

Correlation between the secondary β -relaxation time at T_g with the Kohlrausch exponent of the primary α relaxation or the fragility of glass-forming materials

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A strong correlation between the logarithm of the secondary β -relaxation time, $\log_{10}[\tau_\beta(T_g)]$, and the Kohlrausch exponent, $(1-n)$, or the fragility index m of the primary α -relaxation correlation function $\exp[-(t/\tau_\alpha)^{1-n}]$, all at the glass transition temperature T_g , has been found in glass-forming materials in general. The β relaxations considered are restricted to a class that merges or tends to merge with the α relaxations. For β relaxations in polymeric glass formers that involve side groups, the class is further restricted to those that entail some motions of the polymer backbone. The correlation found indicates the existence of a connection between the β and α relaxations. A possible origin of this connection is rationalized by the conceptual basis of the coupling model. [S1063-651X(98)10406-3]

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In the study of the dynamics of the glass transition, emphasis has often been placed on the primary or α relaxation which is responsible for the major aspects of the phenomenon [1], including Kohlrausch's stretched exponential correlation function, $\exp[-(t/\tau_\alpha)^{1-n}]$, and the Vogel-Fulcher temperature dependence, the α -relaxation time τ_α . However, the secondary or β relaxations also seem to be a universal feature of glass-forming materials [2-4] observed at lower temperatures or higher frequencies than the α relaxation by isochronal and isothermal measurements. However, in some glass formers no evidence of a β -relaxation peak or shoulder has been found so far [3-7]. To avoid possible confusion, I hasten to point out that the β relaxations considered in this work have nothing to do with the β process in the mode coupling theory. A recent work using neutron scattering [8] to explore the origin of the β relaxation indicates continued interest in this area of research. The most probable relaxation time τ_β of the β relaxation has a mild Arrhenius temperature dependence $\tau_\beta(T) = \tau_{\beta\infty} \exp(E_\beta/RT)$ compared with the strong temperature dependence of τ_α . Typically, $\tau_{\beta\infty}$ falls within the [2-8] range $10^{-16} \leq \tau_{\beta\infty} \leq 10^{-13}$ s. Values of $\tau_{\beta\infty}$ in the vicinity of the upper limit correspond to molecular vibrational times, and the lower limit may be rationalized by an additional entropy contributions [2]. E_β has magnitudes that are identifiable with real energy barriers. The magnitudes of both quantities point to the origin of the β relaxation in simple molecular motions. Whatever the origin of the potential barriers, intramolecular or intermolecular, the experimental facts clearly indicate that the β relaxation arises from molecular mobility which remains even in the glassy state; i.e., below T_g . The molecular motion must be much simpler than the cooperative α relaxation. Molecular interpretations of the β relaxation have been offered [2-4,8-11].

In this work, experimental data of many glass formers are used to show that at the glass transition temperature T_g the value of $\tau_\beta(T_g)$ is not random, but strongly correlated with the Kohlrausch (K) exponent $(1-n)$ at T_g . Empirically, the exponent $(1-n)$ at T_g correlates with the T_g -scaled temperature dependence defined by the fragility index [12] m .

Thus a corollary of the finding is the correlation that $\log \tau_\beta(T_g)$ decreases with increasing fragility of the glass formers. A smaller K exponent of the α relaxation in more fragile glass formers corresponds to a shorter $\tau_\beta(T_g)$ or a smaller $\log[\tau_\beta(T_g)]$. Since $\tau_{\beta\infty}$ corresponds approximately to a vibrational frequency, the entire Arrhenius temperature dependence of τ_β is determined by value of $\tau_\beta(T_g)$. Thus the correlation found implies that the location of $\tau_\beta(T)$ in the relaxation map is roughly fixed by the characteristics of the α relaxation. This correlation is remarkable because it relates the secondary relaxation to the primary α relaxation, and should be of interest to any theory of either α or β relaxation.

The correlation to be established is between $\tau_\beta(T_g)$ and the Kohlrausch exponent $(1-n)$ of the α relaxation at T_g . Naturally, only glass formers for which experimental data of both quantities are available are included. I exclude from consideration all β relaxations that clearly bear no relation to the α relaxation. These include isolated rotations of methyl groups, motion of a side group without any involvement of the main chain in some amorphous polymers, and those β relaxations which do not merge with the α relaxation below a reasonably high frequency, say, 10 GHz. I also exclude the β relaxation of polystyrene, that has a $\tau_{\beta\infty}$ very much shorter than vibrational frequencies, making them impossible to be considered as a simple molecular motion like most others. In this work, T_g is defined as the temperature where $\tau_\alpha(T_g)$ reaches 10^4 s. The choice of 10^4 s to be the structural relaxation time at T_g is somewhat arbitrary, but the conclusion about the results to be given below are independent of the other possible choice of $\tau_\alpha(T_g) = 10^2 - 10^4$ s for the definition of T_g . The β -relaxation time $\tau_\beta(T_g)$ can be obtained either directly from the experimental data at T_g or by extrapolating the Arrhenius temperature dependence of $\tau_\beta(T)$ to T_g . The results, together with the K exponent $(1-n)$ at T_g , are listed in Table I, and are classified loosely into several groups according to similar chemical and physical characteristics. Due to length limitation, the T_g 's are not included in Table I, but approximate values can be found in tables of

TABLE I. The value of $(1-n)$ is the Kohlrausch exponent in the Kohlrausch function used to fit the shape of the dielectric, mechanical, photon correlation or NMR data of the α relaxation at $T=T_g$. The β -relaxation time at T_g , $\tau_\beta(T_g)$, is taken directly from the experimental data of the β relaxation whenever it is observable.

Glass former	$1-n$	$\log_{10}[\tau_\beta(T_g)]$	Glass former	$1-n$	$\log_{10}[\tau_\beta(T_g)]$
Amorphous polymers			Small molecules		
Poly(vinylchloride) [23]	0.27	-6.7	17.2% Chlorobenzene/cis-decaline [3,4]	0.37 ^b	-5.3
Poly(aryletheretherketone) [24]	0.32	-8.2	Toluene [35]	0.49	-4.7
Poly(oxy-1,4-phenylene sulfoneyl-1,4-phenylene) [24]	0.33	-9.4	<i>ortho</i> -terpheny [3-5]	0.55	-5.1
Polycarbonate (β') [43]	0.35	-5.1	Isopropylbenzene [3,4,31]	0.56	-4.3
Poly(cyclohexylmethacrylate) [25]	0.37	-6.2	Phenyl salicylate (salol) [36,37]	0.58	-4.3
Poly(2-chlorocyclohexylacrylate) [26]	0.36	-6.0	2-hydroxy-diphenyl-methane (α -phenyl- <i>o</i> -cresol) [36,37]	0.53	-3.8
Polymethylmethacrylate [10,24(b),27]	0.37	-5.2	Tritolylphosphate [31]	0.60	-4.2
Poly(butadiene) [8,12]	0.42	-4.7	3-bromopentane [31,38]	0.63	-3.3
Poly(vinylacetate) [43]	0.48	-4.5	bis-methoxy-phenyl-cyclohexane [5,36]	0.60	-2.8
Poly(isoprene) [43]	0.50	-4.6	N-methyl- ϵ -caprolactam [5,36]	0.74	^a
Poly(propyleneglycol) [6,28]	0.50	-5.0	2-methyltetrahydrofuran [39]	0.64	^a
Combined main-chain side group liquid-crystalline polymer-43 [29]	0.33	-6.7	3-methylpentane [39]	0.72	^a
Alcohols and related materials			Phenolphthalein-dimethylether [36]	0.77	^a
Propanol [5]	0.60	-2.8	Cresolphthalein-dimethylether [36]	0.77	^a
Sorbitol [27,30]	0.48	-4.6	Propylene carbonate [3,4,40]	0.74	^a
Maltitol [27]	0.40	-6.0	<i>m</i> -tricresyl phosphate [36]	0.70	^a
Glucose [24(b),24(c),31]	0.33	-7.0	Plastic Crystals		
Fructose [32]	0.34	-6.7	1-cyanoadamantane [41]	0.62	-1.8
Glycerol [7]	0.71	^a	Cyclo-octanol [13]	0.77	-0.44
Propylene glycol [6,33]	0.75	^a	(CF ₄) _{0.46} (CClF ₃) _{0.54} [42]	0.30 ^c	-5.7
Aqueous solutions of 0.50 mole fraction of dimethylsulfoxide [34]	0.76	^a	Inorganic Glass formers		
Aqueous solutions of 0.50 mole fraction of ethyleneglycol [34]	0.76	^a	Boron trioxide [43]	0.60	-1.3
Aqueous solutions of 0.50 mole fraction of methanol [34]	0.78	^a	Silica [24(c)]	0.70	^a

^aA peak or shoulder indicating the presence of a β relaxation has not been observed experimentally either by isochronal or isothermal measurement.

^bThe K function does not give a good fit to the loss spectrum.

^cValue from the K stretched exponential fit to the dielectric relaxation data may be an overestimate of the actual $(1-n)$ because of additional broadening caused by concentration fluctuation of the CClF₄ probe molecules in the CF₄ host lattice.

Ref. [12]. The existence of a correlation is shown by a plot of $\log[\tau_\beta(T_g)]$ against $(1-n)$ in Fig. 1. The data shown as points exhibit the trend that $\log[\tau_\beta(T_g)]$ increases with $(1-n)$. Different symbols are used for different classes of glass formers. The correlation is even stronger when comparisons are confined to members of a closely related family of glass formers.

Points lying on the solid line (to be described) and inside the parallelogram in Fig. 1 are not real experimental data of $\log[\tau_\beta(T_g)]$. Only the x values of these points correspond to the actual values of the K exponents, $(1-n)$, of the α relaxation of these glass formers in which the β relaxation has not been resolved either as a peak or a shoulder in the loss spectrum. These ‘‘fictitious’’ data of $\log[\tau_\beta(T_g)]$ are plotted in the manner described to highlight the observation that the glass formers in Table I, on which the β relaxation has not been resolved, all have larger values of $(1-n) \geq 0.7$, except for 2-methyltetrahydrofuran, which has a slightly larger $(1-n)$

$= 0.64$. Consistent with the correlation between $\log[\tau_\beta(T_g)]$ and $(1-n)$ found from glass formers that show β relaxation, the glass formers inside the parallelogram in Fig. 1 may have $\log[\tau_\beta(T_g)]$'s so long, and so close to $\log[\tau_\alpha(T_g)]$, as to make it difficult or impossible to resolve the β relaxation from the more dominant α -relaxation peak. In other words, the correlation found may explain why β relaxation of the kind of interest to this work has not been found in some glass formers. There is one point (filled circle) which has $(1-n) = 0.77$, but lies outside the parallelogram, and this represents *actual* data of $\log[\tau_\beta(T_g)]$ of the plastic crystal cyclo-octanol. The dielectric loss dispersion of cyclo-octanol [13] is very similar to other glass formers inside the parallelogram (e.g., glycerol, propylene glycol, and propylene carbonate [3-7]), showing no shoulder or peak to indicate the presence of a β relaxation, however, a special circumstance in cyclo-octanol enabled the authors of Ref. [13] to resolve the β -relaxation peak. This work [13] strengthens the proposal that

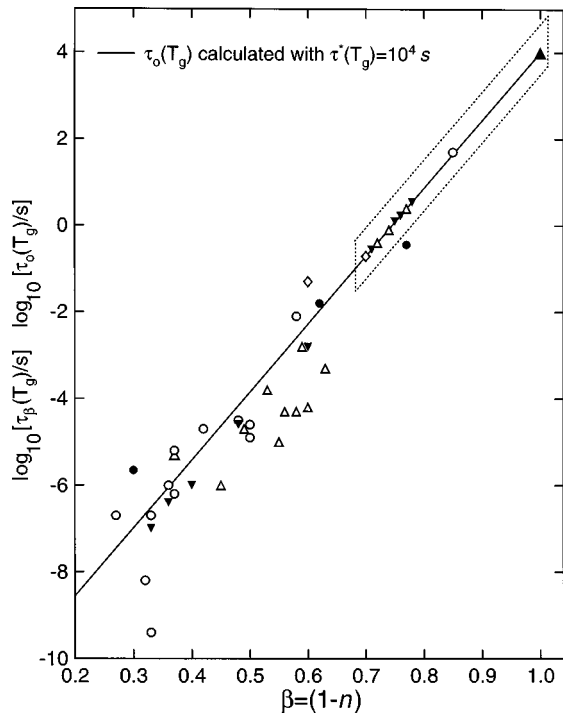


FIG. 1. Solid line represents $\log_{10}[\tau_0(T_g)]$ calculated from the coupling model. Symbols outside the parallelogram represent the experimental values of $\log_{10}[\tau_\beta(T_g)]$ for glass formers with different chemical structures. (1) Open circles for amorphous polymers. (2) Open triangles for small molecule van der Waal liquids. (3) Filled inverted triangles for small molecule liquids with hydrogen bonding and the alcohols. (4) Filled circles are for the plastic crystals. For points inside the parallelogram, see text. The lone filled triangle represents the extreme case of a linear exponential α relaxation, which has $\tau_0(T_g) = \tau_\alpha(T_g)$, and the β and α relaxations are expected to become inseparable from each other.

the unobservability of β relaxation in strong glass formers is due to their $\log[\tau_\beta(T_g)]$ being long, as suggested by the locations of the fictitious data points inside the parallelogram in Fig. 1.

A possible origin of the correlation can be rationalized by the concept of the coupling model (CM) [14,15]. In the CM, there exists a temperature insensitive crossover time t_c with a magnitude determined by the strength of the intermolecular interaction. At times shorter than t_c , the basic molecular units relax independently of each other and exponentially (i.e., via the primitive α -relaxation mode) according to the normalized correlation function, $\phi(t) = \exp(-t/\tau_0)$ for $t < t_c$, where τ_0 is the primitive α -relaxation time. At times longer than t_c , the intermolecular interactions (i.e., cooperativity) slow down the relaxation, and the averaged correlation function assumes the Kohlrausch stretched exponential form $\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}]$ for $t > t_c$. Continuity of $\phi(t)$ at t_c leads to the relation $\tau_\alpha = [t_c^{-n} \tau_0]^{1/(1-n)}$ between the two times. Existence of the crossover time has been shown by simple Hamiltonian models that exhibit chaos [15]. Experi-

mental proofs for the existence of such a crossover at a time, $t_c \approx 2$ ps, come from quasielastic neutron scattering measurements in poly(vinylchloride) [16], poly(isoprene), and polybutadiene [17] performed at temperatures high above T_g where τ_α becomes short, and on the order of ten picoseconds or less. Under this condition, the primitive α relaxation, decaying linearly exponentially, is directly evident from the relaxational part of the experimental data. There are also proofs for the crossover at $t_c \approx 2$ ps from (a) analysis of molecular dynamics data of *ortho*-terphenyl [18], (b) high frequency dielectric measurement of a molten salt [19], (c) molecular dynamics simulations [20,21] and neutron scattering experiment [21] performed in polyethylene, and (d) molecular dynamics simulation data of polystyrene [22]. The β relaxation being a simple molecular motion bears some resemblance to the primitive α relaxation; however, they cannot be the same. Otherwise the former like the latter will be slowed down by intermolecular interactions to become the cooperative α relaxation observed at longer times. Therefore, it makes sense to compare the experimental values of $\tau_\beta(T_g)$ in Table I and Fig. 1 with $\tau_0(T_g)$ calculated as a function of $(1-n)$ by solving the equation $\tau_\alpha(T_g) = [t_c^{-n} \tau_0(T_g)]^{1/(1-n)}$ with $t_c = 2$ ps and $\tau_\alpha(T_g) = 10^4$ s. The result is shown as the solid line in Fig. 1 and the experimental values of $\tau_\beta(T_g)$ are remarkably close in order of magnitude to $\tau_0(T_g)$ for many glass formers, as can be anticipated by the resemblance between the two processes. It is worth emphasizing once more that the value of $t_c = 2$ ps used to calculate the solid line is not arbitrary, and had been predetermined by experiment [16–22]. Also, although we use $\tau_\alpha(T_g) = 10^4$ s to define T_g and obtain the data of $\tau_\beta(T_g)$ in Fig. 1 at the same temperature, we could use any other reasonable choice like $\tau_\alpha(T_g) = 10^2$ or 10^3 s to define T_g . The line calculated with, say, $\tau_\alpha(T_g) = 10^2$ s and the same $t_c = 2$ ps occupies a different position in Fig. 1, but so do the $\tau_\beta(T_g)$ data points in Fig. 1 because of a slightly higher new value of T_g . However, both the line and the data points shift in the same direction. Hence the proximity of the solid line to the data points in Fig. 1 is a result which is independent of the choice of the value for $\tau_\alpha(T_g)$.

Although I have rationalized the occurrence of a correlation between $\log[\tau_\beta(T_g)]$ and $(1-n)$ in the framework of the coupling model, the emphasis of this work is on the existence of the correlation as an empirical fact. This principal result deserves attention from workers in the glass transition from all points of view on both the α and β relaxations, because it correlates a quantity of the former with another of the latter. It would be interesting to examine the correlation in light of other physical interpretations of the β relaxation including (1) the island of mobility of Johari and Goldstein [3,4], (2) the quasipoint defect model of Perez and Cavaille [9], (3) the model of Garwe *et al.* [10(b)], (4) the dynamically “uncorrelated” regions of Fujimori and Oguni [11], and (5) the view of β relaxation as the precursor of α relaxation by Arbe *et al.* [8].

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