Glass transition [pln24]

Characteristic attributes of glassy materials:

- solid-like behavior mechanically,
- liquid-like behavior structurally,
- infinite viscosity and finite shear modulus,
- no translational or orientational long-range order,
- amorphous state,
- optical transparency (sometimes).

Importance of time scales:

Viscosity η and stress relaxation time τ exhibit anomalous dependence on temperature (deviation from Arrhenius law).

Recall the relation, $\eta = G_0\tau$, from [pln23].

• Arrhenius law:

$$\eta = \eta_0 \exp\left(\frac{B}{T}\right) \quad \Rightarrow \quad \ln\frac{1}{\tau} \sim -\frac{B}{T}.$$

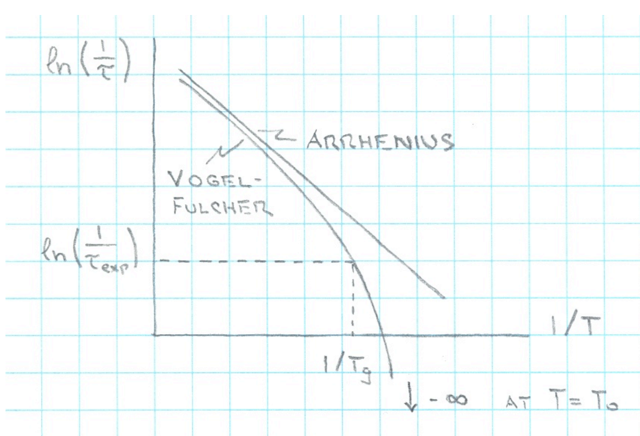
• Vogel-Fulcher model:

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \quad \Rightarrow \quad \ln\frac{1}{\tau} \sim -\frac{B}{T}\left[\frac{1}{1 - T_0/T}\right].$$

▷ T_0: Vogel-Fulcher temperature,

▷ T_g: glass transition temperature,

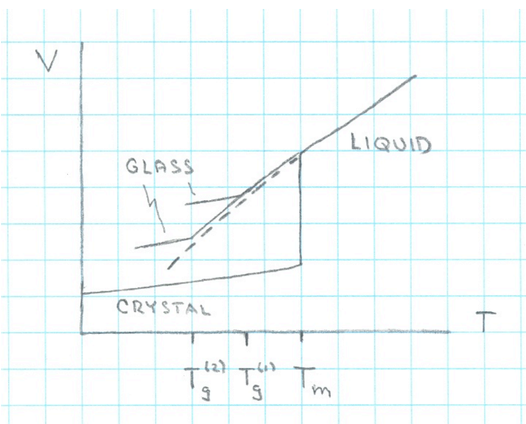
▷ $\tau_{\rm exp}$: time scale of experiment.

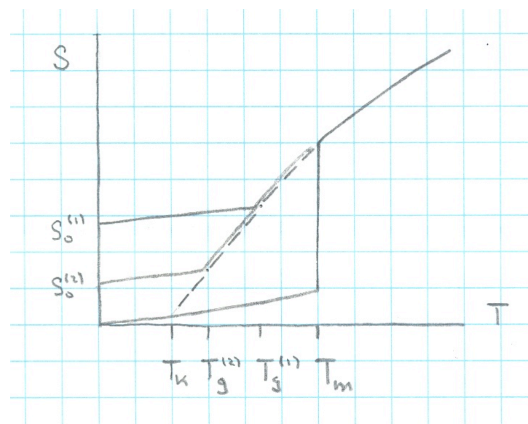


Nature of transition:

- liquid → crystal: first-order transition (discontinuous),
- liquid → glass: more akin to second-order (continuous).

  ▷ $T_{\rm g}^{(n)}$: glass transition temperature for given cooling rate,
  ▷ $T_{\rm m}$: melting temperature,
  ▷ $T_{\rm K}$: Kauzmann temperature,
  ▷ $S_0^{(n)}$: residual entropy of glass for given cooling rate,
  ▷ $--$: undercooled liquid.





Entropy:

The volume V can be measured directly whereas the entropy S must be determined from the heat capacity via integration:

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \quad \Rightarrow \quad S(T) = S(T_0) + \int_{T_0}^{T} dT' \frac{C_p(T')}{T'}.$$

[in part from Jones 2002]

Comments:

- Undercooled liquid is in metastable state. Nonequilibrium glass state with quenched randomness falls out of undercooled liquid.
- At constant $T \lesssim T_\mathrm{g}$ glass state undergoes slow ageing associated with densification toward density of undercooled liquid state. Ageing proceeds by spatial rearrangement of groups of molecules. As groups that need rearrangement grow larger, energy barriers grow higher and times scales longer.
- High density glasses are more durable due to more efficient packing of molecules. High-density assembly is achievable via vapor deposition. Molecules near surface have high mobility and thus produce efficient packing.
- Melting process of glass upon reheating depends on quality of packing:
  - loosely packed glass tends to gradually soften,
  - efficiently packed (high-density) glass tends to exhibit narrow moving front between soft and hard material.
- Quality of packing also leaves characteristic signature in heat capacity:
  - LDG: $C_p \sim T$ (typical for excitations of amorphous matter),
  - HDG: $C_p \sim T^3$ (typical for phonons in crystalline matter).
- Tempered glass is produced in a process that uses differential cooling rates for surface and interior parts, putting surface under compression and interior under tension. Cracks grow into explosive fragmentation. Small fragments are less dangerous than large shards.
- Deformation of glass produces irreversible rearrangements of molecules in spatially localized shear transformation zones. STZs have been interpreted as a defect structure that becomes manifest only under stress. With increasing stress, STZ have been observed to organize into bands that then mark the locations of initial failure.

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