A stress relaxation approach to glass transition

LETTER TO THE EDITOR

A stress relaxation approach to glass transition

Kostya Trachenko

Department of Earth Sciences, University of Cambridge, Downing Street,
Cambridge CB2 3EQ, UK

Abstract
We propose that the onset of a glass transition can be defined as the point at
which a supercooled liquid acquires the stress relaxation mechanism of a solid
glass. We translate this condition into the rate equation for local relaxation
events. This equation simultaneously gives two main signatures of a glass
transition: stretched-exponential relaxation and the Vogel–Fulcher law. In the
proposed picture, the increase of non-exponentiality of relaxation and deviation
from the Arrhenius law both originate from the lag behind the new equilibrium
state, to which the system is driven by external perturbation. This lag can be
quantified by the number of local relaxation events, and we propose that this
number is related to the system's fragility. The proposed theory reproduces
several general correlations, including the correlation of fragility with non-
exponentiality of relaxation and bonding type.

If a liquid is cooled down fast enough, it forms glass. At the onset of the glass transformation
range, a liquid qualitatively changes its properties, and the two main features that distinguish it
from a high-temperature liquid are the stretched-exponential relaxation (SER) and the Vogel–
Fulcher (VF) law. When a perturbation, in the form of stress or external field, is applied to a
liquid near the glass transition, a relaxing quantity $q(t)$ decays following a universal SER [1]:

$$q(t) \propto \exp(-(t/\tau)^{\beta}) \tag{1}$$

where $0 < \beta < 1$. This behaviour is seen in many different systems, and is considered as a
universal signature of the 'glassy' relaxation [2–5]. Another universal feature of relaxation near
a glass transition is that the viscosity, or relaxation time τ, follows a non-Arrhenius dependence,
which in most cases is well approximated by the VF law:

$$\tau \propto \exp(A/(T - T_0)) \tag{2}$$

where A and T_0 are constants [5].

A substantial amount of research in the area has revolved around the origin of these two
anomalous, yet universal, relaxation laws. A successful theory of the glass transition, as widely

perceived, should provide a common justification for equations (1) and (2) [3, 6]. Recently, the need for a theory of the glass transition to give equations (1) and (2) *simultaneously* has been reiterated on the basis of the close relationship between β and τ: it has been found that β is invariant to different combinations of pressure and temperature that hold τ constant [7]. It has therefore been suggested that this correlation should constrain any theory of the glass transition, in that if a given formalism gives equation (2), it should also be able to give equation (1) [7].

Several decades ago, Goldstein proposed [8] that at a glass transition, flow becomes dominated by potential barriers which are high compared to thermal energies, whereas at high temperature, the opposite is true: barriers are much smaller than thermal energies. Hence it can be argued that, while in a liquid at high temperature local stress is relaxed on the timescale of microscopic trajectory reversal times, in the supercooled regime local regions can support a finite stress (i.e. maintain local structure unchanged) on timescales that are considerably larger. This has opened the possibility to discuss the stress relaxation mechanism in a liquid approaching the glass transition. However, practical realization of this approach, in particular the relationship between the stress relaxation mechanism and the origin of equations (1) and (2), has remained elusive.

Following this approach, we consider that as the temperature decreases, a liquid acquires a 'solid-like' ability to support local stresses on timescales that considerably exceed trajectory reversal times. Our main proposal is that a liquid near the glass transition also starts to *redistribute* local stresses in a solid-like manner. Hence the onset of the glass transition can be robustly defined as the point at which a liquid and a solid glass under stress begin to redistribute local stresses in the same way. In other words, we propose that *the onset of the glass transition is the point at which the liquid acquires the stress relaxation mechanism of solid glass*. We show that this condition is *sufficient* to recover both anomalous relaxation laws, equations (1) and (2). We also show that the proposed theory gives a simple definition of a system's fragility in terms of the number of local relaxation events induced by external perturbation, recovers fragility plots and predicts correlations of fragility with β and the nature of the chemical bond.

How do local stresses redistribute in glass under pressure? In the same paper [8], Goldstein considered this question: he argued that because a local region supports less stress after the relaxation event than before, all other local regions support more of the external stress after the event than before. Generally, increasing stress on other local regions makes their relaxation more difficult, as is seen in the molecular dynamics simulations of relaxation in glass under pressure [9]. This can be understood by noting that relaxation paths for local events with the smallest activation barriers are anisotropic [10], and are oriented at random relative to each other and to external stress; hence the increase of stress (for example, shear stress) on region $n + 1$ depends on the local relaxation path of event n, and is not, on average, 'aligned' with the reaction path of event n (in Goldstein's terminology, relaxation paths of local events are 'non-concordant' [8]). As a result, activation barriers increase for later events.

In what follows, we consider that relaxation proceeds by local relaxation events (LREs). In the literature, these jump or flow events have been given different names (for a review, see [11]); in this discussion we borrow the term LRE from our previous studies of relaxation in glasses [9, 10, 12, 13]. In glass under high enough pressure, an LRE involves several localized atomic jumps which include breaking old bonds, forming new ones and the subsequent relaxation of the local structure [10]. An animation of an LRE in SiO_2 glass is available in the electronic form of [10]. Each LRE carries a microscopic change of a macroscopic relaxing quantity, e.g., volume. By considering the dynamics of LREs and their coupling to the structural rigidity of glass, it has been possible to explain several interesting aspects of glass relaxation, including the origin of slow relaxation [9, 12] and the origin of temperature-induced densification in the pressure window, centred at the rigidity percolation point [13, 14].

We introduce LREs as local relaxation 'quanta' which a liquid uses to adjust to external perturbations. Each LRE carries a microscopic change of a liquid's relaxing quantity (i.e. volume, external stress, etc). In a high-temperature liquid, an LRE is an atomic jump from the surrounding 'cage', followed by local relaxation. As the temperature decreases, atomic rearrangements become more cooperative, due to the need to cross higher activation barriers. In this regime, each LRE is associated with the transition over the activation barrier in the Goldstein picture of activated flow [8]. In the supercooled regime and below, LREs, induced in different parts of a system, have different relaxation times, i.e. they are dynamically heterogeneous [15], as discussed below in more detail.

We now derive the rate equation for LREs in a liquid at the onset of a glass transition. For this, we use our main proposal that at the glass transition, liquid acquires the stress relaxation mechanism of solid glass. So first we find how to express the stress relaxation mechanism in glass in mathematical terms. In particular, we find how activation barriers for LREs change as a result of redistribution of local stresses. Let N be the total number of relaxing units in the structure, and P the external force (hydrostatic or shear) per area unit. Each unit supports local stress p_0 such that $P = p_0 N$. Since, as discussed above, after relaxation, a local unit supports stress $p_1 < p_0$, the stress on other local regions is $p_2 = (P - p_1 n_c)/(N - n_c)$, where n_c is the current (instant) number of LREs induced by external perturbation. If $n = n_c/N \ll 1$, $p_2 = p_0 + (p_0 - p_1)n$. It has been argued that the main contributor to the activation barrier V is elastic energy [11]. Hence the increase of V is proportional to the increase of work needed to overcome the barrier created by elastic force due to additional stress $\Delta p = p_2 - p_0 = (p_0 - p_1)n$. So $V \propto \Delta p \propto n$ for small n:

$$V(n) = V_0 + V_1 n \tag{3}$$

where V_0 is the energy barrier in an unperturbed system, and V_1 is defined such that $V(n_r)$ is the maximal energy barrier, where n_r is the total number of LREs caused by an external perturbation, $n(t) \to n_r$ as $t \to \infty$.

Note that equation (3) cannot be applied to a liquid above the glass transition, because at high temperature, externally induced stresses are quickly removed by thermal fluctuations, and redistribution of stresses between different local regions does not take place. More precisely, at high temperature, the stress relaxation mechanism, as described by equation (3), only exists on short microscopic timescales. On experimental timescales, over which equations (1) and (2) are measured, V is independent of n at high temperature.

We now apply equation (3) to the liquid approaching the glass transition. We do so by writing the rate equation for LREs which uses equation (3). The rate equation should reflect two main features of the relaxation. First, the rate of LREs, $\frac{dn}{dt}$, depends on the event probability, $\exp(-V/kT)$. According to our main proposal, the onset of the glass transition is defined as the point at which a liquid acquires the stress relaxation mechanism of a solid glass; hence V is given by equation (3). Second, the rate equation should contain a term that ensures that a finite external perturbation induces a finite number of relaxation events, n_r, such that $\frac{dn}{dt} = 0$ as $n(t) \to n_r$ at $t \to \infty$. Hence the rate of LREs should have a saturation term to reflect the depletion of LREs. We assume that relaxed events are removed from further relaxation, hence the saturation term has the linear $-\alpha n$ dependence. This is analogous to the process of nuclear decay, in which the decay rate decreases linearly with the number of decayed nuclei, $dn/dt \propto -n$. Hence, using equation (3) and noting that in a liquid $V_0 \ll kT$, we write

$$\frac{dn}{dt} = \exp(-Cn) - \alpha n$$

where $C = V_1/kT$ and t is rescaled as $t \to t/t_0$, where t_0 is the characteristic relaxation time.

α is defined from the condition that $\frac{dn_r}{dt} = 0$ when $n = n_r$, giving $\alpha = \exp(-Cn_r)/n_r$:

$$\frac{dn}{dt} = \exp(-Cn) - \frac{n}{n_r}\exp(-Cn_r). \tag{4}$$

Before solving equation (4), we discuss its two different regimes with known solutions. The first regime is at high temperature, in which case the right part of equation (4) contains the $\propto n$ term only. This is because, as discussed above, the stress distribution mechanism, equation (3), does not apply at high temperature, but comes into play at lower temperature only, signalling the onset of the glass transition. In this case, the solution of equation (4) is exponential, with Arrhenius-type dependence of the relaxation time on temperature since $C \propto 1/T$.

The second regime is at low temperature, when equation (3) applies, but when the saturation effects are small and can be ignored. In this case, the right-hand part of equation (4) contains only the $\exp(-Cn)$ term, giving a logarithmic $n \propto \ln(t + t_0)$ solution. This result is consistent with experiments in three aspects. First, the experiments clearly show a logarithmic relaxation of the macroscopic properties (e.g., volume) of SiO_2 and GeO_2 glasses under pressure [16]. Second, the calculation of the slope of logarithmic relaxation from microscopic parameters gives a quantitative agreement with the slope obtained in the pressure experiments [9]. Third, by considering the dynamics of LREs that give logarithmic relaxation, it has been possible to explain the origin of the difference between relaxation in SiO_2 and GeO_2 glass: because GeO_4 tetrahedra are less stiff than SiO_4 ones, LREs are induced in GeO_2 glass at lower pressure as compared with SiO_2 glass [13]; hence logarithmic relaxation due to LREs sets in in GeO_2 glass at lower pressure, consistent with experiments [16].

We now show that equation (4) gives SER and the VF law, equations (1) and (2). First, we solve equation (4) in the wide range of its parameters C and n_r. Remembering that $n(t) \to n_r$ as $t \to \infty$, we fit the solution to $n = n_r(1 - \exp(-t/\tau)^\beta)$. We note that this form of SER and equation (4) contain two parameters each, which suggests that if a good fit exists, it is not accidental, but probably reflects the involved physics. Figure 1 shows that fits of the solution to SER are very good. We find that this is the case in a wide range of parameters (C, n_r), except when $Cn_r \gg 1$.

We find that β decreases as Cn_r increases (see the legend in figure 1). Hence non-exponentiality can increase as a result of either decrease of temperature $T \propto 1/C$, or increase of n_r. The first correlation is consistent with many experiments that find that β decreases with T [2–4]. The second correlation means that, physically, the origin of non-exponentiality of relaxation is related to the lag behind the new equilibrium state, to which the system is driven by external perturbation. The degree of the lag is quantified by n_r: a larger lag gives a larger n_r, resulting in larger stretching (smaller β) in our picture. We will return to this point below.

Second, for several different n_r, we solve equation (4) as a function of C, and fit the solution to the SER form above to obtain relaxation time τ. We plot τ as a function of $1/(n_rC) = T/T_0$, where $kT_0 = V_1 n_r$. We find that the dependence of τ on temperature collapses on the curve $\ln(\tau/n_r) = f(1/(n_rC)) = f(T/T_0)$. We also find that $f(x)$ cannot be represented by the Arrhenius-type dependence $\propto 1/x$; however, a good fit is obtained if

$$\ln\frac{\tau}{n_r} = \frac{a_1}{1/(Cn_r) - a_2} = \frac{a_1}{T/T_0 - a_2} \tag{5}$$

where a_1 and a_2 are constants. This is the form of the VF law, equation (2). We find that a good fit to equation (5) exists in both $T/T_0 > 1$ and $T/T_0 < 1$ regimes, with $\ln(\tau/n_r)$ spanning over 15 decades (see figure 2).

We can therefore conclude that equation (4) gives SER and the VF law, equations (1) and (2). It could be argued that there may be an alternative way to write the right-hand part of
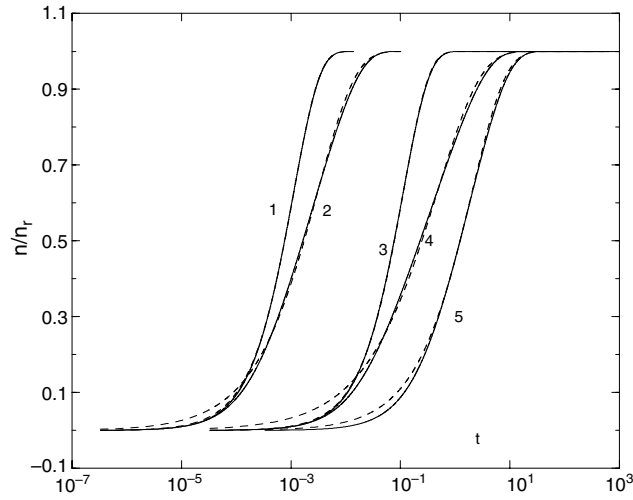
Figure 1. Solid lines are the solutions of equation (4) for several pairs of parameters (n_r, C): 1—(0.001, 1000), 2—(0.001,4000), 3—(0.1, 10). 4—(0.1, 50), 5—(1, 3). Dashed lines are the least-square fits to SER, giving the following parameters of (β, τ): 1—(0.93, 0.0011), 2—(0.63, 0.0031), 3—(0.94, 0.114), 4—(0.55, 0.478), 5—(0.71, 2.05), respectively. For each value of n_r, the solution of equation (4) for n has been divided by n_r so that $0 < n/n_r < 1$.
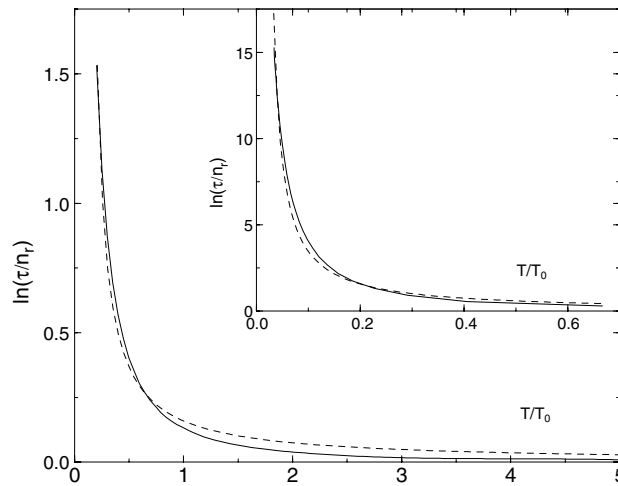

Figure 2. The solid line is the solution of equation (4), fitted to SER to obtain τ. The dashed line is the fit to equation (5), with $a_1 = 0.141$ and $a_2 = 0.116$. The inset shows the fit in the $T/T_0 < 1$ regime; $a_1 = 0.288$ and $a_2 = 0.017$.

equation (4), for example as $(1 - n/n_r)\exp(-Cn)$. This form, just as equation (4), contains two essential ingredients: it incorporates equation (3) in the activation term, and ensures that under a finite external perturbation, the number of LREs is finite, $\frac{dn}{dt} = 0$ as $n(t) \rightarrow n_r$ at $t \rightarrow \infty$. Interestingly, we find that in this case, the solution can also be successfully fitted to the SER form, suggesting that SER can be obtained as long as the two main ingredients of the model are present. However, the saturation term in the alternative form, proportional to $n\exp(-Cn)$, contains an exponential factor. There is no reason why this needs to be so, as the

saturation term should only reflect the fact that the relaxed events are linearly removed from further dynamics. This is ensured by the $\propto n$ term as in equation (4).

We now suggest that the proposed theory clarifies the origin of the system's 'fragility', its correlation with the non-exponentiality of relaxation [4, 6] and the nature of the chemical bond.

First, n_r, a parameter in equation (4), quantifies the overall atomic motion in a system due to external perturbation that comes in addition to thermally induced motion. At a given temperature, n_r depends on the magnitude of external perturbation and, more importantly, on the system's ability to resist structural changes at the microscopic level. This ability has been termed the system 'fragility', and it constitutes the basis of fragility plots, which are essentially plots of equation (5) with a varying parameter that measures the deviation from Arrhenius dependence: the larger this deviation, the larger the fragility [5]. Qualitatively, a 'strong' system has a built-in resistance to temperature-induced structural changes, whereas the structure of a 'fragile' system is easy to disrupt [5]. In our picture, this means that a strong system responds to external perturbation with little retardation and smaller n_r, whereas relaxation in a more fragile system involves a larger number of LREs, required to come to equilibrium with new external conditions. In other words, a more fragile system is more retarded in terms of larger n_r. Hence our picture offers the quantification of fragility in terms of n_r, and we recover the fragility plots as follows. At a given temperature, small n_r results in $1/(Cn_r) \gg a_2$, and equation (5) becomes Arrhenius. As n_r increases, corresponding to a more fragile system in our picture, $1/(Cn_r) \gg a_2$ does not hold, and the relaxation becomes VF-type, according to equation (5).

We therefore find that, similarly to the SER, the physics behind the VF law is related to the lag behind the new equilibrium state, to which the system is driven by external perturbation. The degree of the lag is quantified by n_r: a larger lag gives a larger n_r, corresponding to a larger deviation from the Arrhenius relaxation in the form of the VF law (see equation (5)).

Second, we find that the proposed picture reproduces the relationship between fragility and non-exponentiality. Experimental data of more than 70 systems show that β decreases, approximately linearly, with fragility [4]. In our picture, fragility is defined by n_r, and in figure 3, we plot β as a function of n_r for different values of C. It is indeed seen that β decreases with n_r, reproducing the experimental correlation well. Note that at a given n_r, higher temperature $T \propto 1/C$ results in the increase of β (see figure 3), in agreement with experimental observations [2–4].

Third, we can discuss how the proposed picture relates a system's fragility to its microscopic parameters. Other conditions being equal, one expects that an external perturbation induces generally larger n_r in a system with ionic bonding as compared with a system with covalent bonding. In the covalent case, an atomic pair lowers its energy through sharing electrons between two atoms, resulting in a binding energy as high as several eV, and an LRE necessarily involves breaking these stable electronic configurations (breaking 'covalent bonds') with associated high energy cost. In the ionic case, atomic rearrangements can proceed without a change in the electronic state of the atoms. As a result, activation barriers generally increase with covalency of bonding. Since, as discussed above, the fragility increases with n_r, one readily predicts that covalent systems should be generally stronger and ionic systems should be more fragile, in good agreement with experimental results [5]. Other factors, in addition to the nature of the chemical bond, may also affect n_r, including, for example, the ratio of ionic radii.

Before concluding, we make three remarks. First, it is important to note that equation (4) yields SER and the VF law *simultaneously*, suggesting that *LRE dynamics are behind both anomalous 'glassy' relaxation laws*. This clarifies an open question of why the relaxation function is non-exponential at temperatures at which the relaxation time is non-Arrhenius [6]: in our theory, larger n_r increases the non-exponentiality of relaxation (see figures 1 and 3)
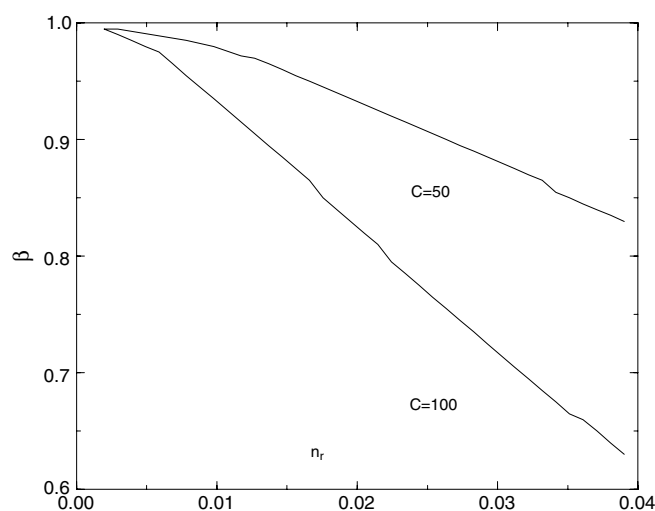
Figure 3. Decrease of β with n_r (fragility), at various values of C. At constant n_r, β increases with $T \propto 1/C$.

and, at the same time, increases departure from the Arrhenius relaxation as follows from equation (5).

A second related point is that the relationship between SER and the VF law has recently been reiterated: it has been discovered that β is invariant to different combinations of pressure and temperature that hold τ constant [7]. It has therefore been suggested that this correlation should constrain any theory of the glass transition [7]. In our theory, temperature and pressure define parameters C and n_r in equation (4). C and n_r, in turn, unambiguously define β and τ. Due to the monotonic character of the solution of equation (4), we find that only one value of β corresponds to a given τ. In other words, we find that β is invariant to different combinations of pressure and temperature that hold τ constant, satisfying the experimental result [7].

Finally, we note that in order to derive equations (1) and (2), we considered a system under external stress, which allowed us to discuss the stress relaxation mechanism at the onset of non-exponential and non-Arrhenius behaviour, equations (3) and (4). At the same time, equations (1) and (2) are observed in supercooled liquids in the absence of pressure as well, from the decay of correlation functions. This behaviour directly follows from the considered situation of the system under stress, by applying the fluctuation-dissipation theorem.

In summary, we have proposed a new simple way of defining the onset of a glass transition: a liquid enters the glass transformation range when it begins to redistribute local stresses in the same manner as solid glass. We have shown how this condition simultaneously gives two main signatures of 'glassy' relaxation: the stretched-exponential relaxation and the Vogel–Fulcher law. In the proposed picture, the increase of non-exponentiality of relaxation and deviation from the Arrhenius law both originate from the lag behind the new equilibrium state, to which the system is driven by external perturbation. We have proposed that the degree of this lag can be quantified by the number of local relaxation events n_r: a larger lag gives a larger n_r. In our theory, larger n_r results in smaller β and a larger deviation from the Arrhenius relaxation in the form of the VF law. Consistent with recent experiments, we found that β is invariant to different combinations of pressure and temperature that hold τ constant. Finally, we have discussed how the proposed theory offers the definition of the system's fragility in terms of n_r,

and recovers experimental correlations of fragility with non-exponentiality of relaxation and the nature of the chemical bond.

References

[1] Kohlrausch R 1854 *Pogg. Ann. Phys. Chem.* **91** 179
[2] Phillips J C 1996 *Rep. Prog. Phys.* **59** 1133
[3] Ngai K L 2000 *J. Non-Cryst. Solids* **275** 7
[4] Bőhmer R *et al* 1993 *J. Chem. Phys.* **99** 4201
[5] Angell C A 1995 *Science* **267** 1924
[6] Angell C A 2000 *J. Phys.: Condens. Matter* **12** 6463
[7] Ngai K L *et al* 2005 *J. Phys. Chem.* B **109** 17356
[8] Goldstein M 1969 *J. Chem. Phys.* **51** 3728
[9] Trachenko K *et al* 2003 *J. Phys.: Condens. Matter* **15** L743
[10] Trachenko K and Dove M T 2002 *J. Phys.: Condens. Matter* **14** 7449
[11] Dyre J C 1998 *J. Non-Cryst. Solids* **235–237** 142 and references therein
[12] Trachenko K and Dove M T 2004 *Phys. Rev.* B **70** 132202
[13] Trachenko K *et al* 2004 *Phys. Rev. Lett.* **93** 135502
[14] Trachenko K and Dove M T 2003 *Phys. Rev.* B **67** 212203
[15] Bőhmer R *et al* 1998 *J. Non-Cryst. Solids* **235–237** 1
[16] Tsiok O B *et al* 1998 *Phys. Rev. Lett.* **80** 999