Glass transition theory based on stress relaxation

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Abstract. We propose that an onset of 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 glass transition, stretched-exponential relaxation and the Vogel-Fulcher law. The proposed theory quantifies system fragility in terms of the number of retarded local relaxation events and reproduces its correlation with the non-exponentiality of relaxation and bonding type.

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If a liquid is cooled down fast enough, it forms glass. At the onset of 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 glass transition, a relaxing quantity \( q(t) \) decays following a universal SER:

\[
q(t) \propto \exp\left(-\frac{t}{\tau}\right)^\beta
\]

where \( 0 < \beta < 1 \). This behaviour is seen in many systems, and is considered a signature of the “glassy” relaxation \cite{1, 2, 3, 4, 5}. Another universal feature of this regime is that viscosity, or relaxation time \( \tau \), follows non-Arrhenius dependence, which in most cases is well approximated by the VF law:

\[
\tau \propto \exp\left(\frac{A}{T - T_0}\right)
\]

where \( A \) and \( T_0 \) are constants \cite{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 Eq. (1) and (2) \cite{3, 4, 5}. Recently, the need for a theory of the glass transition to give Eq. (1) and (2) simultaneously has been reiterated on the basis of the close relationship between \( \beta \) and \( \tau \): it has been found that \( \beta \) is invariant to different combinations of pressure and temperature that hold \( \tau \) constant \cite{7}. It has therefore been suggested that this correlation should constrain any theory of the glass transition, in that if a given formalism gives Eq. (2), it should also be able to give Eq. (1) \cite{7}.

Several decades ago, Goldstein proposed \cite{8} that at 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
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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 glass transition. However practical realizations of this approach, in particular the relationship between the stress relaxation mechanism and Eq. (1) and (2) have remained elusive.

Following this approach, we consider that as temperature decreases, 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 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 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, Eq. (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 $\beta$ 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. The increased stress they need to support is aligned along the direction of external pressure. On the other hand, local relaxation paths for local events with the smallest barriers are generally oriented at random relative to the external pressure, because they are defined by the symmetry of local ordering [9] (in Goldstein’s terminology, local reaction paths are “non-concordant” to the external stress [8]). As a result, activation barriers increase for later local relaxation events.

In what follows, we consider that relaxation proceeds by local relaxation events (LRE). In the literature, these jump or flow events have been given different names (for review, see Ref. [10]); in this discussion we borrow the term LRE from our previous studies of relaxation in glasses [9,11,12,13]. In glass under high enough pressure, a LRE involves several localized atomic jumps which include breaking old bonds, forming new ones and the subsequent relaxation of the local structure [9]. An animation of a LRE in SiO$_2$ glass is available in the electronic form of Ref. [9]. Each LRE carries a microscopic change of a macroscopic relaxing quantity, e.g., volume. By considering the dynamics of LRE and their coupling to structural rigidity of glass, it has been possible to explain several interesting aspects of glass relaxation, including the origin of slow relaxation [11,12] and the origin of temperature-induced densification in the pressure window, centered at the rigidity percolation point [13].

We introduce LRE 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, a LRE is an atomic jump from the surrounding “cage”, followed by local relaxation. As 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, LRE, induced in different parts of a system, have different relaxation times, i.e. they are dynamically heterogeneous \(^{14}\), as discussed below in more detail.

We now derive the rate equation for LRE in a liquid at the onset of glass transition. For this, we use our main proposal that at 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 LRE change as a result of redistribution of local stresses. Let \(N\) be the total number of relaxing units in the structure. Under external (hydrostatic or shear) stress \(P\), each unit supports 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 LRE 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 \(^{10}\).

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 \(n\):

\[
V(n) = V_0 + V_1 n
\]

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 LRE caused by an external perturbation, \(n(t) \to n_r\) as \(t \to \infty\).

Note that Eq. (3) can not be applied to a liquid above 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, stress relaxation mechanism, as described by Eq. (3), only exists on short microscopic timescales. On experimental timescales, over which Eqs.(1) and (2) are measured, \(V\) is independent of \(n\) at high temperature.

We now apply Eq. (3) to the liquid approaching glass transition. First, the rate of LRE, \(d\frac{dn}{dt}\), 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 Eq. (3). Second, because an external perturbation induces a finite number of relaxation events, \(n_r\), the rate of LRE should also have a saturation term to reflect the depletion of LRE. The most natural choice for the saturation term is linear \(-\alpha n\) dependence, which reflects the fact that relaxed events are removed from further dynamics. This is analogous to, for example, the process of nuclear decay, in which the decay rate decreases linearly with the number of decayed nuclei, \(\frac{dn}{dt} \propto -n\). Hence, using Eq. (3) and assuming 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 re-scaled as \(t \to t/t_0\), where \(t_0\) is the characteristic relaxation time. \(\alpha\) is defined from the condition that \(\frac{dn_r}{dt} = 0\) when \(n = n_r\), giving \(\alpha = \exp(-Cn_r)/n_r\):

\[
\frac{dn}{dt} = \exp(-Cn) - \frac{n}{n_r} \exp(-Cn_r)
\]
Before solving Eq. (4), we note that the only assumption in its derivation is that the increase of the activation barrier is linear, Eq. (3). We argued that this is justified for \( n \ll 1 \), and here we note that Eq. (3) is consistent with experiments in common glasses. If the saturation effects are small and the second term in the right part of Eq. (4) is ignored, \( n \propto \ln(t + t_0) \). Thus linear expansion (3) gives logarithmic dependence of \( n \), which is consistent with the logarithmic relaxation of macroscopic properties (e.g., volume) of \( \text{SiO}_2 \) and \( \text{GeO}_2 \) glasses under pressure [12]. In addition to the qualitative agreement, Eq. (3) also gives a quantitative agreement with the experiment, as is found by the calculation of the slope of logarithmic relaxation of volume under pressure [11].

Eq. (4) has two parameters, \( C \) and \( n_r \). When \( Cn_r \ll 1 \) (and hence \( Cn \ll 1 \) since \( n < n_r \) ), the right part of Eq. (4) becomes \( 1 - n/n_r \), leading to the usual Debye-type relaxation. This takes place when either the temperature \( T \propto 1/C \) is high, or when \( n_r \) is small. At \( Cn_r \approx 1 \), one expects the onset of non-exponential relaxation. This sets the scale for the non-exponentiality temperature \( T_n \):

\[
kT_n \approx V_1n_r
\] (5)

Below we show that in the \( T \approx T_n \) regime, Eq.(4) gives SER and the VF law, Eqs. (1) and (2). Note that \( T_n \) is higher than the glass transition temperature \( T_g \). \( T_g \) is often defined from the condition of viscosity reaching some large value, corresponding to the relaxation time exceeding the time of experiment, whereas \( T_n \) defines the preceding temperature regime at which relaxation becomes non-exponential and non-Arrhenius.

First, we solve Eq. (4) for a wide range of parameters \((C, n_r)\) that satisfy condition \( Cn_r \geq 1 \), i.e. define the non-exponential region of solution of Eq. (4). 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 Eq. (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 the wide range of parameters \((C, n_r)\), except when \( Cn_r \gg 1 \).

An important observation from Figure 1 (see the legend) is that \( \beta \) decreases as \( Cn_r \) increases. Hence non-exponentiality can increase as a result of either increase of \( n_r \), or decrease of temperature \( T \propto 1/C \). This is consistent with many experiments in which \( \beta \) decreases with \( T \) [2, 3, 4]. We will return to this point below.

Second, for several different \( n_r \), we solve Eq.(4) as a function of \( C \), and fit the solution to the SER form above to obtain \( \tau \). We plot the solution as a function of \( 1/(n_r C)= T/T_n \), where \( T_n \) is defined from Eq. (4). We find that the dependence of relaxation time \( \tau \) on \( T/T_n \) collapses on the curve \( \ln(\tau/n_r) = f(T/T_n) \). We also find that \( f(x) \) can not be represented by the Arrhenius-type dependence \( \propto 1/x \), however a good fit is obtained if

\[
\ln \frac{\tau}{n_r} = \frac{a_1}{1/(Cn_r) - a_2} = \frac{a_1}{T/T_n - a_2}
\] (6)

where \( a_1 \) and \( a_2 \) are constants. This is the form of the VF law, Eq. (2). We find that a good fit to Eq. (6) exists in both \( T > T_n \) and \( T < T_n \) regimes, with \( \ln(\tau/n_r) \) spanning over 15 decades (see Figure 2).

The transition from Eq. (6) to Arrhenius dependence directly follows from the condition that solution of Eq. (4) is exponential, \( Cn_r \ll 1 \). Since \( a_2 < 1 \) (see the legend to Figure 2), this condition means \( 1/(Cn_r) \gg a_2 \), and dependence (6) becomes Arrhenius. If, on the other hand, \( Cn_r \ll 1 \) does not hold, relaxation is VF-type.
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Figure 1. Solid lines are the solutions of Eq. (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 $(\beta, \tau)$: 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 Eq.(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 Eq. (4), fitted to SER to obtain $\tau$. The dashed line is the fit to Eq. (6), with $a_1=0.141$ and $a_2=0.116$. The insert shows the fit in the $T < T_n$ regime; $a_1=0.288$ and $a_2=0.017$.

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

First, $n_r$, a parameter in Eq. (1), 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 a system “fragility”, and constitutes the basis of fragility plots, which are essentially plots of Eq. (6) with a varying parameter that measures the deviation from Arrhenius dependence; the larger this deviation, the larger the fragility [5].
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Figure 3. Decrease of $\beta$ with $n_r$ (fragility), at various values of $C$. At constant $n_r$, $\beta$ increases with $T \propto 1/C$.

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. 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 LRE, 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 can immediately recover fragility plots in this approach. As discussed above, small $n_r$ corresponds to a stronger system. At a given temperature, small $n_r$ results in $1/(Cn_r) \gg a_2$, and Eq. (6) 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 relaxation becomes progressively non-Arrhenius (see Eq. (6)). Another way of discussing this effect is to note that $n_r$ is proportional to $Tn$ (see Eq. (5)); hence larger $n_r$ in a fragile system corresponds to higher $Tn$. Physically, this means that the increase of the degree of system’s retardation, quantified by $n_r$, requires a higher temperature to remove this retardation by a more efficient equilibration and make the system relax exponentially.

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

Finally, one 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 a 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, 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 Eq. (4) yields SER and the VF law simultaneously, suggesting that LRE dynamics are behind both anomalous “glassy” relaxation laws that kick in at the onset of the glass transition. 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) and, at the same time, increases departure from the Arrhenius relaxation as follows from Eq. (6).

A second related point is that the relationship between SER and the VF law has recently been reiterated: it has been discovered that $\beta$ is invariant to different combinations of pressure and temperature that hold $\tau$ 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 Eq. (4). $C$ and $n_r$, in turn, unambiguously define $\beta$ and $\tau$. Due to the monotonous character of the solution of Eq. (4), we find that only one value of $\beta$ corresponds to a given $\tau$. In other words, we find that $\beta$ is invariant to different combinations of pressure and temperature that hold $\tau$ constant, satisfying the experimental result [7].

Finally, we note that in order to derive Eq. (1) and (2), we considered a system under external stress, which allowed us to discuss the stress relaxation mechanism near glass transition, Eq. (3-4). At the same time, Eq. (1) and (2) are observed in supercooled liquids in the absence of pressure as well, from 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 proposed a new simple way of defining the onset of glass transition: a liquid enters glass transformation range when it begins to redistribute local stresses in the same manner as solid glass. We showed how this condition simultaneously gives two main signatures of “glassy” relaxation, the stretched-exponential relaxation and the Vogel-Fulcher law. Consistent with recent experiments, we found that in the proposed theory, $\beta$ is invariant to different combinations of pressure and temperature that hold $\tau$ constant. We have discussed that the proposed theory offers the definition of system’s fragility in terms of the number of local relaxation events, and recovers experimental correlations of fragility with non-exponentiality of relaxation and the nature of the chemical bond.

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[1] Kohlrausch R 1854 Pogg. Ann. Phys. Chem. 91 56/179
[2] Phillips J C 1996 Rep. Prog. Phys. 59 1133
[3] Ngai K L 2000 J. Non-Cryst. Sol. 275 7
[4] Böhmer R et al 1993 J. Chem. Phys. 99 4201
[5] Angell C A 1995 Science 267 1924
[6] Angell C A 2000 J. Phys.: Cond. Matt. 12 6463
[7] Ngai K L et al 2005 J. Phys. Chem. B 109 17356
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[8] Goldstein M 1969 J. Chem. Phys. 51 3728
[9] Trachenko K and Dove M T 2002 J. Phys.: Cond. Matt. 14 7449
[10] Dyre J C 1998 J. Non-Cryst. Sol. 235-237 142 and references therein.
[11] Trachenko K, Dove M T, Brazhkin V V and Phillips J C 2003 J. Phys.: Cond. Matt 15 L743
[12] Trachenko K and Dove M T 2004 Phys. Rev. B 70 132202
[13] Trachenko K et al 2004 Phys. Rev. Lett. 93 135502; Trachenko K and Dove M T 2003 Phys. Rev. B 67 212203
[14] Böhmer R et al 1998 J. Non. Cryst. Sol. 235-237 1
[15] Tsiok O B et al 1998 Phys. Rev. Lett. 80 999