Glass transition of metaphosphate glass in the viscosity-temperature relation

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Viscosity of several glasses

![Graph showing viscosity of several glasses](image)
Viscosity of glass
Definitions of shear stress and shear strain

Strain $\varepsilon = \frac{\Delta l}{h}$

Stress $\sigma = \frac{G}{S}$
Time-dependence of strain under step-type stress

\[ \varepsilon(t) = a + b \left[ 1 - \exp\left(\frac{-t}{\tau}\right) \right] + dt \]

\[ \varepsilon'(t') = c + b \exp\left(-\frac{t}{\tau}\right) \]
Definition of shear viscosity

stress $\sigma$, strain $\varepsilon(t)$
$\sigma = \varepsilon \frac{d \varepsilon(t)}{dt}$

viscosity $\eta$
$\eta = \frac{\sigma}{d}$

experimental conditions
$\varepsilon(t) \leq 10^{-3}$, $t \leq 5$ min.
Schematic diagram of apparatus

- Detector
- Probes
- Mobile plate
- Pulley
- Furnace
- Specimen
- Fixed plate
- Weight
Viscosity of metaphosphate glass

\[ (\text{AgI})_{0.5}(\text{AgPO}_3)_{0.5} \]
Viscosity of polystyrene

- polystyrene
- ○ sandwich
- △ rotation

Log $\eta$ (Pa·s)

$1000/T$
Viscosity of metallic glasses

By Prof. H. Numakura
of Kyoto Univ.
Viscosity of polymer glasses

- Polystyrene ($T_g = 366 K$)
- PMMA ($T_g = 388 K$)
- Polycarbonate ($T_g = 418 K$)

Graph showing the relationship between $\log \eta$ (Pa·s) and $T_g/T$.
Viscosity of aromatic hydrocarbon

![Graph showing viscosity as a function of reciprocal absolute temperature](image)

**Fig. 1.** Log $\eta$ (base 10) (poise) of T-xNB as a function of the reciprocal absolute temperature, degrees Kelvin. Open circles from torsional creep measurements (Ref. 2); the filled circles are the capillary results of Magill and Ubbelohde (Ref. 1). The new capillary results are represented by the triangles. The position of the conventional (1 deg/min cooling) glass temperature $T_g$ is indicated. Viscosity of an annealed glass is also shown (Ref. 2).

Glass transition

- Rearrangements of **groups** with many molecules.
- Metals with **complex** molecules or with **different size** compositions tend to be glasses.

Big aging effects

Effects of **different** compositions, and **thermal** and **mechanical** treatments on viscosity
Viscosity of metaphosphate glass with different compositions

$$\log (\text{Pa} \cdot \text{s})$$

$$\text{Tg/T}$$

- (AgI)$_{0.5}$(AgPO$_3$)$_{0.5}$
- AgPO$_3$
Viscosity of polystyrene

with different treatments

![Graph showing viscosity of polystyrene with different treatments.](image)
Temperature-rate dependence of $T_g$

Two transition temperatures were discovered.
In glass

Disorders \(\rightarrow\) Properties different from crystals

Intermediate Range Orders \(\rightarrow\)

Particular properties of glasses including the glass transition

Intermediate Range Order (IRO)

Cooperative Rearranging Region (CRR)

Spatial Heterogeneity (SH)

Cluster
Short range orders in liquids
  Size of them is about 2 Å.
  This situation is the same as that in glasses and crystals.

Medium range structures in supercooled liquids
  Icosahedron in metallic glasses
  Size of them is about 5 Å.
  They are precursors of IROs.

Intermediate range orders in glasses
  Crystalline nanoclusters or compound nanoclusters
  Size of them is about 2 nm.
  They yield their small interfacial energy to form glasses.

Long range orders in glasses
  No
Theories for glass transition

- Free volume theory: phenomenal theory
- Adam-Gibbs theory: phenomenal theory
- Mode coupling theory: basic theory
- Molecular dynamic theory: simulation
- Energy landscape theory: simulation
- Renormalization group theory: basic theory

No theory can explain the glass transition phenomena.

IROs, which increase in size and number decreasing to $T_g$, suppress the crystallization of the super liquids and generate the glass states below $T_g$. 
Activation process with double well potential

Potential barrier height $U$  \quad \rightarrow \text{Activation energy } E

Constant $E$ in \textbf{Arrhenius} state \quad \rightarrow \text{Freezing of } IROs \text{ in glasses}
Adam-Gibbs theory (1965) shows
\[ \tau = \tau_0 \exp\left(\frac{C}{T S_c}\right) \]
\( \tau \) : relaxation time
\( \tau_0, C \): constants
\( T \): temperature
\( S_c \): configurational entropy

When \( S_c \) is proportional to \( (T - T_0)/T_0 \),
\[ \eta = \eta_0 \exp\left(\frac{D T_0}{(T - T_0)}\right) \quad (\text{VTF equation}) \]
\( \eta \): viscosity
\( \eta_0, D, T_0 \): constants

When \( S_c \) is constant,
\[ \eta = \eta_0 \exp\left(\frac{E}{RT}\right) \quad (\text{Arrhenius equation}) \]
\( E \): activation energy
\( R \): gas constant
Conclusions

- Viscosities do not diverge at any temperature.
- Process is a phase transition from the VTF state to the Arrhenius state at $T_g$ with no latent heat.
- Viscosity is more sensitive to the composition, thermal and mechanical treatments in the glass state than in the supercooled liquids.
- New (viscous) transition temperature was discovered at lower than $T_g$ by the DSC.
- Idea of IROs for the glass transition is proposed to explain our data.
The glass transition is due to a self-organization of the IROs of nanometer orders in size in the glass state.