Slow dynamics and stress relaxation in a liquid as an elastic medium

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We propose a framework to discuss the transition from exponential relaxation in a liquid to the regime of slow dynamics. For the purposes of stress relaxation, we show that a liquid can be treated as an elastic medium. We discuss that, on lowering the temperature, the feed-forward interaction mechanism between local relaxation events becomes operative and results in slow relaxation.

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At high temperature, a liquid under external perturbation relaxes exponentially fast: a relaxing quantity $q(t) \propto \exp(-t/\tau)$, where τ is associated with the transition over a single activation barrier. This is known as Debye relaxation. On lowering the temperature, relaxation becomes qualitatively different. In many cases, it is well approximated by the stretched-exponential function, $q(t) \propto \exp[-(t/\tau)^{\beta}]$, where $0 < \beta < 1$; smaller β corresponds to slower relaxation. Slow relaxation is universally seen in many supercooled liquids, glasses, and other disordered systems.[1–3] It describes a very sluggish dynamics: in the wide data range, it decays as a logarithm of time. The transition to slow relaxation signals the onset of glass transformation range,[1] which ends with the dynamical arrest at T_g, glass transition temperature. T_g is conventionally defined from the condition that relaxation time τ exceeds the experimental time scale of $100–1000$ s. Slow relaxation can be seen below T_g as well, although stronger perturbation (e.g., large pressure[4]) is needed to induce relaxation.

The universal character of slow relaxation strongly suggests that there should be some fundamental slowing down mechanism that kicks in on lowering the temperature. Since stretched-exponential relaxation (SER) was introduced by Kohlrausch in 1854,[5] it has proven difficult to rationalize it from the first principles, without invoking postulates or assumptions. This has contributed to the lack of consensus about its physical origin.[6,7] For a more detailed discussion, the reader is referred to papers that review slow relaxation.[1–3]

Our thinking of the liquids is shaped by the idea that unlike elastic solids, they do not support static stresses. At the same time, it has been long known that liquids are no different to solids in supporting stresses at very high frequencies,[1] at times smaller than the system's relaxation time. Whether the general idea of liquids being able to relax stress can be related to slow relaxation has remained unknown.

In this Brief Report, we propose a framework to discuss the origin of nonexponential dynamics in a liquid. We show that, on a temperature decrease, the feed-forward interaction mechanism between local relaxation events becomes operative, resulting in slow relaxation. This result is discussed solely on the basis of elastic response of a liquid, without invoking any additional assumptions or postulates.

It is interesting to recall the previous discussion about the elastic aspects of liquid behavior. Some time ago, Orowan introduced "condordant" local rearrangement events.[8] A concordant local rearrangement is accompanied by a strain agreeing in direction with the applied external stress and reduces the energy and local stress (see Fig. 1). A discordant rearrangement, on the other hand, increases the energy and local stress. This has led to a general result that stress relaxation by earlier concordant events leads to the increase of stress on later relaxing regions in a system. Orowan used this result for a heterogeneous system, in which stresses are relaxed by local rearrangements in certain regions of the system only.[8] Goldstein applied the same argument to a viscous liquid[9]: consider a system under external stress which is counterbalanced by stresses supported by local regions. When a local rearrangement to a potential minimum, biased by the external stress, occurs (a concordant event), this local region supports less stress after the event than before; therefore, other local regions in the system should support more stress after that event than before.[9] Noting that "… a molecular theory of this process will be extremely complicated," Goldstein proposed that "the least any model of the flow process must acknowledge is that the extra stress must be supported elsewhere."[9] Note that this proposal implies that a supercooled liquid should be considered as an elastic medium that can support stress relaxation and redistribution.

We begin the discussion with introducing local relaxation events (LREs) which a system uses to relax stress locally. These activated events have been given different names in
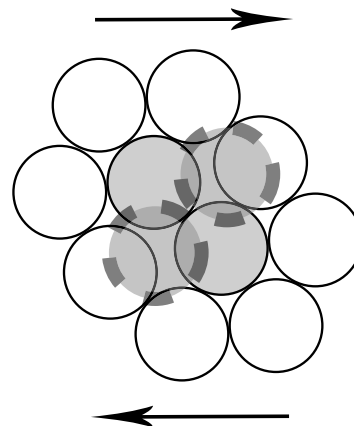

FIG. 1. Orowan's illustration of a concordant local rearrangement. Solid and dashed lines around the shaded atoms correspond to initial and final positions of a rearrangement, respectively. Arrows show the direction of external stress.

the literature (e.g., molecular rearrangements, "flow events," etc.[1]). Because each event carries a microscopic change of a macroscopic quantity (e.g., volume, etc.), the number of events governs the dynamics of relaxing observables. To illustrate the argument of Orowan and Goldstein above, let us consider the current number of LREs $n(t)$ induced in a liquid by an external perturbation. As discussed by Orowan and Goldstein, because an external perturbation introduces bias toward concordant relaxation events, which support less stress after relaxation, later LREs should support more stress in order to counterbalance. The increase of stress on a current relaxing region, Δp, is therefore a monotonically increasing function of n.

It has been shown that activation barrier for a LRE V is essentially defined by the elastic energy. In the Shoving model, for example, V is given by the work of the elastic force needed to shove aside the surrounding liquid in order for a relaxation event to take place.[10] The increase of stress Δp, on a current relaxing region, increases the activation barrier for a LRE since it requires more work to expand the cage around the escaping atom. This can be easily shown to be the case for a hydrostatic or shear component of the strain due to Δp. Hence, the increase of V is given by the increase of work needed to overcome the additional barrier created by the elastic force due to the additional stress Δp: $\Delta V = \int \Delta p \, dq$, where the integral is taken over the reaction path of a LRE. If q_a is the characteristic activation volume,[10] $\Delta V = \Delta p q_a$, giving

$$V(n) = V_0 + q_a \Delta p, \tag{1}$$

where V_0 is the initial value of the barrier.

Because Δp is a monotonically increasing function of n, we find that $V(n)$ is also a monotonically increasing function of n. This describes the *feed-forward interaction mechanism* between LREs, in that activation barriers increase for later events.

It is important to discuss the condition under which the feed-forward interaction mechanism is operative. Let t_s be the time needed for elastic interaction to propagate between LREs, d the distance between neighboring LREs of about 10 Å, c the speed of sound, and τ_0 the oscillation period or inverse of Debye frequency ($\tau_0 = 0.1$ ps). Because c is on the order of a/τ_0, where a is the interatomic distance, we find that $t_s = d/c = \tau_0 d/a$ and is temperature independent. On the other hand, relaxation time $\tau = \tau_0 \exp(V/kT)$, which is also the time between two consecutive relaxation events,[1] increases on lowering the temperature. It is easy to see that at high enough temperature, when $\tau = \tau_0$, $t_s > \tau$ is always true because $d/a > 1$. In this case, local events relax independently of each other because at high temperature, the time between the events is shorter than the time needed for elastic interaction to propagate between them. Because LREs are independent, we obtain the expected high-temperature result that relaxation is exponential. On cooling the system down, a certain temperature always gives the opposite condition $t_s \leq \tau$. When the time between local relaxation events exceeds the time of propagation of elastic interaction between the events, local relaxation events do not relax independently but "feel" the presence of each other.
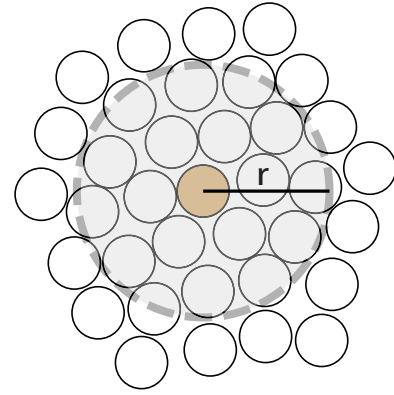

FIG. 2. (Color online) Illustration of the feed-forward interaction mechanism between local relaxation events. This mechanism operates within the sphere of radius $r = d$. Shaded and open circles represent local relaxing regions inside and outside, respectively, of the interaction sphere.

The maximal distance between those LREs which are involved in the elastic feed-forward interaction mechanism is obtained by setting $t_s = \tau$,

$$d = a \frac{\tau}{\tau_0}, \tag{2}$$

where d is now the range of elastic interactions in a liquid.

At high temperature, when $\tau = \tau_0$, d is on the order of interatomic distances but quickly increases on lowering the temperature. Since $\tau = \tau_0 \exp(V/kT)$, we obtain

$$d = a \exp\left(\frac{V}{kT}\right), \tag{3}$$

where V is the activation barrier. For super-Arrhneius increase of V, it is easy to show[11] that d exceeds the system size well above T_g.

It follows from the above discussion that when d exceeds the distance between neighboring LRE in a liquid on the order of 10 Å, the *crossover* from exponential to nonexponential relaxation takes place due to the feed-forward interaction mechanism. The crossover temperature T_c can be calculated from Eq. (3).

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 in a sphere of radius $r = d$. $n(t)$ starts from zero and increases to its final value n_r, $n(t) \rightarrow n_r$ as $t \rightarrow \infty$. We consider relaxation at a fixed temperature, which, according to Eq. (3), corresponds to a fixed value of d. Let us consider the current LRE about to relax to be in the center of the sphere (see Fig. 2). All previous concordant LREs that are located within distance r from the center participate in the feed-forward interaction, increasing stress on the central region and hence the activation barrier for the central LRE. Let $\Delta p_i(0)$ be the reduction of local stress due to a remote concordant LRE i. Generally, Δp_i decays with distance, hence we denote $\Delta p_i(r)$ as its value at distance r from the center. In what follows, we assume, for simplicity, that $\Delta p_i(0)$ are constant, $\Delta p_i(0) = \Delta p_0$. The increase of stress

on the central rearranging region, Δp, can be calculated by integrating $\Delta p_i(r)$,

$$\Delta p = \rho \int_{d_0/2}^{d} 4\pi r^2 \Delta p_i(r)dr, \tag{4}$$

where d_0 is on the order of the size of a relaxing region (central region in Fig. 2), $d_0 \geqslant 3a$ (see Fig. 1), and ρ is the density of LREs, $\rho = 6n/\pi d^3$.

It is important to note that Eq. (4) describes the redistribution of local stresses in an elastic medium. Unlike a solid, a liquid does not support static shear stresses. However, it supports shear stresses at high frequencies in a solidlike manner.[1] These frequencies correspond to times smaller than relaxation time τ. We introduce the distance over which interactions in a liquid are elastic, liquid elasticity length d_{el}. If c is the speed of sound, $d_{el} = c\tau$. Because $c = a/\tau_0$, we find $d_{el} = a\tau/\tau_0$. As follows from Eq. (2), $d_{el} = d$. We therefore find that the distance in which the feed-forward interaction mechanism between LREs operates is also the liquid elasticity length. Hence, we are justified to use $d/2$ as the upper limit of integration in Eq. (4).

In an elastic medium, stresses decay as $\Delta p(r) \propto 1/r^3$.[12] Since $\Delta p(r) = \Delta p_0$ at $r = d_0/2$, $\Delta p(r) = \Delta p_0(d_0/2r)^3$. A straightforward integration of Eq. (4), combined with Eq. (1), gives

$$V = V_0 + V_1 \frac{n}{n_r}, \tag{5}$$

where $V_1 = \pi/2\rho_r q_a \Delta p_0 d_0^3 \ln(2d/d_0)$ and $\rho_r = 6n_r/(\pi d^3)$ is the density of the final number of events in the sphere.

Equation (5) describes the feed-forward interaction mechanism in a liquid at $T < T_c$.

We are now set to derive slow relaxation. As discussed above, at high temperature above T_c, the feed-forward interaction mechanism is absent, and LREs relax independently of each other. The rate of LREs dn/dt is proportional to the number of unrelaxed events $(n_r - n)$ and the event probability $\rho = \exp(V_0/kT)$, where V_0 is the high-temperature activation barrier. Introducing $q = n/n_r$, we write

$$\frac{dq}{dt} = \exp\left(-\frac{V_0}{kT}\right)(1 - q), \tag{6}$$

where t is dimensionless time $t \rightarrow t/\tau_0$. The solution of Eq. (6) is the expected high-temperature exponential relaxation $q \equiv n/n_r = 1 - \exp(-t/\tau)$, where $\tau = \tau_0 \exp(V_0/kT)$.

As temperature is lowered below T_c, the feed-forward interaction mechanism between consecutive LREs becomes operative as discussed above. Because this mechanism is described by Eq. (5), the event probability ρ becomes dependent on n (or q), and the rate equation is [compare with Eq. (6)]

$$\frac{dq}{dt} = \exp\left(-\frac{V_0}{kT}\right)(1 - q)\exp(-\alpha q), \tag{7}$$

where $\alpha = V_1/kT$.

Unlike Eq. (6), Eq. (7) describes slow relaxation due to the factor $\exp(-\alpha q)$. Nonexponential relaxation becomes ex-
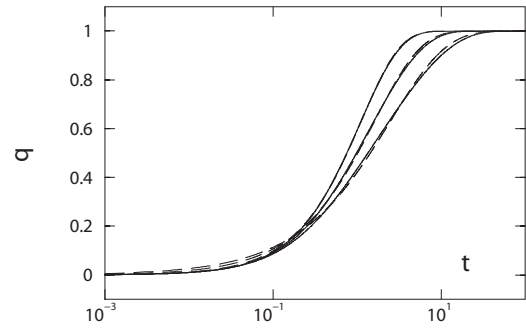

FIG. 3. Solid lines are solutions of Eq. (7), and dashed lines are fits to SER. From left to right, $\alpha = 0.3$, 1.2, and 2.2. SER parameters (β, τ) are (0.94, 1.12), (0.78, 1.62), and (0.66, 2.51) in the same order.

ponential at high temperature when α is small. Since SER is one of the simplest functions that describes slow relaxation, we attempt to fit the solution of Eq. (7) to $q = 1 - \exp[-(t/\tau)^\beta]$. Because the degree of nonexponentiality of the solution of Eq. (7) is controlled by α only, we set $\exp(-V_0/kT) = 1$. This affects τ but not β. In this form, Eq. (7) is a one-parameter description of nonexponential relaxation. We solve Eq. (7) numerically for different values of α and fit the solution to SER using the least-squares method. A reasonably good quality of the fits is illustrated in Fig. 3. Note that smaller temperature (larger α) gives smaller β (see the legend in Fig. 3), consistent with experimental results.[2,3]

It is interesting to note that on lowering the temperature, we expect to find the crossover of β to the lower slope. Using Eq. (3), we find $V_1 \propto \ln(d/d_0) = [\ln(a/d_0) + V/kT]$. This relation remains true as long as, on lowering the temperature, $d < L$, where L is the system size. For propylene carbonate, for example, a simple calculation shows that $d = L$ takes place at temperature above T_g.[11] When $d \geqslant L$, the upper limit of integral in Eq. (4) is L, and $V_1 \propto \ln(L/d_0)$, and is temperature independent. Hence, at $d = L$, V_1 shows a kink and starts to saturate to a constant value. Because β decreases with $\alpha = V_1/kT$ [see Eq. (7)], we find that $d = L$ should mark the crossover of β to the lower slope. This is indeed what is seen in several glass-forming systems at low temperature.[13]

We also note that the proposed picture of slow relaxation gives rise to the property that has been discussed quite intensely recently, namely, that relaxation in supercooled liquids and glasses is dynamically heterogeneous.[14] Dynamic heterogeneity naturally arises in our picture, since activation barriers increase for later LREs that are located in different regions of the system. This gives different waiting times in different regions of the system and dynamic heterogeneity.

In this Brief Report, our main intention has been to identify and discuss the origin of slow relaxation in a liquid. We proposed that slow relaxation can be understood solely on the basis of liquid elasticity, without invoking any additional assumptions or postulates. We have shown that on lowering the temperature, the feed-forward interaction mechanism between LREs becomes operative and sets slow relaxation. We note that it is an encouraging sign that we can discuss slow relaxation in a liquid using only concepts from elasticity, one of the most robust areas of physics.

Compared with other models of slow relaxation, our picture is probably the closest in its spirit to the coupling model (CM) of the glass transition.[2] The main assumption of the CM model is the postulate that nonexponentiality is the result of some sort of cooperativity of relaxation that kicks in on lowering the temperature. Here, we discussed that the origin of cooperativity is the feed-forward interaction mechanism between LREs. Absent at high temperature, it becomes operative on lowering the temperature, setting the cooperative character of relaxation and slow dynamics.

We have recently shown that the feed-forward interaction mechanism, which gives nonexponential relaxation, is also responsible for the Vogel-Fulcher-Tamman (VFT) law for relaxation time. Here, super-Arrhenius behavior is associated with increase, on lowering the temperature, of the range of the feed-forward interaction.[11] Joining this result with the present discussion, we can conclude that the two most important open questions in the area of glass transition, the origin of SER and the VFT law,[1] can be understood on the basis of elasticity of a liquid.

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