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# Stress-induced glass transitions

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ABSTRACT

In 1995, Chudnovsky and coworkers (Zhou, Chudnovsky, Bosnyak, & Sehanobish, 1995) interpreted cold drawing in polymeric glasses as a dual glass transition, first from glass state to a liquid, and then, after drawing turned the glass into a non-isotropic oriented polymeric liquid, from oriented liquid to a new glass state. On the microscopic scale, a glass is a system with local arrangements of particles frozen. At the glass–liquid transition temperature, these arrangements become changeable at an observable time scale. Assuming that cold drawing is caused by slip-stick rearrangements in small clusters throughout the material, we investigate the relations of conventional glass transition to the onset of cold drawing; our theory is based on a generalization of Eyring's ideas of stress-dependent rearrangement activation energies.

Upon cooling, liquids solidify. In many liquids, solidification takes the path of crystallization, a discontinuous phase transition. In other liquids (glass-formers), crystallization can be avoided; then, the supercooled liquid remains liquid until freezing at the glass–liquid transition temperature $T_g$. Freezing transition is not accompanied by strong energy effects or volume changes, it happens in a narrow temperature interval, and can be reversed by heating the glass back to liquid state temperatures. Glassy solidification only freezes particles arrangements in small parts (clusters) of the glass: each particle (atom, molecule) still vibrates in a cage made of surrounding nearest neighbors while keeping the same neighbors for a macroscopically long time. No real singularity is associated with the glass transition; the glass transition temperature $T_g$ is defined (Howard & Young, 1997) by convention that the viscosity at this temperature is $\eta(T) - 10^{13}$ *Poise*, or equivalently the dielectric relaxation time $\theta \sim 10^3$ s. In practical terms, the difference between the glassy and the liquid state can be tested, and the glass–liquid transition detected by onset of deformation, under moderate stress. These and other tests of structural mobility show that changing temperature is not the only way to solidify a liquid or to de-freeze a glass; another, frequently used in applications, way is to apply mechanical stress. Here, we study and discuss relations between these methods of facilitating a glass transition.

A widely accepted explanation of long lifetimes of particles arrangements in small clusters (cages) of glasses and glass-formers is that a change in this arrangement (a local rearrangement) is a thermally activated process that needs activation energy $\Delta \gg k_BT$ where $k_B$ is the Boltzmann constant and $T$ the temperature. The rate $R$ of a thermally-activated process is described by the Arrhenius formula

$$R(\Delta, T) = \frac{N(\Delta)}{\theta(\Delta)}, \quad \theta(\Delta, T) = \theta_0 \exp\left(\frac{\Delta}{k_BT}\right), \tag{1}$$

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here $N(\Delta)$ is the number of clusters characterized by the activation energy $\Delta$ and the time $\theta_0$ (reciprocal to the frequency of rearrangement attempts) is of the order of particles vibration periods (for small particles $\sim 10^{-12}$ s (Howard & Young, 1997). Due to the amorphous nature of the glass, particles arrangements in small cluster vary, and one assumes that also lifetimes $\theta$ of cages have a distribution. Then, a more accurate statement about glass transition is that at glass transition, the lifetime of the local (in a small cluster) arrangement in most parts of the material is $\theta \sim 10^3$ s. This statement does not exclude the possibility that an insignificantly small fraction of clusters may have smaller lifetimes, and some clusters may remain frozen at the glass transition temperature. In glassforming liquids, an insight into the spectrum of rearrangement times can be obtained from the temperature dependence of the viscosity. Angell (2008) analyzed a large database of glassforming liquids and found that formula (1) fits the viscosity data for some ("strong") but not for all glassforming liquids; there are other ("fragile") liquids where the apparent excitation energy $\Delta(T)$ in the fit increases with decreasing temperatures. The packing energy of interacting particles depends on particles arrangement. Then, the statistics of these arrangements (the local structure) in glassforming liquid changes with decreasing temperature until it becomes frozen at the glass transition. Fragility is than explained by assuming that the activation energy $\Delta$ for a rearrangement has a substantial dependence on the changing arrangements. In strong glassformers, the main part of the energy to change any configuration is the energy to break a strong chemical bond; this energy is not collective, and not sensitive to the local structure.

In contrast to liquids, the local structure in the glass and the spectrum of activation energies for rearrangements are frozen. On increasing temperature in the glassy state, one can observe, at least in principle, an increase in the frequency of spontaneous rearrangements in some clusters. However, until the material remains glassy, structurally frozen clusters form a percolated frozen matrix that acts as an elastic body and forbids non-elastic deformation on the macroscopic scale. The onset of growing macroscopic changes in a sample under moderate stress is a signature signals of the glass–liquid transition, but it also assumes that the glass transition condition $\theta \sim 10^3$ is met in a significant fraction of clusters in the frozen matrix. The activation energy $\Delta$ for this fraction defines the glass transition temperature and sets the condition that the Gibbs number $G = \frac{\Delta}{k_B T}$ in the Arrhenius formula (1) has the value $G = G_g \approx 40$.

The activation energy $\Delta$ can be changed at constant $T$ using a variety of means: changing the arrangements in clusters by ionizing radiation or fast neutrons, initiating chemical reactions, and/or applying external force that stresses the glass. A general condition for glass transition in a system where the activation energy depends on a parameter $X$ is

$$G = \frac{\Delta(X)}{k_B T} = G_g; \tag{2}$$

this condition defines the glass transition line in the ($X$–$T$) plane. A known example is the shift in glass transition temperature under a hydrostatic pressure $P$. In most (but not in all) glassforming liquids, an increase in pressure increases activation energies, and thus $T_g(P)$. A liquid can be solidifies (vitrified) at a fixed temperature by applying a sufficiently high pressure, and a reverse glass–liquid transition can be facilitated by diminishing the pressure back to liquid state values.

The behavior of the glass becomes more complex when changing pressure also leads to a phase transition. Recently, phase transitions between liquid phases differing in local structure (polyamorphous phase transitions) have been demonstrated in some liquids (Angell, 2008; Brazhkin et al., 2008; Mitus, Patashinskii, & Shumilo, 1985); similar phenomena can be expected in glasses (Mishima & Stanley, 1998). It is important that glass is a non-equilibrium, structurally frozen system: even when the thermodynamic conditions for a phase transition in the glass are met, actual changes are forbidden until the glass is brought to the glass–liquid transition. Once the transition starts, relaxation from a strongly non-equilibrium state may destroy the sample. For example, a negative pressure $P < 0$ creates a universal instability that relaxes to a stable two-phase state by cavitation, nucleation and then growth of voids. In a glass, onset of structural mobility starts nucleation and growth of supercritical bubbles, and results then in a foam-like state in parts (as in crazing Howard & Young, 1997) or in the entire material (as in foaming). Another case of instable state is a glass under anisotropic, for example uniaxial, stress $\sigma$. The free energy of the system can be diminished by elongation in the direction of the stress and a corresponding contraction in other directions to keep the volume constant. The related industrial process is cold drawing of materials. Again, relaxation can only start when the glass is brought to the glass transition line (2) by increasing the temperature to $T_g$ or by diminishing the activation energy $\Delta$. Chudnovsky and coworkers (Brazhkin, Buldyrev, Ryzhov, & Stanley, 2002) investigated cold drawing in polymeric glasses and identified it as a combination of two glass transitions, a glass–liquid transition on the onset of drawing followed by plastic elongation, and then a liquid–glass transition structurally freezing the oriented polymer. In the experimental or industrial setup, glass transition conditions (2) are met in some parts of a sample while other parts are still in frozen glassy or mobile liquid states. To account for this non-uniformity, one needs to understand first the properties in parts of the system where the conditions can be approximated as spatially uniform. Here, we consider a glassy material under uniform uniaxial (true) stress. A quasistatic increase of stress in the glass results in an elastic deformation of the material as described by the Hook's law; detectable plastic changes start when the force diminishing the activation energy $\Delta$ reaches the glass transition threshold.

The idea of activation energies changing under stress was long ago formulated by Eyring (1936) and Tobolsky and Eyring (1943). Eyring considered a degree of freedom described by a coordinate $x$ and an energy landscape $U(x)$ characterized by two energy basins near corresponding energy minima $U_1$ and $U_2$, and a maximum $U_{max}$ (Fig. 1) separating the basins. In a thermal bath, the coordinate $x$ fluctuates between basins; the frequency of basin switches is regulated by the activation energy $\Delta_1 = U_{max} - U_1$ for switching from basin 1 to basin 2, and $\Delta_2 = U_{max} - U_2$ for switching back. The system is in thermal