly calculate $C_1^{(g)}$ and $C_2^{(g)}$ from the GET and explore how the computed parameters are influenced by monomer molecular structure, chain stiffness, and interactions. We also consider the physical conditions under which $C_2^{(g)}$ of the WLF relation becomes constant and develop a polymer classification scheme based on these conditions.

II. BASIC FEATURES OF THE GET FOR GLASS-FORMATION IN POLYMER LIQUIDS

The GET is the synthesis of the lattice cluster theory^{5,9} (LCT) for the temperature variation of the configurational entropy density $s_c(T)$ of semiflexible, monomer structured polymers and the Adam-Gibbs (AG) relation¹⁰ between the configurational entropy density $s_c(T)$ and the structural relaxation time τ ,

$$\tau = \tau_0 \exp[(\Delta\mu/k_B T) s_c^*/s_c], \quad (4)$$

where k_B is Boltzmann constant, $\Delta\mu$ is the free energy of activation at high enough temperatures at which an Arrhenius dependence of τ approximately holds, and s_c^* is the high temperatures limit of $s_c(T)$, which is estimated as the maximum of $s_c(T)$ as a function of temperature T for a fixed pressure P . (For more recent insights into AG theory, see Ref. 10) The free energy of activation $\Delta\mu$ is assumed to be only of enthalpic origin, i.e., an entropic contribution to $\Delta\mu$ is neglected, following the original assumption of Adam and Gibbs.¹⁰ Moreover, $\Delta\mu$ is estimated within the GET by invoking the simple semi-empirical approximation,^{5,9}

$$\Delta\mu/k_B \approx 6T_c, \quad (5)$$

where the crossover temperature T_c is determined^{5,9} from the condition

$$\partial^2[Ts_c]/\partial T^2|_P = 0. \quad (6)$$

The parameters $C_1^{(g)}$ and $C_2^{(g)}$ evaluated from the GET are functions of molecular parameters, such as the strength of the nearest neighbor van der Waals interaction energy ϵ and the magnitudes of the bending energies $E_b \equiv E$ and E_s in the chain backbone and side chains, respectively. The microscopic interaction energy ϵ quantifies the strength of the cohesive interactions, while the *gauche* conformational energy penalties E and E_s (for pairs of sequential bonds) determine the degree of chain stiffness.^{5,9} We next calculate the WLF parameters $C_1^{(g)}$ and $C_2^{(g)}$ directly from the GET and then assess the universality of the computed parameters and their significance.

III. RESULTS

Our illustrative calculations for the thermodynamic and dynamic properties of glass-forming polymer liquids are performed for model melts of polymers with the monomer structure of poly(α -olefins), as depicted in Fig. 1, and are restricted to the low temperature regime of glass-formation ($T_g < T < T_c \approx T_g + 100$ K), where both the VFT and WLF equations apply. Each polymer species of Fig. 1 is composed of a chain backbone and side chains, and these two portions of the polymer chain generally have different rigidities, as reflected in the magnitudes of the bending energies E and E_s , respectively. Within the extended lattice model⁵ underlying the GET, each united atom group represents a portion of a single monomer (in the polymer chain) and occupies a single lattice site on a simple cubic lattice with coordination number $z = 6$. Each united atom group interacts with its nearest neighbors through a common, monomer averaged, van der Waals energy ϵ . Besides the monomer structure, a given polymer melt is thus specified within

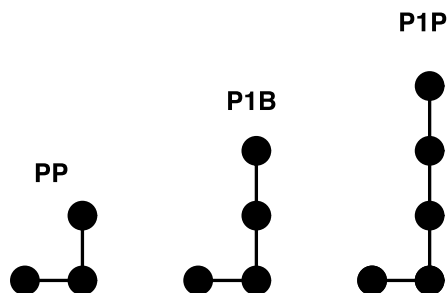


FIG. 1. Cartoons of monomers of PP, P1B, and P1P. Each monomer of a given polymer species i contains m_i united atom CH_n groups (solid circles) that are connected by $m_i - 1$ consecutive bonds (lines). Polymer chains of species i are constructed by successively linking the backbone united atom groups of monomers of this species. The total number M_i of united atom groups in a chain equals $M_i = m_i N_i + 1$, where the polymerization index N_i denotes the number of monomers in a chain.

the GET by three microscopic energetic parameters ϵ , E , and E_s , the polymerization index N (the number of monomers in a single chain), and by the temperature T and the pressure P . The consideration of a nonzero pressure imposes the requirement that the lattice model for a polymer melt contains empty lattice sites. All calculations described below refer to a pressure $P = 0.101\,325$ MPa and to a unit volume v_{cell} associated with a single lattice site, $v_{\text{cell}} = 2.7^3 \text{ \AA}^3$.

We begin with the computational analysis of the VFT equation³ because the GET validates this equation in the low temperature regime of glass-formation ($T_g < T < T_g + 100 \text{ K}$).^{5,11} Since the GET enables independent determination of both the fragility parameter D and the segmental relaxation time $\tau(T)$, the VFT temperature can be extracted from a plot of $\log[\tau(T)/\tau_0]$ versus $D T_{\text{VFT}} / [(T - T_{\text{VFT}}) \ln 10]$ that should yield a universal straight line for all the systems. Figure 2 presents this type of analysis for high molar mass models of poly(propylene) (PP), poly(1, butene) (P1B), and poly(1-pentene) (P1P) polymer melts, each with the nearest neighbor van der Waals energy $\epsilon = 200 \text{ K}$, the bending energy $E = 400 \text{ K}$ for the chain backbone, and the bending energy $E_s = 400 \text{ K}$ for the side chains for P1B and P1P.¹² The shifts ΔT between the fitted VFT temperatures T_{VFT} and the Kauzmann temperatures T_0 (where the extrapolated $s_c(T)$ vanishes) are specified in the figure. Since Fig. 3 demonstrates that the fragility parameter D scales in a universal linear fashion with $\Delta T \equiv T_{\text{VFT}} - T_0$, larger values of D (i.e., a smaller fragility) should be accompanied by greater departure of T_{VFT} from T_0 , an observation that has never been made before and that is important in analyzing our calculations of $C_2^{(g)}$ below.

Next, we describe the method of determining the WLF parameters $C_1^{(g)}$ and $C_2^{(g)}$ from the GET and discuss their basic characteristic features. Reexpressing the original form of the WLF equation (2) in the more convenient fashion,

$$\frac{-1}{\log[\tau(T)/\tau(T_g)]} = \frac{1}{C_1^{(g)}} + \frac{C_2^{(g)}}{C_1^{(g)}} \frac{1}{T - T_g}, \quad (7)$$

indicates that plots of the left hand side of Eq. (7) versus $1/(T - T_g)$ are straight lines with slopes $b \equiv C_2^{(g)}/C_1^{(g)}$ and intercepts $a \equiv 1/C_1^{(g)}$. Since both the shift factor $\alpha^{(g)} = \tau(T)/\tau(T_g)$ and the glass transition temperature T_g (conventionally taken as the

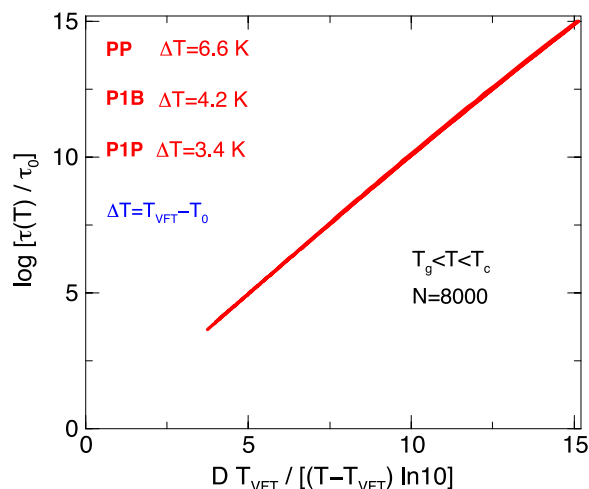


FIG. 2. Analysis of the VFT relation in Eq. (1) by plotting the logarithm of the calculated reduced relaxation time $\tau(T)/\tau(T_g)$ (where T_g is the glass transition temperature) versus $D T_{\text{VFT}} / [(T - T_{\text{VFT}}) \ln 10]$ (where D is the fragility parameter evaluated from the GET, T is a variable temperature, and T_{VFT} is the VFT temperature) for the PP, P1B, and P1P polymers (see Fig. 1) in Fig. 1. The chains of these three polymers are assumed to have the van der Waals interaction energy $\epsilon = 200 \text{ K}$, the bending energy $E = 400 \text{ K}$ in the chain backbone, the bending energy $E_s = 400 \text{ K}$ in the side group chains (in the case of P1B and P1P), and the polymerization index $N = 8000$. The VFT temperature T_{VFT} is fit for each melt to the straight line $y = x$ that emerges from Eq. (1) when $y = \log[\tau(T)/\tau_{\text{VFT}}]$ is plotted versus $x = D T_{\text{VFT}} / [(T - T_{\text{VFT}}) \ln 10]$. The shifts $\Delta T = T_{\text{VFT}} - T_0$ are indicated in the figure. The pressure $P = 0.101\,325$ MPa and the cell volume v_{cell} is $v_{\text{cell}} = a_{\text{cell}}^3 = (2.7)^3 \text{ \AA}^3$ in all Figs. 2–10.

temperature corresponding to $\tau = 100 \text{ s}$) can each be evaluated from the GET,^{5,9} the GET along with Eq. (7) enables the determination of $C_1^{(g)}$ and $C_2^{(g)}$ without adjustable parameters beyond those specifying the system (ϵ , E , E_s , and N). Figure 4 depicts typical plots of $-1/\log \alpha^{(g)}$ versus $1/(T - T_g)$ for model polymers with a PP structure and chain polymerization indices ranging from those for short chains ($N = 33$) to the high molar mass limit ($N = 8000$). Another method of estimating $C_1^{(g)}$ and

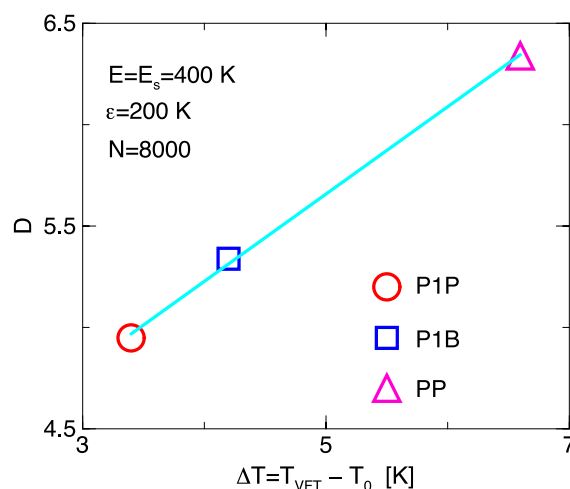


FIG. 3. Dependence of the temperature shift $\Delta T = T_{\text{VFT}} - T_0$ (determined from the analysis illustrated in Fig. 2) on the fragility constant D as computed from the GET for the glass-forming poly(α -olefin) polymers illustrated in Fig. 1.

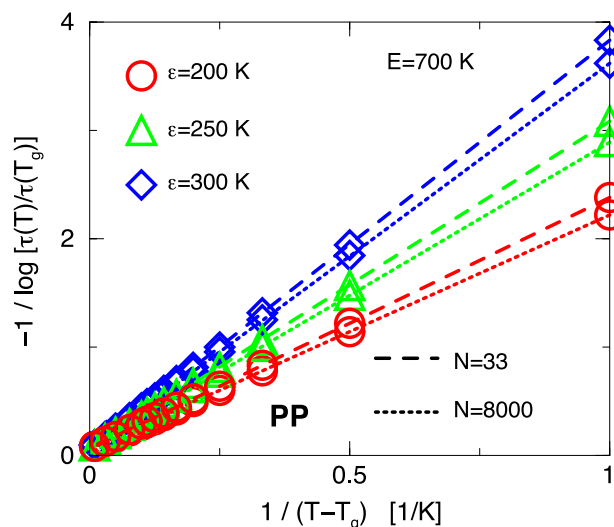


FIG. 4. The reciprocal of the logarithm of the computed WLF shift factor $\alpha^{(g)}$ [defined as the ratio of the structural relaxation times at temperature T and at the glass transition temperature T_g , $\alpha^{(g)} = \tau(T)/\tau(T_g)$] as a function of the reciprocal of the temperature difference $T - T_g$ evaluated from the GET. Chains are assumed to have the structure of PP, a common bending energy $E = 700$ K, and different van der Waals interaction energies ϵ as indicated in the figure. The temperature T ranges from T_g to $T_g + 100$ K. Symbols denote the calculations, and dotted and dashed lines are the least square fits for polymers with polymerization indices $N = 33$ and $N = 8000$, respectively.

$C_2^{(g)}$ follows from their alternative definitions,

$$C_1^{(g)} = DT_{VFT}(T_g - T_{VFT}) \ln 10 \quad (8)$$

and

$$C_2^{(g)} = T_g - T_{VFT}, \quad (9)$$

and the equivalence of the VFT and WLF equations in the low temperature regime of glass-formation. This assumption leads to identical numerical results for $C_1^{(g)}$ and $C_2^{(g)}$, as deduced from Eq. (7), provided the VFT temperature T_{VFT} is determined by the procedure indicated in Fig. 2.

Figure 5 collects the computed $C_1^{(g)}$ for model polymer melts with the monomer structures of PP, P1B, and P1P. Data for a particular polymer structure and a given nearest neighbor van der Waals interaction energy ϵ refer to different bending energies E (PP) or different pairs of bending energies E and E_s (P1B and P1P). Computed values of $C_1^{(g)}$ generally span the narrow range from 15 to 16. This parameter exhibits small variability with monomer structure, the degree of chain stiffness, the strength of cohesive interactions, and even the polymerization index N . In contrast to these findings for $C_1^{(g)}$, a similar plot for $C_2^{(g)}$ versus ϵ for high molar mass model melts of polymers with the structure of PP indicates that $C_2^{(g)}$ depends significantly on both ϵ and E , ranging from around 30 K to about 70 K for this family of model polymer melts, a range that is similar to the observed range (24 K–104 K) noted by Angell for synthetic polymers.⁶ Figure 6 exhibits the linear variation of $C_2^{(g)}$ with ϵ for fixed E . The slope decreases with chain stiffness. A similar behavior emerges from our calculations for polymers with the P1B and P1P structures. When all the computed values of $C_2^{(g)}$ for the three model

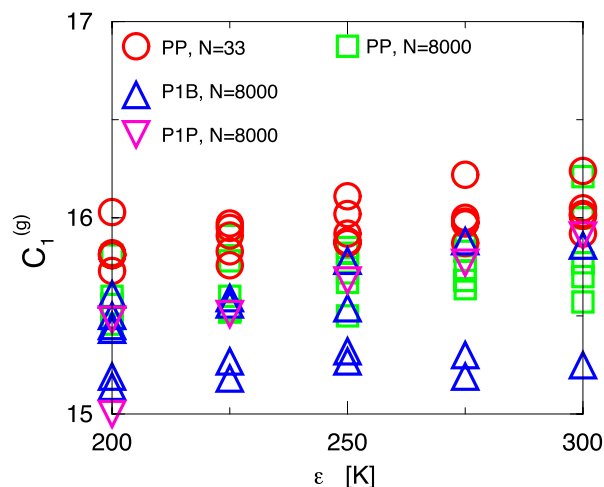


FIG. 5. The WLF parameter $C_1^{(g)}$ (determined from plots like those in Fig. 4) as a function of ϵ for poly(α -olefin) polymers with the monomer structures specified in Fig. 1 and the polymerization indices N as indicated in the figure. Symbols of the same type for a given ϵ correspond to PP polymers with different bending energies E (ranging from 400 K to 1200 K) or to P1B or P1P polymers with different combinations of the bending energies in the backbone (E) and side chains (E_s).

polymer melts and various $\{N\}$, $\{\epsilon\}$, and $\{E, E_s\}$ are divided by the corresponding glass transition temperatures T_g and are collected together onto one figure, the data remarkably exhibit a universal scaling of $C_2^{(g)}/T_g$ with the fragility parameters D or $K_s = 1/D$. Figure 7 displays this universal correlation between the ratio $T_g/C_2^{(g)}$ and the fragility parameter K_s . The calculations in Figs. 2–7 demonstrate that the GET reproduces general trends in observed experimental WLF parameters for polymeric fluids, thus providing a predictive capacity beyond the reach of any other statistical mechanical theory. We now turn to understanding the relationship between the VFT and WLF descriptions of $\tau(T)$.

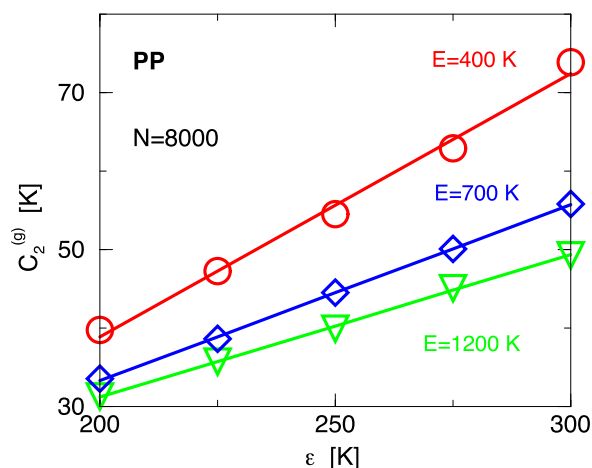


FIG. 6. A typical dependence of the calculated WLF parameter $C_2^{(g)}$ (determined from the plots exemplified in Fig. 4) on the interaction energy ϵ for the high molar mass ($N = 8000$) polymers with the structure of PP and different bending energies E as indicated in the figure. Symbols denote the calculations, and lines provide the least square fits.

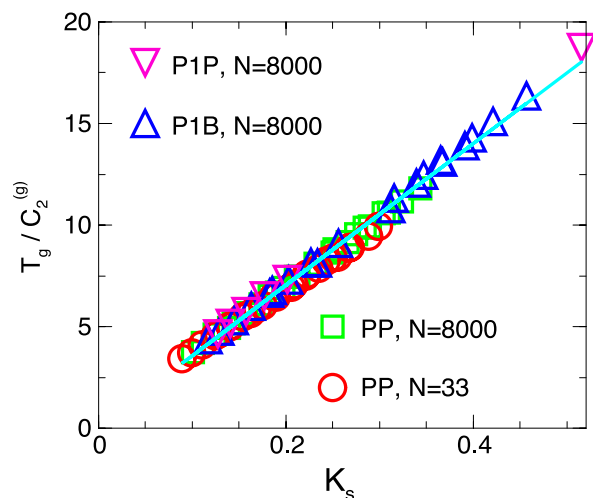


FIG. 7. The relation between the ratio $T_g/C_2^{(g)}$ and the fragility constant K_s , as computed from the GET for polymers indicated in the figure (where T_g is the glass transition temperature and $C_2^{(g)}$ is the WLF parameter). Symbols denote the calculations, and the line is the least square fit. Symbols of the same type refer to the polymers with a given monomer structure, but different combinations of ϵ ($200 \text{ K} \leq \epsilon \leq 300 \text{ K}$) and the bending energies E ($400 \text{ K} \leq E \leq 1200 \text{ K}$) [or for P1B and P1P, with combinations of ϵ , E , and E_s].

IV. DISCUSSION

Although the calculations described in Sec. III demonstrate agreement with experiment that the $C_1^{(g)}$ and $C_2^{(g)}$ parameters of the WLF equation are not really universal, many “typical” polymers approximately follow this relation,^{1,2} clearly indicating something important about the nature of glass-forming polymer liquids as a material class. Moreover, the assumption that $C_1^{(g)}$ and $C_2^{(g)}$ are constants is shown to produce conclusions incompatible with the equivalence of the WLF and VFT equations since constant WLF parameters would imply that the segmental relaxation time τ in the WLF equation then depends only on the temperature difference, $T - T_g$, completely independent of the fragility D . The observation of an approximate constancy for a number of polymers of $C_1^{(g)}$ and $C_2^{(g)}$ explains why many polymer scientists simply discount consideration of glass fragility.¹³ The resolution of these apparent inconsistencies is discussed below.

Restricting attention to the temperature range between T_g and T_c , where the VFT equation provides an excellent description of both the measured τ and the GET prediction for τ , the WLF equation can be deduced mathematically from the formally equivalent VFT equation, as described in the Introduction. Pushing our manipulations of the VFT equation further, it is also possible to show that the “steepness” index, $m = d \log \tau / d(T_g/T)|_{T=T_g}$, a widely reported⁴ measure of fragility, can be directly expressed in terms of $C_1^{(g)}$ and $C_2^{(g)}$ as¹⁴

$$m = (C_1^{(g)}/C_2^{(g)})T_g = \alpha T_g. \quad (10)$$

The constancy of the “universal” WLF constants $C_1^{(g)} = 17.44$ and $C_2^{(g)} = 51.6 \text{ K}$ in conjunction with Eq. (10) then would imply that m is proportional¹⁴ to T_g , i.e., $m \approx 0.34T_g$, a relation that is certainly not implied directly by the VFT equation alone.

A roughly linear correlation between m and T_g has indeed been reported¹⁴ for both polymeric and metallic glass-forming liquids when all available experimental data are superimposed on a common plot and an average least-square type fit is made for α of a given class of materials. The fits of α yield about 0.28 for the polymers, while a value of about 0.17 is found for metallic glasses.¹⁴ Qin and McKenna report¹⁴ the absence of systematic correlation between m and T_g for small molecule inorganic glass-forming materials which cover wider range of cohesive interaction strengths than found for metallic and synthetic polymer glasses, so it would be incorrect to assume that Eq. (10) holds generally for glass-forming materials. Nonetheless, the relation between m and T_g seems to be a characteristic of restricted classes of materials, a dependence illuminated by the GET.

Some insight into the proportionality between m and T_g in measurements for polymeric materials and thus into the origin of the “universal” WLF parameters can be directly obtained from the calculations of Sec. III. The approximate constancy of $C_1^{(g)}$ and $C_2^{(g)}$ can only be expected for polymers of similar “types,” e.g., polymers in a homologous series in which, for instance, the side chains have a variable length or polymers of different molar masses. An example of this behavior is displayed in Fig. 8, which depicts the steepness index m as a function of T_g for three different polymers having poly(α -olefin) monomer structures (see Fig. 1). Choosing representative values of the nearest neighbor van der Waals interaction energy $\epsilon = 250 \text{ K}$ and the bending energies, $E = E_s = 400 \text{ K}$, deduced from fits¹⁵ to thermodynamic data for PP,¹⁶ and assuming that our representative polymer has a simple poly(α -olefin) type structure, the steepness index m is found to vary nearly linearly with T_g , where the proportionality constant $\alpha = C_1^{(g)}/C_2^{(g)}$ for all three polymers differs by only a few percent. Moreover, α almost perfectly coincides with the value of 0.34 required to rationalize the observed “universality” of WLF parameters [see Eq. (10)]. This explains why data for

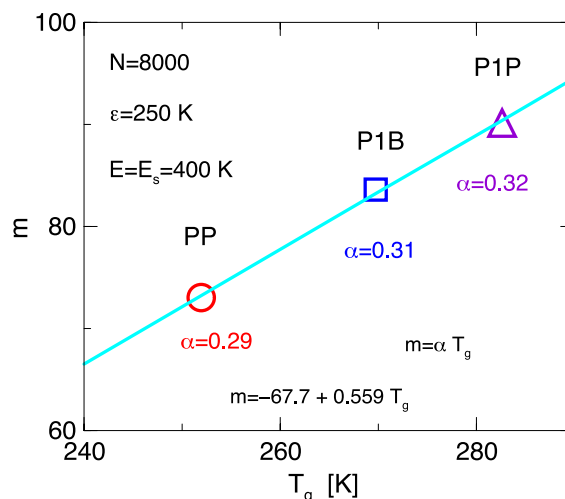


FIG. 8. The steepness index m as a function of the glass transition temperature T_g , as calculated from Eq. (10) for polymers with the monomer structures illustrated in Fig. 1, $\epsilon = 250 \text{ K}$,¹⁵ $E = E_s = 400 \text{ K}$,¹⁵ and polymerization index $N = 8000$. Symbols denote the calculations, and the line is the least square fit. The slope $\alpha = m/T_g$ is in units of K^{-1} .

“typical” flexible polymers interacting through relatively weak van der Waals forces might give the impression of “universality” in relaxation in the sense proposed by WLF.

Of course, not all polymers have such a weak intermolecular interaction strength ϵ and flexibility. More generally, the proportionality constant α between m and T_g depends on the type of polymer. In particular, direct computations with the GET reveal deviations of α from the “universal” value of $\alpha = 0.34$ when the strength of the van der Waals interaction is varied over a broad range, as illustrated in Fig. 9 for a family of model PP structured polymers having $\epsilon = 200$ K, 250 K, and 300 K. Additional calculations indicate that α also changes with the size and stiffness of the polymer side groups. For example, $\alpha = 0.602$ and 0.654 emerge, respectively, for the high molar mass ($N = 8000$) PIB and P1P model polymers when $\epsilon = 200$ K and $E = E_s = 1200$ K. Our computational analysis further reveals that α is insensitive to the polymer molar mass (see Fig. 10) or to details in the chemical structure of the polymers of the same “type,” provided the polymerization index is not so small that the chain cannot really be characterized as a polymer. The ratio $C_1^{(g)}/C_2^{(g)}$ is then a *constant* for a given class of polymers, albeit with values of $C_2^{(g)}$ not generally equal the “universal” constant $C_2^{(g)} = 51.6$ K. This predicted insensitivity of $C_1^{(g)}/C_2^{(g)}$ to the molar mass of the polymer accords with experiment.¹⁷

Evidently, when considering polymers with diverse monomer structures, chain stiffness, and intermolecular interactions, the proportionality between m and T_g and fixed $C_1^{(g)}$ and $C_2^{(g)}$ cannot reasonably be assumed to apply. The large variability of $\alpha = C_1^{(g)}/C_2^{(g)}$, noted before by Angell,⁶ is further evidenced by the large scatter of data in Fig. 1(a) of Ref. 14, which attempts to determine a relationship between m and T_g for *all* polymers. The validity of the WLF equation with constant values of $C_1^{(g)}$ and $C_2^{(g)}$ is strictly limited to polymers having very similar chemical structure. Rather than representing a shortcoming of the WLF method of data reduction, the ratio $\alpha = C_1^{(g)}/C_2^{(g)}$ becomes an attractive parameter for *quantifying* both polymer “type” and fragility.⁶

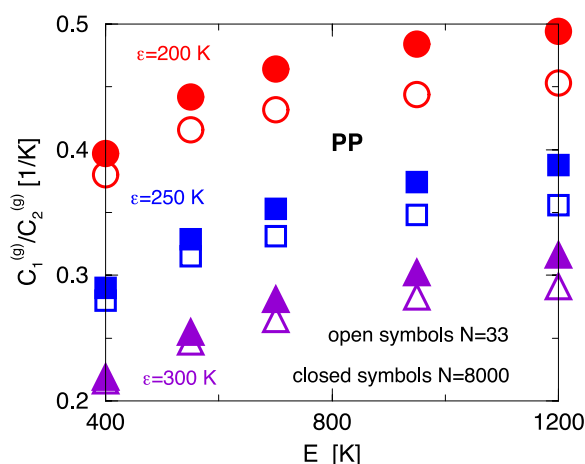


FIG. 9. Ratio $C_1^{(g)}/C_2^{(g)}$ of the WLF parameters computed from the GET for model polymers with a PP structure and various interaction energies $\{\epsilon\}$ (indicated in the figure) as a function of the bending energy E . Open and closed symbols refer to polymerization indices $N = 33$ ($M = 100$) and $N = 8000$ ($M = 24001$), respectively.

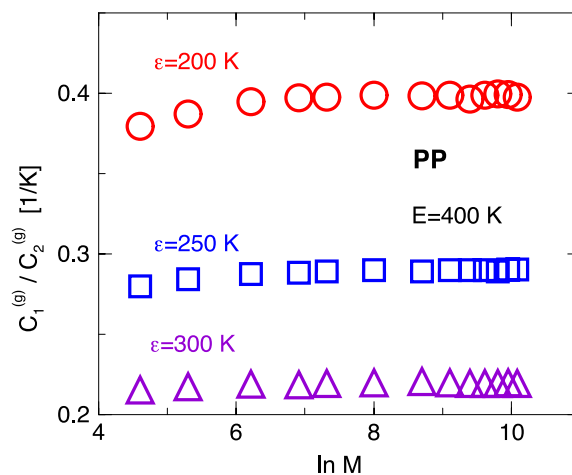


FIG. 10. Ratio $C_1^{(g)}/C_2^{(g)}$ of the WLF parameters computed from the GET for model polymers with a PP structure, the bending energy $E = 400$ K, and various nearest neighbor van der Waals interaction energies $\{\epsilon\}$ (indicated in the figure) as a function of the logarithm of the number M of united atom groups in a single chain, which is proportional to the polymer molar mass.

In summary, we determine the dependence of $C_1^{(g)}$ and $C_2^{(g)}$ on the molecular parameters that specify model polymer melts within the GET, including the strength of the molecular cohesive interaction energy ϵ , the degree of chain stiffness, and the polymer molar mass. The approximate “universal” WLF equation (with the originally proposed constant values of $C_1^{(g)}$ and $C_2^{(g)}$) emerges from the GET only when attention is restricted to polymers having $\epsilon \approx 250$ K, a simple polymer backbone structure, and a chain stiffness representative of reasonably flexible polymers. However, when ϵ and E vary over larger ranges or when the monomer structure is complex, the calculated $C_2^{(g)}$ differs appreciably. The GET predicts that $C_1^{(g)}$ and $C_2^{(g)}$ are constant and that $m = \alpha T_g$ for a *fixed homologous series* of polymers with similar chain structure and chemistry, suggesting that α might provide a good means of classifying polymers.

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