Freezing a liquid to obtain glass may seem a familiar and conceptually simple process, and yet its theoretical description remains elusive. Such a description, as widely perceived, should provide a consistent theory for the two main properties that a liquid acquires in the glass transformation range: non-exponential relaxation and super-Arrhenius temperature dependence of relaxation time [1].

At high temperature, a liquid under external perturbation relaxes exponentially fast: a relaxing quantity \( q(t) \) decays as \( \exp(-(t/\tau)) \), where \( \tau \) is associated with the transition over a single activation barrier. This is known as Debye relaxation. On lowering the temperature, relaxation changes markedly, and is described by a stretched-exponential function, \( q(t) \propto \exp\left(-\frac{t}{\tau}\right)^\beta \), where \( 0 < \beta < 1 \) [2, 3]. The transition from Debye relaxation to stretched-exponential relaxation (SER) marks the onset of glass transformation range. The transformation is complete when, by convention, the relaxation time \( \tau \) increases to the experimental time scale of \( 100-1000 \) seconds, corresponding to the glass transition temperature \( T_g \). In the glass transformation range, \( \tau \) often increases faster than Arrhenius, and is well approximated by the Vogel-Fulcher-Tamman (VFT) law, \( \tau = \tau_0 \exp\left(\frac{A(T - T_0)}{T - T_0}\right) \), [1].

\( \beta \) and \( \tau \) are therefore two fundamental parameters that describe a liquid in the glass transformation range. A challenge for a theory of the glass transition is to propose a description of these parameters. \( \beta \) and \( \tau \) have been discussed in a number of popular theoretical approaches [1, 2, 3, 4]. An outstanding feature of these approaches is that \( \beta \) and \( \tau \) are often treated separately. One group of theories has offered the mechanism of the increase of \( \tau \), and includes the Adam-Gibbs entropy theory [5], free volume theory [6], elastic models and other approaches (for a recent review, see Ref. [1]). Another group of theories has derived \( \beta \) for SER (see, e.g., Refs. [2, 3, 4]).

In view of this, it remains unclear what the relationship between \( \beta \) and \( \tau \) is, or if one exists at all. On the other hand, because the increase of non-exponentiality and relaxation time are the two signatures of glass transformation, it is natural to ask if there exists a fundamental process of slowing down of molecular motion that affects both quantities. If a single mechanism affects both \( \beta \) and \( \tau \), it should be reflected in a well-defined relationship between these parameters at different temperatures in the glass transformation range.

By analyzing the experimental data for various glass-forming liquids and polymers, we find that non-exponentiality \( \beta \) and the relaxation time \( \tau \) are uniquely related: \( \log(\tau) \) is an approximately linear function of \( 1/\beta \), followed by a crossover to a higher linear slope. We rationalize the observed relationship using a recently developed approach, in which the problem of the glass transition is discussed as the elasticity problem.

In this paper, we show that a universal relationship between \( \beta \) and \( \tau \) exists for all temperatures in the glass transformation range: \( \log(\tau) \) is an approximately linear function of \( 1/\beta \), followed by a crossover to a higher linear slope. We discuss the observed behaviour in the elastic picture of the glass transition.

We have analyzed the experimental data on dielectric relaxation, including our recent results, as well as earlier data [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. At each temperature, \( \beta \) and \( \tau \) were determined from the location and width of the dielectric loss peak, respectively. Prompted by our recent work on glass transition [22, 23], we have plotted \( \log(\tau) \) as a function of \( 1/\beta \). In Figure 1, this dependence is shown for 15 different glass-forming systems.

Figure 1 immediately highlights our central point, namely that a universal relationship \( f(\beta, \tau) = 0 \) can be identified for the studied systems in the entire range of glass transformation. First, at high temperature, \( \log(\tau) \) is approximately proportional to \( 1/\beta \). Second, as the temperature is reduced, a crossover to another higher slope takes place.

We note here that generally, presenting the data as in Figure 1 is attractive since it does not require scaling by \( T_g \), an arbitrary quantity from a theoretical point of view. In addition to providing a universal relationship between \( \beta \) and \( \tau \), the plot in Figure 1 can serve as a convenient comparative representation of non-exponentiality in different systems approaching their glass transition.

We also note that the universality of the pattern in Figure 1 is extended to the domain of high pressure. In the dielectric spectroscopy experiment, the increase of \( \tau \) at higher pressure can be counter-balanced by an increase of temperature. For many systems, it has been shown that different combinations of pressure and temperature that keep \( \tau \) constant, always give the same value of \( \beta \). This signifies the universal relationship between \( \beta \) and \( \tau \).

Relationship between non-exponentiality of relaxation and relaxation time at the glass transition

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Figure 1 is attractive since it does not require scaling to a higher linear slope. We rationalize the observed relationship using a recently developed approach, in which the problem of the glass transition is discussed as the elasticity problem.
There is no a-priori reason why the location of the dielectric loss peak (\(\tau\)) should be correlated with its width (\(\beta\)). Hence the existence of a universal relationship between \(\beta\) and \(\tau\) strongly suggests that they reflect the same slowing-down mechanism operative in the glass transformation range.

Figure 1 presents a challenge for a theory of the glass transition. In order to rationalize the observed behaviour, one requires an approach to the glass transition that offers descriptions of both \(\beta\) and \(\tau\). Some have been proposed \[26, 27\], and it would be interesting to see the predictions of these approaches regarding the observed behaviour. Here, we discuss the observed relationship based on the recently developed approach, in which the problem of the glass transition is discussed as the problem of elasticity \[23, 24\]. Below we briefly review the model, followed by a discussion of its prediction about the relationship between \(\beta\) and \(\tau\).

A glass is different from a liquid by virtue of its ability to support shear stresses on experimental time scales \[1\]. In our picture, we discuss that when considering stress relaxation, a liquid can be treated as an elastic medium. In other words, we show that the problem of glass transition can be formulated as the elasticity problem. Important to this discussion is the elastic feed-forward interaction between local relaxation events (LREs) \[23, 24\]. Let \(\Delta p\) be the increase of shear stress on a current LRE due to previous concordant LREs. If \(n\) is the current number of LREs, \(\Delta p\) is a monotonically increasing function of \(n\). The increase of stress, on a currently relaxing region increases its activation barrier \(V\). It has been argued that \(V\) is given by the elastic shear energy of a surrounding liquid \[30\]. This result was confirmed by the experimental measurements of the shear modulus, showing that the activation barrier increases with the shear energy \[30\]. Because, as discussed by Orowan and Goldstein, previous LREs reduce stress in the direction “concordant” to the external stress, the increase of shear stress on later rearranging regions consistently increases shear strain on them in the same direction, increasing shear energy and therefore \(V\). The increase of \(V\) due to the additional stress \(\Delta p\), \(\Delta V\), is given by work \(\int \Delta p dq\). If \(q_a\) is the characteristic volume \[30\], \(\Delta V = \Delta pq_a\), and we find \(V = V_0 + q_a \Delta p\), where \(V_0\) is the high-temperature activation barrier.

Because \(\Delta p\) is a monotonically increasing function of \(n\) and \(V = V_0 + q_a \Delta p\), we find that \(V\) is also a monotonically increasing function of \(n\). This provides the feed-forward interaction mechanism between LREs, in that activation barriers increase for later events.
It is important to discuss how the feed-forward interaction mechanism operates on lowering the temperature. The elastic wave that propagates stress created by a LRE is stopped when another LRE takes place at the front of the wave. If $\tau$ is the structural relaxation time, the elastic wave propagates without dissipation distance $d = ct$, where $c$ is the speed of sound. $d$ can therefore be called the liquid elasticity length. Because $c$ is on the order of $a/\tau_0$, where $a$ is the interatomic separation of about 1 Å and $\tau_0$ the oscillation period, or inverse of Debye frequency ($\tau_0 = 0.1$ ps),

$$d = \frac{a \tau}{\tau_0} \quad (1)$$

Let $d_m$ be the distance between neighbouring LREs. $d_m$ is the distance between the centres of neighbouring molecular cages of about 10 Å. At high temperature, when $\tau \approx \tau_0$, $d < d_m$ (see Eq. (1)). This means that neighbouring LREs do not elastically interact. Because events are independent, we obtain the expected high-temperature result that relaxation is exponential in time and Arrhenius in temperature. Because $\tau = \tau_0 \exp(V/kT)$, a certain temperature always gives the opposite condition, $d > d_m$, at which point the elastic feed-forward interaction mechanism between LREs becomes operative. Note that the maximal time between two neighbouring LREs is given by $\tau$, hence $d = c\tau < d_m$ ($d = c\tau > d_m$) also means that the time between the neighbouring LREs is shorter (longer) than the time of elastic propagation between the events $d_m/c$. This is another way of showing that local events relax as independent at high temperature, but start to interact as the temperature is lowered. We have recently shown that this results in the crossover from exponential to stretched-exponential relaxation $22$. The crossover temperature $T_c$ is calculated by putting $d = d_m$ in Eq. (1).

To calculate how $V$ depends on the current number of LREs $n$, we introduce the dynamic variable $n(t)$, the current number of relaxing events induced by an external perturbation (i.e., in addition to thermally-induced events). We consider relaxation at constant temperature. According to Eq. (1), this sets the range of the feed-forward interaction $d$. $n(t)$ starts from zero and increases to its final value $n_r$, $n(t) \rightarrow n_r$ as $t \rightarrow \infty$. Let’s consider the current LRE to relax in the centre of the sphere of diameter $d$. As discussed above, all previous remote concordant LREs within distance $d$ from the centre participate in the feed-forward interaction, increasing stress $\Delta p$ on the central region and hence increasing $V$ for the central LRE. $\Delta p$ can be calculated by integrating the contributions of remote concordant LREs. A straightforward integration, together with $V(n) = V_0 + q_0 \Delta p$ from the above, gives $22$:

$$V(n) = V_0 + V_1 \frac{n}{n_r} \quad (2)$$

where $V_1 = \pi/2 \rho_c \Delta \rho_0 d_0^3 \ln(2d/d_0)$, $d_0$ is on the order of the size of a relaxing region, $\rho_c$ is the density of relaxing regions, $\rho_c = 6n_r/\pi d^3$, and $\Delta \rho_0$ is the decrease of stress due to a remote concordant LRE.

In Eq. (2), $V_1$ depends on temperature through $d$ (see Eq. (1)). As we have recently shown $24$, using $\tau = \tau_0 \exp(V/kT)$ in Eq. (1) and eliminating $d$ from Eq. (2), gives the VFT law for $\tau$. Here, $\tau$ corresponds to $n = n_r$, i.e. maximal relaxation time of the system $24$.

Eq. (2) describes the feed-forward interaction mechanism in a liquid at $T < T_c$. We are now set to write the equation that relates $\beta$ and $\tau$. The rate of LREs, $dn/dt$, is proportional to the number of unrelaxed events, $(n_r - n)$, and the event probability, $\rho = \exp(V/kT)$. Since $V$ depends on $n$ (see Eq. (2)), $\rho$ becomes dependent on $n$. Introducing $q = n/n_r$, and reduced time $t/\tau_0$, we write:

$$\frac{dq}{dt} = (1 - q) \exp \left( -\frac{V_0 + V_1 q}{kT} \right) \quad (3)$$

Eq. (3) has two parameters, $V_0/kT$ and $\alpha = V_1/kT$. We have recently shown $23$ that its solution is well approximated by the two-parameter SER, $q(t) = 1 - \exp(-t/\tau^2)$. Whereas $\tau$ depends on both $V_0/kT$ and $\alpha$, $\beta$ depends on $\alpha$ only; the smaller $\alpha$, the larger $\beta$ ($\alpha = 0$ gives exponential relaxation, $\beta = 1$). We solve Eq. (3) for different values of $\alpha$, fit the solution to the form of SER above, and find that $1/\beta = 1 + C\alpha$, where $C$ is a constant (see Figure 2). Joining this result with $V_1 \propto \ln(d) \propto \ln(\tau)$ (see Eqs. 1-2), we find that $\ln(\tau)$ is a quasi-linear function of $1/\beta$.

To discuss the crossover to the second higher slope in Figure 1, we note that our picture predicts crossovers of both $\tau$ and $\beta$ when at low temperature $d$ reaches the system size $L$. The crossover of $\tau$ takes place because $V$ is proportional to $V_1 \propto \ln(d)$ (see Eq. (2)) $24$. As long as $d < L$, $V$ increases with temperature, because $d$ is temperature-dependent (see Eq. (1)), giving the VFT dependence of relaxation time $24$. When $d \geq L$, $V$ can not increase by way of increasing $d$, resulting in a weak temperature dependence of $V$ at $d > L$ and thus the crossovers observed experimentally $8, 31$. The same

![FIG. 2: $\beta$ as a function of $\alpha$, obtained from the solution of Eq. (3).](image)
reasoning is applied to the crossover of $\beta$. $V_1$ increases on lowering the temperature because $V_1 \propto \ln(d)$ in Eq. (2). This remains true as long as, on lowering the temperature, $d < L$. When $d \geq L$, $V_1 \propto \ln(L/d_0)$, and is temperature-independent. Hence at $d = L$, $V_1$ shows a kink and starts to saturate to a constant value. Because $\beta$ decreases with $V_1/kT$ (see Figure 2), we find that $d = L$ should mark the crossover of $\beta$ to the lower slope. Using salol as an example, $d = L \approx 1$ mm in Eq. (1), and the VFT parameters $A = 839$ K and $T_0 = 195$ K for $\tau$ [22], we find the crossover temperature of 247 K. This agrees well with the crossover of $\beta$ shown in Figure 3.

Because our picture predicts the crossover of $\beta$ to the lower slope, the crossover of $\log(\tau)$ vs $1/\beta$ to the higher slope also takes place, as is seen in Figure 1.

The crossover of $\beta$ at $d = L$ is expected to be more pronounced than that of $\tau$, because the activation barrier is the sum of a constant term and a temperature-dependent term $\ln(d/d_0)$ [24], whereas $\beta$ is solely defined by $\alpha = V_1/kT$ (see Eqs. (2-3)). Consistent with this, we find that the crossover in Figure 1 is affected mostly by the crossover of $\beta$. In Figure 3 we observe that for salol at low temperature, $1/\beta$ trails off at about 1.5, the same value of $1/\beta$ associated with the crossover to the higher slope in Figure 1. The crossover in Figure 1 takes place in the temperature range in which $T$ shows a crossover as well, although the latter is less pronounced as compared with the crossover of $\beta$.

In summary, we have shown that the non-exponentiality parameter $\beta$ and relaxation time $\tau$ are uniquely related in the glass transformation range, and rationalized this relationship in the approach that discusses the problem glass transition from the elastic point of view.

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