

## Two factors governing fragility: Stretching exponent and configurational entropy

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We derive an analytical expression showing that the fragility of a supercooled liquid is a result of (i) a thermodynamic term depending on change in configurational entropy and (ii) a kinetic term depending on change in the nonexponentiality or “stretching” of the relaxation function, as quantified by the exponent  $\beta$  of the Kohlrausch-Williams-Watts (KWW) relaxation function. Our expression indicates that there is not a direct correlation between the non-Arrhenius scaling of liquid viscosity and the nonexponential nature of glassy relaxation. Rather, the temperature dependence of the stretching exponent  $\beta$  provides a lower limit for fragility, which can be increased through changes in the configurational entropy. Our result explains the apparent contradiction between those researchers showing a correlation between  $\beta$  and fragility and those who question such a correlation due to the spread of the data.

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Among all the technologically useful properties of a glass-forming system, the shear viscosity  $\eta$  of the melt is undoubtedly the most important. Shear viscosity controls the rates of melting and of fining in a glass melting tank. Each glass-forming operation, e.g., fiber forming or the final annealing of container glass, requires a certain well defined viscosity range [1] and consequently a specific temperature range for that operation. Viscosity also determines the relaxation rate of a final glass product.

The scaling of viscosity with temperature can be described in terms of its fragility  $m$ , defined by Angell as [2–4]

$$m \equiv \left. \frac{\partial \log_{10} \eta(T)}{\partial (T_g/T)} \right|_{T=T_g}, \quad (1)$$

where  $T$  is absolute temperature and  $T_g$  is the glass transition temperature, here defined as the temperature where the supercooled liquid viscosity is  $\eta_g = 10^{12}$  Pa s. As noted by Angell [2], in the limit of infinite temperature the extrapolated viscosity of all liquids approaches roughly  $\eta_\infty = 10^{-5}$  Pa s. Hence, a liquid exhibiting perfectly Arrhenius scaling of viscosity—known as a “strong” liquid—has a fragility of  $m_0 \approx 17$ ; examples of strong liquids include silica and germania. Strong behavior is an exception to the usual non-Arrhenius or “fragile” behavior observed with most liquids. Since the values of  $\eta_g$  and  $\eta_\infty$  are independent of composition, from Eq. (1) it follows that a greater value of fragility  $m > m_0$  leads to an increasingly non-Arrhenius scaling of the viscosity curve.

While fragility is strictly a property of the liquid state, recent experimental and theoretical studies have shown that fragility has a profound impact on the properties of the corresponding glass [5–10] and on relaxation behavior [11–18]. Of particular interest here is the work of Plazek, Ngai, Böhrner, and Angell [11–13], who found an empirical correlation between fragility and the shape of the relaxation function; specifically, as the viscosity becomes more non-Arrhenius the relaxation function becomes increasingly nonexponen-

tial. However, a recent paper by Dyre [19] questions whether such a correlation exists. Dyre writes, “In our view—to a considerable extent based on measurements performed in our laboratory during the last 20 years on simple, organic glass-forming liquids—there is no such clear correlation.” [19]

In the current paper we show that while there is no direct correlation between fragility and nonexponentiality, the temperature dependence of nonexponentiality introduces a positive additive term to the fragility. The value of fragility can be increased further through an independent term controlled by the temperature dependence of configurational entropy. The analytical expression derived in the current paper helps reconcile the “noisy correlation” observed in experiment. Our expression also supports the recent work of Mauro and Loucks [18], who, treating fragility in the enthalpy landscape approach, found that there is no theoretical upper limit to the value of fragility.

We begin with the Kohlrausch-Williams-Watts (KWW) relaxation function [20,21]

$$\phi(t) = \exp[-(t/\tau_{\text{KWW}})^\beta] = \int_0^\infty g(\tau) \exp(-t/\tau) d\tau, \quad (2)$$

which has achieved extraordinary success in modeling the relaxation behavior of glass-forming systems [22]. With the KWW expression—also termed the “stretched exponential” decay function—the distribution of relaxation times  $\tau$ , and hence the nonexponentiality of the relaxation process, is governed by the stretching exponent  $\beta$ . A value of  $\beta=1$  gives simple exponential relaxation; lower values of  $\beta$  yield increasingly nonexponential relaxation.

As indicated by the integral in Eq. (2), stretched exponential relaxation can be written in terms of a continuum of simple exponential decays with weighting factors  $g(\tau)$ . Using a Riemann zeta function  $\zeta(2)$ , Richert and Richert [23] showed that the variance of the logarithm of relaxation times  $\sigma_{\ln \tau}^2$  is a simple function of  $\beta$ :

$$\sigma_{\ln \tau}^2 = \langle (\ln \tau)^2 \rangle - \langle \ln \tau \rangle^2 = \frac{\pi^2}{6} \left( \frac{1 - \beta^2}{\beta^2} \right). \quad (3)$$

We assume that the distribution of relaxation times  $g(\tau)$  is the result of a distribution of activation barriers  $p(B)$ .

For a given activation barrier  $B$ , the temperature dependence of the relaxation time can be described using the Adam-Gibbs relation [24]

$$\ln \tau(B) = \ln \tau_\infty + \frac{B}{TS_c(T)}, \quad (4)$$

where  $S_c(T)$  is the configurational entropy of the liquid and  $\tau_\infty$  is the extrapolated relaxation time in the limit of infinite temperature. While not derived rigorously from fundamental physics, the Adam-Gibbs equation has met with remarkable success in fitting experimental data for a wide variety of systems [25–28]. With the Adam-Gibbs relation,  $\sigma_{\ln \tau}^2$  is related to the variance of the activation barriers  $\sigma_B^2$  by

$$\sigma_{\ln \tau}^2 = \frac{\sigma_B^2}{[TS_c(T)]^2}, \quad (5)$$

where  $\sigma_B^2$  is given by

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

With these expressions, we can derive an equation for fragility  $m$  in terms of configurational entropy  $S_c$  and stretching exponent  $\beta$ .

With the Adam-Gibbs relation and a distribution of activation barriers  $p(B)$ , the average relaxation time is

$$\langle \tau \rangle = \tau_\infty \int p(B) \exp\left(\frac{B}{TS_c}\right) dB, \quad (7)$$

which can be rewritten as

$$\langle \tau \rangle = \tau_\infty \exp\left(\frac{\langle B \rangle}{TS_c}\right) \int p(B) \exp\left(\frac{B - \langle B \rangle}{TS_c}\right) dB. \quad (8)$$

Expanding the integrand about  $\langle B \rangle$  and neglecting terms above second order, we obtain

$$\langle \tau \rangle \approx \tau_\infty \exp\left(\frac{\langle B \rangle}{TS_c}\right) \left[ 1 + \frac{\sigma_B^2}{2(TS_c)^2} \right]. \quad (9)$$

Substituting Eq. (6) for  $\sigma_B^2$ ,

$$\langle \tau \rangle = \tau_\infty \exp\left(\frac{\langle B \rangle}{TS_c}\right) \left[ 1 + \frac{\pi^2}{12} \left( \frac{1 - \beta^2}{\beta^2} \right) \right]. \quad (10)$$

Shear viscosity is simply the product of the infinite frequency shear modulus  $G_\infty$  and the average relaxation time  $\eta(T) = G_\infty(T) \langle \tau(T) \rangle$ . Since most of the temperature dependence of  $\eta(T)$  is due to the relaxation time  $\eta(T) \approx G_\infty \langle \tau(T) \rangle$ .

Combining Eqs. (1) and (10), we obtain the final result

$$m = m_0 \left( 1 + \frac{\partial \ln S_c(T)}{\partial \ln T} \Big|_{T=T_g} \right) + \frac{1}{\ln 10} \left( \frac{2\pi^2}{12[\beta(T_g)]^2 + \pi^2\{1 - [\beta(T_g)]^2\}} \right) \times \frac{\partial \ln \beta(T)}{\partial \ln T} \Big|_{T=T_g}. \quad (11)$$

In the limit of constant  $S_c$  and  $\beta$ , we recover  $m = m_0$ , the fragility of a strong liquid. Since  $S_c$  and  $\beta$  both increase with temperature for the vast majority of liquids [22,34,35], both the thermodynamic and kinetic terms in Eq. (11) will make positive contributions to the fragility.

We note that

$$\frac{\partial \ln S_c(T)}{\partial \ln T} \Big|_{T=T_g} = \frac{C_p^{\text{conf}}(T_g)}{S_c(T_g)}, \quad (12)$$

where  $C_p^{\text{conf}}(T_g)$  is the configurational heat capacity of the liquid at the glass transition temperature. The thermodynamic term in Eq. (11) is thus identical to that obtained by Mohanty *et al.* [29]. Cangialosi, Alegría, and Colmenero [30] present a similar expression but where the configurational entropy is replaced by an excess entropy. Similar forms have been reported by other authors; for example, Wang *et al.* [31] present an empirical fragility expression of  $m = 40C_p^{\text{conf}}(T_g)/\Delta S_m$ , where  $\Delta S_m$  is the entropy of fusion. A comparable expression has been derived by Lubchenko and Wolynes [32] within the framework of random first-order transition theory. None of these expressions, however, include the dependence of fragility on  $\beta$ . Our result in Eq. (11) supports the notion of Ruocco *et al.* [33] that configurational entropy alone is insufficient for determining the value of fragility. Vilgis [5] has also previously reported a relation between  $m$  and  $1/\beta$ .

Thus, there are two contributions to fragility: (i) a thermodynamic term governed by the change in configurational entropy and (ii) a kinetic term determined by the stretching exponent  $\beta$ . While there is a minimum fragility associated with any  $S_c(T)$  or  $\beta(T)$ , there is no inherent upper limit to fragility. This result is confirmed by the enthalpy landscape analysis of Mauro and Loucks [18], which made no assumption of Adam-Gibbs theory or the stretched exponential form for relaxation. Mauro and Loucks also show that in the limit of infinite fragility the glass transition becomes an ideal second-order phase transition. Such an ideal transition would occur in the limit of  $C_p^{\text{conf}}(T_g) \rightarrow \infty$ .

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