

Strong and fragile glasses: A powerful classification and its consequences

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In the strong versus fragile classification of simple liquids near their glass transition, a simple model is used to quantify this distinction, which sheds light on mechanisms in glass-forming liquids near freezing. From this model it is shown that the fragility parameter, one of the most important material constants, can be mapped onto the fluctuation of the coordination number, Δz : $\Delta z = 0$ for network glasses; hence they are strong glasses. Systems with $\Delta z > 0$ are always fragile. Implications on the relaxation behavior are shown to be in qualitative and quantitative agreement with experimental results. The proposed model supports the idea that glass-transition phenomena have universal features.

The question whether glass-transition (GT) phenomena of liquids exhibit universal properties is still one of the most important issues in this active subject.¹ From an experimental point of view, the GT has many universal features,^{1,2} since a typical relaxation time for transport properties for all glass-forming liquids, measured, for instance, by NMR or by the viscosity, becomes unusually large close to a certain material-dependent temperature. Hence the dynamics of such a system is so slow that the liquid has to be defined as frozen. The increase of the relaxation time with decreasing temperatures is much larger than the usual Arrhenius behavior, i.e., $\tau \sim \exp(A/kT)$, where A is an activation energy. The temperature dependence of the relaxation time near the GT seems to be a universal, material-independent function and many glass-forming liquids have been fitted very successfully with a Vogel-Fulcher law (VF), which has been also called the Williams-Landel-Ferry (WLF) equation in the polymer literature:²

$$\tau \sim \exp \left\{ \frac{DT_0}{T - T_0} \right\}. \quad (1)$$

T_0 is a temperature below the actual glass temperature T_g , and D is a material-dependent parameter. The theoretical foundation of this law (containing an essential singularity) is still unclear although there are many attempts to calculate it from particular models.

Some years ago Angell showed that the situation is more subtle, and different glass formers do not follow the phenomenological law in a similar manner. He introduced a very important characterization of glass-forming liquids,³ when he noticed an important issue of temperature dependency of the relaxation time, which shows a very distinguished behavior for different glass formers. He found two extreme limits, called strong and fragile glasses. Strong glasses turn out to have almost an Arrhenius behavior, whereas fragile glasses have a typical Vogel-Fulcher behavior [see Fig. 2(a) below]. With the aid of Eq. (1), a T_g -scaled plot of Fig. 2(a) can be sketched by variation of the, so far unknown, parameter D .^{4,5} The fact that all glass formers in Fig. 2(a) meet at one point $T_g/T = 1$ is due to the definition that the system is

assumed to be frozen if at a time scale ~ 100 s. This classification is important first for the development of basic theoretical ideas for the physics of glass formers and second for practical purposes and materials developments. Angell himself made several striking suggestions to quantify this classification,^{3,4,6} for example, to relate strong glasses to a more modest energy hypersurface with less-deep minima in contrast to fragile glasses possessing a very rough energy landscape in configuration space. Another attempt to relate the classification to an effective coordination number has been made,⁷ but so far no simple theoretical picture for a physical simple model, which quantifies and unifies this classification on a physical basis, has emerged. It has been even argued that the distinction between strong and fragile glasses destroys any universal character of the GT.⁸

This paper attempts to specify, quantify, and unify these ideas and puts forward a simple model that is a basis for further considerations. The starting point is the following: It is generally believed that the energy landscape of the phase space in a glassy system is random. This has been proven for spin glasses,⁹ where the number of "deep minima" (pure states) grows exponentially with the number of quenched spins. Ordinary glasses differ substantially from spin glasses, since the physics of the latter is dominated by the quenched disorder. In ordinary glasses this quenched disorder is missing at high temperatures, but at sufficiently low temperatures in the undercooled phase energy, randomness becomes important, due to random interactions. This can be shown by using Edwards' theorists' ideal glass¹⁰ (TIG) and will be discussed in detail separately. Here we state that the energy landscape is random and has a Gaussian distribution

$$P(E) = \left[\frac{1}{2\pi E_0} \right]^{1/2} \exp \left[-\frac{1}{2} (E/E_0)^2 \right], \quad (2)$$

with zero mean and variance E_0 .

Glass-forming liquids basically have a second random variable, i.e., their coordination number, due to random configurations. The fluctuation range of the coordination number strongly depends on the nature of the liquid. For example, it varies in simple (van der Waals) liquids such

as orthoterphenyl from 11 to 16, whereas in network glasses (e.g., SiO_2) the coordination number is fixed. Figure 1 shows that for a random-close-packing (RCP) structure,¹¹ z is random and has a broad distribution $P(z)$.

The (free) energy surface is generally described by a random function $F(\mathcal{C})$, where \mathcal{C} means "configuration." The form and parameter space of $F(\mathcal{C})$ is unknown but we restrict our model to the variable sets E and z . We then crudely approximate $F(\mathcal{C}) = E \cdot z$, where E and z are random numbers. This is the simplest coupling of the two random variables (minimal model), which is the leading term of a more complicated function. To proceed further we consider the relaxation time

$$\tau(E(\mathcal{C})) \sim e^{\beta F(\mathcal{C})}, \quad \beta = \frac{1}{T}, \quad (3)$$

which has to be averaged over the whole landscape. Equation (3) assumes each valley of the energy hypersurface to contribute to an Arrhenius relaxation time, and non-Arrhenius behavior can be expected after averaging. The average upon the energy distribution equation (2) is straightforward, but the average over $P(z)$ is more difficult and we proceed numerically. To do this it is assumed to replace the distribution given in Fig. 1 by a Gaussian of appropriate width Δz and centered around z_0 (the mean coordination number) and truncate the tails at the minimum and maximum values of z , z_{\min} and z_{\max} . If z_{\min} and z_{\max} are crudely shifted to infinity, the error is controlled and the calculation can be done analytically. It is to leading order¹²

$$\tau \sim \exp \left\{ \frac{1}{2} \left[\frac{z_0}{\Delta z} \right]^2 \frac{1}{1 - (T_0/T)^2} \right\}, \quad (4)$$

where $T_0 = E_0 \Delta z$. It has to be realized that this singularity at $T_0 = T$ appears from the approximation $z_{\min} \rightarrow -\infty$, $z_{\max} \rightarrow +\infty$ and does not appear in reality. Nevertheless, for $T \sim T_0$ (4) can be rewritten to

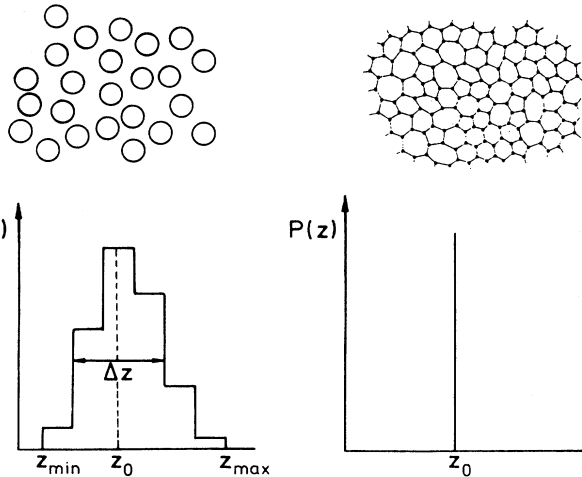


FIG. 1. The distribution of the coordination number in van der Waals glasses and in network glasses. For the computation described later in the text $P(z)$ has been replaced by a Gaussian of width Δz and truncated at the tails at z_{\min} and z_{\max} .

$$\tau \sim \exp \left\{ \frac{1}{4} \left[\frac{z_0}{\Delta z} \right]^2 \frac{T_0}{(T - T_0)} \right\}, \quad (5)$$

which is the celebrated VF equation emerging here as an approximation. For finite values of z_{\min} and z_{\max} , a strong increase of τ can be found by numerical integration and, as usual, a GT has to be defined whenever τ exceeds some time (~ 100 s) corresponding to $\eta \sim 10^{12}$ P. It can be demonstrated by numerical integration that Eqs. (4) and (5) fit the exact values quite well for τ for temperatures not too close to T_0 .

Equation (4) is identical to Eq. (1) and the material constant D can be identified as

$$D = \frac{1}{4} \left[\frac{z_0}{\Delta z} \right]^2. \quad (6)$$

D is determined by the mean coordination number z_0 and its fluctuation. To compare this result with realistic values consider first the random closed packing (RCP), structure, where $z \approx 14$ $\Delta z \approx 4$ for fragile glasses. This leads to $D = 3.1$, which is in very good agreement with the lowest value for $D = 3.2$ found experimentally for simple liquids.^{4,5} Second, as z_0 is constant $\sim 3-5$ and $\Delta z \rightarrow 0$ as in typical network glasses, D becomes very large. But notice that Eq. (4), has a well-defined limit for $\Delta z \rightarrow 0$. It is

$$\tau \sim \exp \left\{ + \frac{1}{2} \left[\frac{z_0 E_0}{T} \right]^2 \right\}, \quad (7)$$

which is of the form proposed by Bässler^{12,13} and has also been fitted to viscosity data (see Ref. 1). Figure 2 represents a T_g -scaled plot based on the numerical integration. A very good verification of the experimental situation is obvious.

How can this be understood? To find a VF-type behavior (at least) two random variables had to be used. The intuitive picture is to have a very complicated energy hypersurface. This corresponds to fragile glasses. Strong glasses have been the result of $\Delta z \rightarrow 0$, i.e., one of the ran-

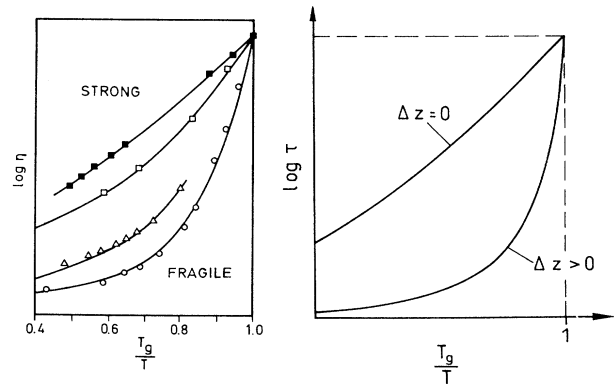


FIG. 2. (a) left: The T_g -scaled plot of the relaxation time of Angell (a) and the result of the computation of Eq. (2). Notice that even the strongest glass SiO_2 (border line at the strong side) does not have a straight line in this representation in agreement with the calculations presented here. (b) right: The computations of the model are shown in the limit $\Delta z = 0$ and $\Delta z = 4$.

dom numbers is quenched out and the energy hypersurface is not as rough as for $\Delta z > 0$. Spin glasses, on the other hand, do have an extremely rough hypersurface^{9,14,15} due to the quenched disorder and frustration (even at $T > T_c$). Hence, spin glasses belong to the extremely fragile class.⁷

The second universal feature for the GT (apart from transport properties) supported by experiments are the relaxation data. These can be uniquely described by a stretched exponential [Kohlrausch-Williams-Watts (KWW) function] $\phi(t) = \exp[-(t/\tau)^\beta]$, where β is another phenomenological material-dependent parameter, which is used for classification of glass-forming liquids. The relaxation function is much slower as for liquids or ordered solids, where $\beta = 1$. The model presented here is also able to predict several correlations of β to the type of the glass-forming system. Consider typical relaxation functions under the same conditions as above:

$$\phi(t) \sim \left\langle \exp \left[-\frac{t}{\tau(\mathcal{C})} \right] \right\rangle. \quad (8)$$

This assumes that every valley of the energy landscape contributes to a single Debye relaxation, which is analogous to the work for spin glasses and the random energy model.¹⁶ The averaging procedure in Eq. (8) cannot be done exactly but the long-time limit is given by

$$\phi(t) \sim t^{-T/(\Delta z E_0)} f(t/T_0). \quad (9)$$

The function $f(x)$ is extremely slow decaying in time and the dominant contribution is the algebraic decay. Notice that the exponent of the power decay is temperature dependent (weak violation of the time-temperature superposition principle) and that it strongly depends on the nature of the liquid (strong and fragile) via Δz . Equation (9) can be fitted very well to a stretched exponential, suggesting $\beta \approx 1 - \Delta z E_0/T$. Thus a relation between the relaxation parameter β at T_g and the material constant D can be established:

$$D = \frac{(T_0/T_g)^2}{[1 - \beta(T_g)]^2}, \quad (10)$$

which shows the same behavior as found by Ngai¹⁷ using his coupling model. Moreover, calculating from the T_g -scaled plot the fragility parameter

$$m = \frac{\delta \ln(\tau)}{\delta(T_g/T)} \Big|_{T=T_g} \quad (11)$$

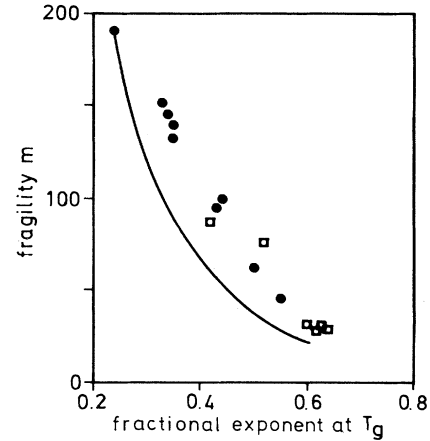


FIG. 3. Fragility m vs KWW exponent at T_g . The experimental values are taken from (Refs. 18 and 19). The line is the fit from Eq. (11).

a relation between m and β can be found:

$$m = A \left[\frac{AT_g}{z_0^2 E_0 \beta^2} + 1 \right]. \quad (12)$$

Here the value of A defines T_g (i.e., $A = 12$ for the viscosity to be 10^{12} P). This can be compared to data by Angell,¹⁸ for a system where the fragility could be altered. Equation (12) is in very good agreement with this result (see Fig. 3). Note that $M = A(A/D + 1)$ and the limiting fragility for strong glasses is thus $m_s = A$ whereas for fragile glasses ($D = 3$) $m_f = \frac{1}{3}A^2 + A$ in our model.

To sum it up, I have presented a simple model which quantifies current ideas about glass-forming liquids. Such disorder models apply below the critical temperature of the singularity calculated by the mode-coupling theory in which energetic disorder is not taken into account. I have succeeded in (1) the classification of strong and fragile glasses, and (2) in deriving a formula that connects fragility and relaxation [Eq. (11)], which is in accord with dielectric measurements.^{19,20} The simple model presented here supports also the idea of the universal behavior of liquids at the GT, since all glasses (strong and fragile) can be described within the same framework. They appear just as different limits. Moreover, our theory predicts differences in the aging behavior of strong and fragile glasses, the glass-transition temperature as a function of the quenching rate q , $T_g \approx T_0(D/\ln q + 1)^{1/2}$, which will be reported elsewhere.

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