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Fragility and temperature dependence of stretched exponential relaxation in glass-forming systems

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Abstract

Relaxation behavior is critically important for nearly all high-tech applications of glass. It is also known as one of the most difficult unsolved problems in condensed matter physics. The relaxation behavior of glass can be described using the stretched exponential decay function $\exp\left(-(t/\tau)^{\beta}\right)$, the shape of which is governed by the dimensionless stretching exponent β. Here, a temperature-dependent model for $\beta(T)$ is proposed. The model is derived based on the Adam-Gibbs relationship and insights from the energy landscape description of glass-forming systems. The model captures previously known limiting values of $\beta(T)$ while also providing a continuous transition between these limits. Additionally, the model captures the effects of fragility and thermal history. The model is validated with experimental data for commercial silicate glasses and a borate glass.

KEYWORDS

glasses, modeling, Monte Carlo, relaxation, statistical mechanics, viscosity

1 | INTRODUCTION

Relaxation is one of the most important properties for designing new glass products, as the thermal history of glass affects all of its properties.[1–8] The mathematical form for glass relaxation (ϕ) was originally proposed by Kohlrausch in 1854 based on the decay of charge in a Leyden jar,[1,3,9–13]

$$\phi(t) = \exp\left(-(t/\tau)^{\beta}\right), \tag{1}$$

where t is time, τ is the relaxation time of the system, and β is the dimensionless stretching exponent. Equation (1) was originally proposed empirically and is known as the stretched exponential relaxation (SER) function.[1,9] The relaxation time, τ, depends on the composition, temperature, thermal history, pressure, and pressure history of the glass, as well as the property being measured.[14,15] For example, the stress relaxation time of a glass can be written as follows[15]:

$$\tau_s = \frac{\eta\left(T_f, T, P_f, P\right)}{G\left(T_f, T, P_f, P\right)} \tag{2}$$

where η is the shear viscosity and G is the shear modulus of the glass-forming system.[9] (Variables are defined in Table 1). In addition to using Equation (2) to describe *stress* relaxation time, *structural* relaxation time has recently been hypothesized to follow Equation (2) with bulk viscosity and the difference of bulk modulus between infinite and 0 frequency replacing shear viscosity and shear modulus.[15] Both η and G vary with the temperature (T) and thermal history of the glass (as quantified via the fictive temperature, T_f) as well as the pressure (P) and its corresponding history (fictive pressure, P_f).[16] The mathematical form proposed empirically by Kohlrausch was subsequently derived by Grassberger and Proccacia from a random trap model[17]; however, this model is unable to provide physical meaning to the stretching exponent at all temperatures.[2,17–19]

TABLE 1 Variable definitions

Variable	Definition
τ; τ_s	Structural relaxation time; stress relaxation time
β	Kohlrausch exponent (i.e., the stretching exponent)
T; T_f; $T_{f,i}$	Absolute temperature; fictive temp.; partial fictive temp.
P; P_f	Pressure; fictive pressure
k_B	Boltzmann's constant
w_i, k_i, $i = 1$ to N	Prony series parameters
B	Adam-Gibbs relaxation barrier
S_c	Adam-Gibbs configurational entropy
σ_B	Distribution of activation barriers
σ^2	Variance
N_a	Number of atoms
f	Topological degrees of freedom per atom
Ω	Degenerate configurations per floppy mode
H	Enthalpy barrier for Relaxation
d	Number of dimensions
f^*	Fraction of activated relaxation pathways
S_∞	Adam-Gibbs entropy in the infinite-temperature limit
m	Kinetic fragility index
m_0	The limit of a strong liquid
γ	Grouped constants $\frac{\sqrt{6}\sigma_B}{\pi N_a k_B \ln\Omega}$
A	Proportionality between fragility and distribution of barriers
x	A given composition
ζ	$\frac{\pi S_\infty}{5.640 A^{1/2}}$
ζ'	Intercept of the linear model of Δ

While it is well known that liquids at high $(T >> T_g)$ temperatures exhibit simple exponential decay (i.e., $\beta = 1$), Phillips[18] derived a model for the limiting value of β at temperatures sufficiently below the glass transition temperature (T_g). According to the Phillips model, β is related to the dimensionality of the relaxation pathways by,

$$\beta = \lim_{T \ll T_g} \frac{df^*}{df^* + 2}. \tag{3}$$

Here, d is the dimensionality of the glass network, and f^* is the fraction of activated relaxation pathways.[2,3,11,12,18] Some examples seen in practice include: a three-dimensional network with all pathways activated ($d = 3$, $f^* = 1$), yielding a value of $\beta = 3/5$; a three-dimensional network with half of the pathways activated ($d = 3$, $f^* = 1/2$), yielding $\beta = 3/7$; and a two-dimensional network with all pathways activated ($d = 2$, $f^* = 1$), yielding $\beta = 1/2$. In the Phillips model, the relaxation pathways can be classified as either long-range or short-range. Structural relaxation involves only long-range pathways ($f^* = 1/2$), whereas stress relaxation involves both long- and short-range pathways ($f^* = 1$).[2] The Phillips model was experimentally validated by Welch et al. in their 1.5-year measurement of the room temperature relaxation of Corning Gorilla® Glass, where β was found to be 3/7 for structural relaxation[12]; an exponent of 3/5 has also been confirmed for stress relaxation of other industrial silicate glasses.[11] The SER equation (Equation 1) has also been derived using graph theory, where the SER form often appears in analytical solutions.[20–30]

The purpose of this work is to provide a physically motivated equation (a model) that reproduces the high-temperature limit of $\beta = 1$ and the low-temperature ($T << T_g$) limit given by Phillips in Equation (3), while providing values for β at in-between temperatures through the glass transition regime. Relaxation behavior is critically important for the design and use of high-tech commercial glasses. Hence, any improvement in the understanding of relaxation can be used to optimize glass composition design and process conditions. The model presented herein is the first model to account for the temperature dependence of the stretching exponent during glass relaxation, and therefore provides a new degree of understanding and control in the design and processing of glassy materials.

2 | MODEL

To connect the stretching exponent of glass-forming systems to its physical origins, we can begin with a result from Richert and Richert[31] that relates β to an underlying structural relaxation time distribution, and then develop equations that determine β from known quantities. Their expression in the limiting case of heterogeneity (as discussed by Richert and Richert[31]) is given by,

$$\sigma_{\ln\tau}^2 = \frac{\pi^2}{6}\left[\frac{1 - \beta^2}{\beta^2}\right], \tag{4}$$

which relates β to the variance of the logarithm $\left(\sigma_{\ln\tau}^2\right)$ of the structural relaxation time τ. For reference, all variables are defined in Table 1. The physical origins of the relaxation time τ are related to the configurational entropy (S_c) as shown by the Adam-Gibbs equation,[32–34]

$$\ln\tau = \ln\tau_\infty + \frac{B}{TS_c}, \tag{5}$$

where τ_∞ is the infinite temperature relaxation time, T is the absolute temperature, and B represents the energy barrier for relaxation.

Combining Equations (4) and (5), Gupta and Mauro[19] proposed that the variance of the energy barriers for relaxation (σ_B^2) could be rewritten as follows:

$$\sigma_B^2 = \left[TS_c(T) \right]^2 \frac{\pi^2}{6} \left(\frac{1 - \beta^2}{\beta^2} \right). \tag{6}$$

Solving for the stretching exponent,

$$\beta = \frac{\pi TS_c(T)}{\sqrt{\left[6\sigma_B^2 + \left(\pi TS_c(T) \right)^2 \right]}}. \tag{7}$$

The work of Naumis et al.[35,36] has shown that the configurational entropy of glass-forming systems is proportional to the topological degrees of freedom in the network, a result that was used in the derivation of temperature-dependent constraint theory[37] and the MYEGA (Mauro-Yue-Ellison-Gupta-Allan) equation for the viscosity of supercooled liquids.[34] The MYEGA equation was derived by expressing the configurational entropy as follows:

$$S_c(T, x) = f(T, x) N_a k_B \ln\Omega. \tag{8}$$

In Equation (8), f is the topological degrees of freedom per atom, N_a is the number of atoms, k_B is Boltzmann's constant, x is a given composition and Ω is the number of degenerate configurations per floppy mode. The temperature dependence of the topological degrees of freedom was approximated using a simple two-state model,

$$f(x, T) = df^* = 3\exp\left(\frac{-H(x)}{k_B T} \right). \tag{9}$$

Here, $H(x)$ is the enthalpy barrier for relaxation, d is the dimensionality of the system, and f^* is the fraction of activated relaxation pathways. Combining Equations (7) and (9) as well as condensing the unknowns into the term defined by

$$\gamma = \frac{\sqrt{6}\sigma_B}{\pi N_a k_B \ln\Omega} \tag{10}$$

we get

$$\beta = \frac{df^*}{\sqrt{\left(\frac{\gamma}{T} \right)^2 + (df^*)^2}}. \tag{11}$$

This can be compared to the prediction made by Phillips[18] for the stretching exponent at temperatures below the glass transition,

$$\beta = \frac{df^*}{2 + df^*}. \tag{12}$$

Comparing the two expressions of Equations (11) and (12), they would agree if

$$\frac{\gamma}{T} = 4 + 4df^*. \tag{13}$$

We will show later (Figure 4) an example where extrapolating our model prediction for β to room temperature (with T in Equation (13) replaced by fictive temperature T_f) gives a result close to the Phillips value of Equation (12). When the temperature T in Equation (11) is high (much larger than γ) then Equation (11) gives us $\beta \to 1$. Thus, the model can interpolate between the low-temperature (Phillips) value and the high-temperature value of 1. In our current model, we do not have access to a value for γ in Equation (10) so this model cannot assess whether the Phillips room temperature value for β is universal, i.e., whether Equation (13) is always satisfied at room temperature.

Zheng et al.[38] showed that the Mauro-Allan-Potuzak (MAP) model for the relaxation time of the nonequilibrium glassy state[39] implies that the configurational entropy can be written as a function of thermal history (T_f), the fragility index (m), the fragility limit of a strong liquid (m_0), the glass transition temperature (T_g), and the limit of infinite temperature configurational entropy (S_∞) as,

$$S_c(T_f) = \frac{S_\infty}{\ln 10} \exp\left[-\frac{T_g}{T_f} \left(\frac{m}{m_0} - 1 \right) \right]. \tag{14}$$

The qualitative relationship between the distribution of activation barriers and fragility was proposed by Stillinger,[40,41] who suggested that the energy landscape of a strong liquid (low fragility) has a small distribution of activation barriers and that a higher fragility is associated with a broader distribution of activation barriers, that is, a higher variance of the activation barriers. This leads to a phenomenological relationship that is here assumed to be valid based on Stillinger's work on energy landscapes,[40,41]

$$\sigma_B^2 = A \left(\frac{m}{m_0} - 1 \right), \tag{15}$$

where A is some constant of proportionality. This expression was chosen because in the limit of a strong glass there is an infinitely sharp distribution of activation barriers. Combining Equations (7), (14), and (15), we obtain the temperature dependence of the stretching exponent for a liquid:

$$\beta(T_f) = \frac{\pi T_f S_\infty \exp\left[-\frac{T_g}{T_f} \left(\frac{m}{m_0} - 1 \right) \right]}{\sqrt{6(\ln 10)^2 A \left(\frac{m}{m_0} - 1 \right) + \pi^2 T_f^2 S_\infty^2 \exp\left[-\frac{2T_g}{T_f} \left(\frac{m}{m_0} - 1 \right) \right]}}. \tag{16}$$

Fictive temperature appears in this new expression because we are deliberately expressing this function as an equilibrium model. This assumption is not physically rigorous but does allow the model to be extended to the nonequilibrium glassy state. Rewriting Equation (16) in terms of one unknown (ζ) and grouping constants,

$$\beta\left(T_\mathrm{f}\right) = \frac{T_\mathrm{f}\zeta\exp\left[-\frac{T_\mathrm{g}}{T_\mathrm{f}}\left(\frac{m}{m_0}-1\right)\right]}{\sqrt{\left(\frac{m}{m_0}-1\right)+T_\mathrm{f}^2\zeta^2\exp\left[-\frac{2T_\mathrm{g}}{T_\mathrm{f}}\left(\frac{m}{m_0}-1\right)\right]}}. \quad (17)$$

Equation (17) is an expression for the stretching exponent as a function of thermal history, glass transition, and fragility index with only one unknown. In Equation (17),

$$\zeta = \frac{\pi S_\infty}{\sqrt{6}\,(\ln 10)\,A^{1/2}}. \quad (18)$$

The only unknown for the compositional dependence of the stretching exponent is the value of ζ. The composition-dependent part of Equation (18) is S_∞ since we approximate A to be independent of composition. The fragility dependence of S_∞ was proposed by Guo et al.,[42]

$$S_\infty(x) = S_\infty(x_\mathrm{ref})\exp\left[\frac{m(x)-m(x_\mathrm{ref})}{m_0}\right], \quad (19)$$

where x is composition and x_ref is a reference composition in the same glass family. Seeking the simplest possible expression

to approximate the unknown ζ, we take the natural logarithm of Equation (18) and of Equation (19) and combine them to get

$$\ln\zeta = \frac{m}{m_0} + \ln\zeta', \quad (20)$$

with the additional definition

$$\ln\zeta' = \ln\left(\frac{\pi S_\infty\left(x_\mathrm{ref}\right)}{\sqrt{6}\,(\ln 10)\,A^{1/2}}\right) - \frac{m\left(x_\mathrm{ref}\right)}{m_0}. \quad (21)$$

The result is that $\ln\zeta'$ varies linearly with fragility m and the intercept $\ln\zeta'$ is independent of composition (depends on one reference composition).

In Figure 1 we plot the data of Böhmer et al.[43] versus the predicted exponent. The work of Böhmer et al. is the summary of the literature data relating fragility index to the stretching exponent at the glass transition, which we use to fit values to Equation (20). The model was then evaluated using the glass transition temperature and fragility of each system. The dataset included in their work covers chalcogenide, oxide, and organic glasses. The fitting (consisting of least-squares minimization of the difference between the predicted stretching exponent and that which was reported) was done twice, once for organic and once for inorganic systems. During the fit it was assumed that $T_\mathrm{g} = T_\mathrm{f}$. Some assumption about thermal history was necessary since the individual thermal histories or T_f values are not known for this whole collection; since we are trying to track overall trends in β values versus composition, this reasonable simplifying assumption is consistent with our program. Given the multiple measurement methods
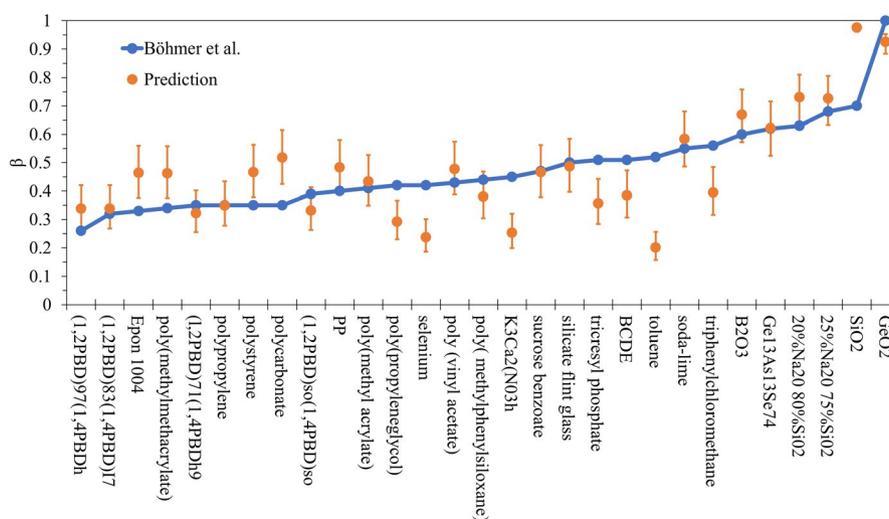
FIGURE 1 β predicted and from literature showing good agreement with a root-mean-square error of 0.1. The fit for organic systems is given by $\zeta' = \mathrm{e}^{-6.6}$ K and for inorganic systems by $\zeta' = \mathrm{e}^{-7.5}$ K. The data are sorted from the lowest experimental value of the stretching exponent to the highest. Error bars are not available for the experimental data since the original source of this data did not report them. The error bars for the model are based on the standard deviation of the calculated intercepts for organic and inorganic systems [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Measured temperatures and their corresponding relaxation values for Corning Jade^{TM} glass and Sylvania Incorporated's SG80

Glass	Temperature (K)	T_g (K)	T_g/T	m	ζ (K^{-1})	β	β Uncertainty	τ (s)
Corning Jade^{TM}	1031	1074	1.042	32	0.002	0.504	0.052	7249
Corning Jade^{TM}	1008	1074	1.065	32	0.002	0.447	0.04	32458
Corning Jade^{TM}	973	1074	1.103	32	0.002	0.395	0.029	419214
SG80	800	800	1	36	0.0057	0.632	0.0294	9.2
SG80	783	800	1.021	36	0.0057	0.593	0.0231	18.2

and the multiple sources of stretching exponent data, it is difficult to make an accurate estimate of the error in the fitted intercepts. Using Equations (17) and (20), the temperature and compositional dependence of the stretching exponent can be described with only one free parameter.

3 | EXPERIMENTAL VALIDATION

Experimental density measurements were made using Corning Jade^{TM} glass as described elsewhere.[11] Changes in the density are normalized to obtain the relaxation functions, which are fit with Equation (1). The resulting values of β are shown in Table 2. A comparison in Figure 2 is shown with data obtained on a soda lime silicate, SG80, where the stretching exponent was obtained using the measurement of the released enthalpy as a function of isothermal annealing time during relaxation below the glass transition. The measurement of the released enthalpy[44] relies on the change in the excess heat capacity in the glass transition range as a function of annealing time. Normalized released enthalpy relaxation functions for each temperature were fit with Equation (1) to obtain the stretched exponent values for SG80. In Figure 2, parts A and B are samples measured below T_g while in part C the samples measured are at T_g and above. The values were then fit with Equation (17) where the only free parameter was ζ, with an equilibrium assumption ($T_f = T$). Figure 2 also includes a comparison of the model fit to the literature values of the stretching exponent reported for glassy B$_2$O$_3$, chosen because of the large collection of β values over a wide temperature range. T_g and m values were determined by equilibrium viscosity measurements[45] in the vicinity of the glass transition range. The deviation seen in Figure 2A,B of the experimental points away from the model calculation are most likely due to the calculation being equilibrium while the datapoints were measured near the glass transition.

4 | DISCUSSION

A combination of the MAP model for non-equilibrium shear viscosity,[39] the model presented here primarily in Equation (17), and the model presented by Wilkinson et al.[49] for the
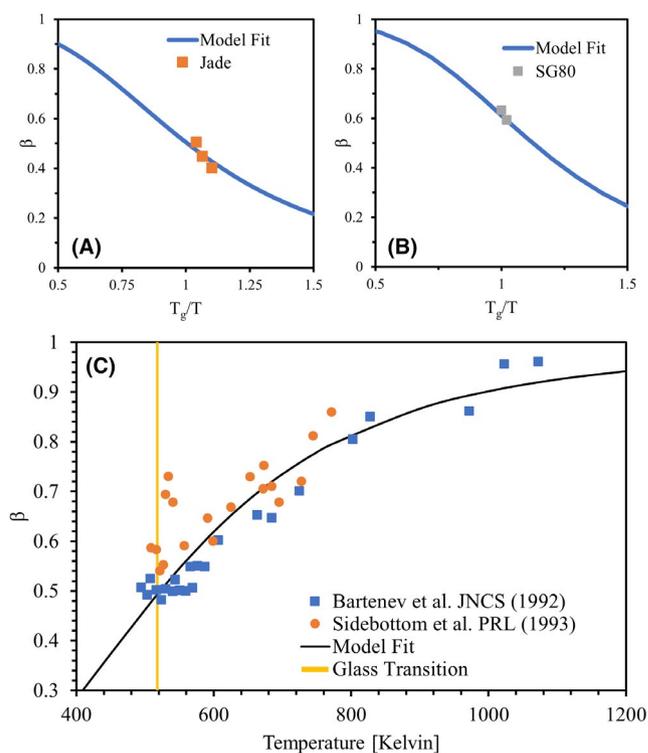
FIGURE 2 Equilibrium model proposed with the experimental points showing good agreement between the experimentally measured data points and the equilibrium derived model. The experimental RMSE was 0.02 for Corning Jade^{TM} (A) and less than 0.01 for SG80 (B). (C) The model fit for B$_2$O$_3$ experimental data.[46,47] The fragility and glass transition temperature of the B$_2$O$_3$ are taken from the work of Mauro et al[48] [Color figure can be viewed at wileyonlinelibrary.com]

temperature dependence of elastic modulus, allows for fully quantitative modeling of stress relaxation behavior. The missing model required to understand *structural* relaxation is the bulk viscosity curve.[15] All previous relaxation (structural or stress) models[9,42] have relied on approximations that use a constant exponent β and on a constant (temperature-independent) modulus value, whereas here, every parameter of Equation (1) may be modeled as a function of temperature. Furthermore, in combination with the relaxation models described by Guo et al.,[42] in which multiple fictive temperatures are described using a Prony series and a temperature-dependent modulus, one can construct a relaxation curve

accounting for the temperature dependence and thermal history dependence of all relevant parameters:

$$\exp\left(-\left(\frac{G(T)t}{\eta(T, T_f)}\right)^{\beta(T_f)}\right) \approx \sum_{i=1}^{N} w_i(T_f)\exp\left(-\frac{G(T)k_i(T_f)t}{\eta(T, T_f)}\right).$$

$$(22)$$

Here, w_i and k_i are fitting parameters that are completely determined by the value of β, and each term in the Prony series is denoted with the subscript i. Usually, 8 or 12 terms are included in the Prony series.[1] Each term in the Prony series is assigned a partial fictive temperature (T_{fi}) whose relaxation is described by the simple exponential in the Prony series. Equilibrium conditions are assumed at the start of the simulation, which allows for a known set of starting probabilities within the energy landscape interpretation of relaxation. The same model also includes the fragility index and glass transition dependence of the non-equilibrium shear viscosity. This method is implemented in RelaxPy,[9] as discussed in the next section. This serves as an approximation for the evolution of the non-equilibrium state; however the temperature dependence of the bulk viscosity and a replacement for fictive temperature need to be quantified to improve the understanding of the underlying physics.[15,16,50]

Separately, we can explore the relationship between this model given by Equation (17) and the underlying energy landscape. In order to better understand the stretching exponent β, consider that there exists a full set of parallel relaxation modes within an energy landscape. The relaxation modes are then weighted by the occupational probability corresponding to a particular mode. This gives a series of transition rates with some probability prefactor and an associated relaxation time (scaled from the mean relaxation time), which gives rise to a Prony series form of Equation (22). Thus, the *distribution* of relaxation times (or barriers) determines the evolution of the stretching exponent while the *average* barrier determines the mean relaxation time. If this Prony series description, in turn, describes the stretching exponent, we arrive at a physical description and origin of the stretching exponent. As the temperature approaches infinity, even though there is a distribution of activation barriers, the distribution of relaxation times approaches a Dirac delta function, and the stretching exponent approaches one (a simple exponential decay). As the temperature decreases, the distribution of relaxation times broadens due to the wide distribution of barriers; however, due to the broken ergodic nature of glass, the value of the stretching exponent will be controlled by the instantaneous occupational probability. The activation barriers may be modeled, for example, using a numerically random set of Gaussian distribution of barriers.[51] The probability of selecting an individual transition is then calculated using a Boltzmann weighting function; the transition also has an associated relaxation time. The Prony
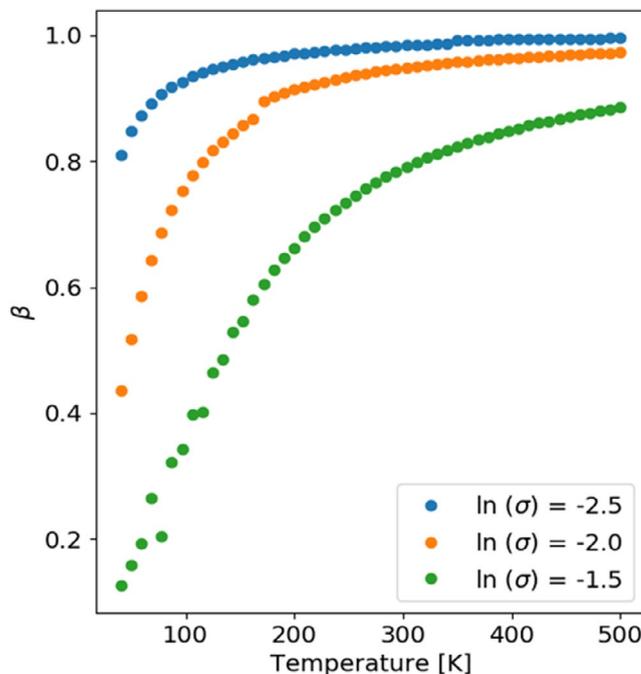
FIGURE 3 Stretching exponent calculated as described in the text for a Gaussian distribution of barriers. This plot shows that the distribution of barriers has a large effect on the stretching exponent. A T_g cannot be described since there is no vibrational frequency included in the model, though the glass transition temperature should be the same for all distributions since the mean relaxation time is the same for all distributions at all temperatures. The deviation is given in ln eV units [Color figure can be viewed at wileyonlinelibrary.com]

series is then recreated with the probability multiplied by the simple exponential relaxation form. The sum of all of these terms is then fit with the stretched exponential form. Figure 3 shows the stretching exponent calculated for the mean activation energy of 1.0 eV and three choices of standard deviation, $\sigma = e^{-2.5}, e^{-2}$ and $e^{-1.5}$ eV as shown in the legend, where Equation (1) has been fit to the Prony series calculated from an equilibrium Boltzmann sampling of a Gaussian distribution of barriers. The temperature dependence for the stretching exponent matches the form derived earlier in this work. This stretching exponent shape has been shown previously though not in a closed-form solution.[51] This secondary method not only validates the generalized form of Equation (17) but also highlights the validity of using the configurational entropy and barrier distributions as the underlying metric controlling the temperature dependence of the stretching exponent.

5 | SOFTWARE IMPLEMENTATION

To create software to model this complex behavior, the authors' existing software RelaxPy[9] has been modified into a new version, RelaxPy v2.0. Instead of fixed values for the

Prony series, the values are chosen dynamically to match the stretching exponent as predicted by Equation (17). The database of values $w_i(\beta)$ and $k_i(\beta)$ was created with a fixed number of terms N in Equation (22) (we chose $N = 12$). This database is available in the same Github repository as the software. The parameters were fit by starting with the values obtained

for $\beta = 3/7$ reported by Mauro and Mauro,[1] to make the new version of the model smoothly reproduce a prior optimal fit, then β was stepped by 0.01 (when less than 0.95) or by 0.001 (when greater than 0.95). Using the previously optimized values of w_i and k_i for starting values for each new β, the w_i and k_i values were then varied to minimize the root-mean-square
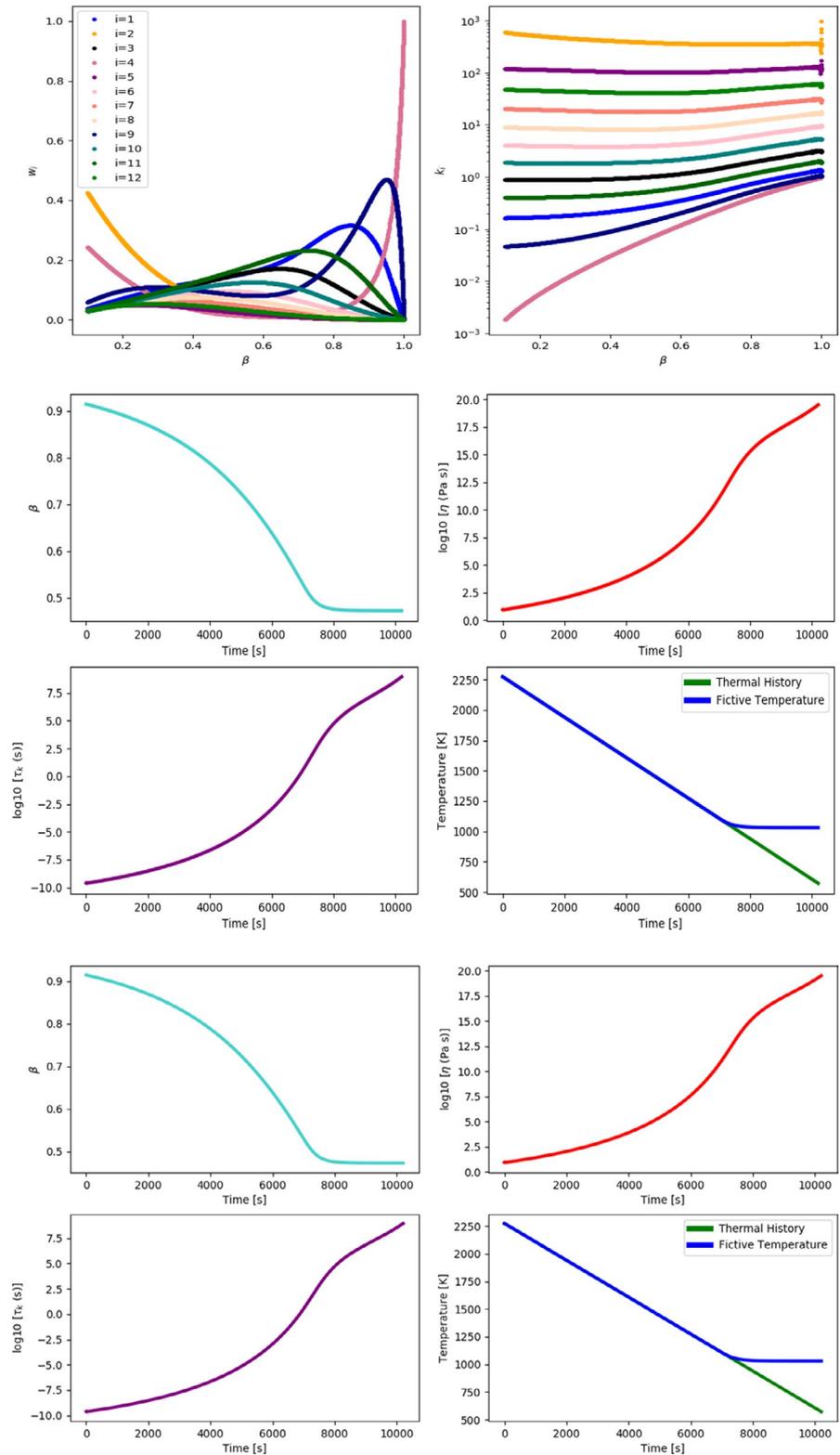
FIGURE 4 (Top) The Prony series parameters as a function of the stretching exponent. Each color designates one term in the series. (Bottom) The output from RelaxPy v.2.0 showing the stretching exponent effects on the relaxation prediction of Corning Jade™ glass. Each quadrant shows one property that is of interest for relaxation experiments. In particular, it is interesting to see the dynamics of the stretching exponent during a typical quench [Color figure can be viewed at wileyonlinelibrary.com]

error between the stretching exponent form and the Prony series form, that is, to satisfy Equation (22) with least error. This list of compiled values makes up the contents of a database that the software accesses. The values of w_i and k_i used for a given β are calculated by finding the closest value in the database to the given value of β. This allows for an efficient implementation of relaxation modeling. Figure 4 shows the fitted parameters to the Prony series and an example RelaxPy output for Corning Jade^{TM} glass undergoing quenching at a rate of 10 K/min. Note that the room temperature stretching exponent value is 0.46, a close match the Phillips's "magic" value of 3/7 (0.43).[6] This prediction for Corning Jade^{TM} is a non-equilibrium prediction, in contrast to the equilibrium high-temperature prediction shown in Figure 2.

6 | CONCLUSION

A model was derived through an understanding of the distribution of barriers for relaxation and the temperature dependence of the Adam-Gibbs entropy. The model outlined herein describes the temperature dependence of the stretching exponent, β, in glass relaxation. It not only considers the extremes at high and low temperature (when compared to the glass transition) as in the Phillips model, but also for any intermediate temperature as a function of the fictive temperature. This model does not have any explicit temperature dependence since it was assumed that an equilibrium model works well to describe the distribution of relaxation times. Given the physical argument and the success of this model when tested by experiments and by another model, it is at least reasonable to formulate the temperature dependence of β in terms of its fictive temperature dependence as we have done here. Including both T and T_f is possible to consider but lies outside our current scope. Using previously derived compositional dependence for the MAP model, a fragility index dependence of the stretching exponent was derived and tested. The model was confirmed using multiple experimental datasets. In addition, a theoretical comparison to a distribution of landscape activation barriers was found to reproduce the same trends as the model.

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