Dynamic Light Scattering in Glassforming Ultraphosphate Liquids

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Network forming glasses

- SiO$_2$ is strong
- alkali addition reduces covalent bonding and increases the fragility
- Why is this?
- In what other ways are dynamics influenced by structure?
Structural Relaxation in Liquids

Two step decay:

– **β relaxation**
  - fast, cage dynamics

– **α relaxation**
  - slow, viscoelastic response

– **nonergodic level**
  - plateau, $f_q$
Viscoelastic ($\alpha$) Relaxation

- Non-exponential
  - Kohlraush or ‘stretched’ exponential
- Non-Arrhenius
  - Vogel-Tamman-Fulcher

$$S_q(t) = f_q \exp\left\{ -\left( \frac{t}{\tau_{\alpha}} \right)^\beta \right\}$$

$$\tau_{\alpha} = \tau_o \exp\left\{ \frac{DT_o}{T - T_o} \right\}$$
Dynamic Light Scattering

Dynamics cause scattered light to undergo energy shifts ...

- **Raman** ... THz
  - vibrational modes
  - gratings
- **Brillouin** ... GHz
  - sound waves
  - *Fabry-Perot*
- **Rayleigh** ... less than MHz
  - thermal diffusion
  - other slow relaxations
  - *Photon Correlation*

Small energy shifts (< MHz) cannot be measured using filter techniques (grating, Fabry-Perot) but are best resolved in the *time domain* ...

\[ S_q(\omega) = \int e^{i\omega t} \langle \delta \rho_q(0) \delta \rho_q(t) \rangle dt \]
Photon Correlation Spectroscopy

- correlate (in time) the intensity of light scattered by the density fluctuations ...

\[
g^{(2)}(t) = \frac{\langle I(0)I(t) \rangle}{\langle I \rangle^2} = 1 + A_{coh}|S(q,t)|^2
\]

instrumental constant (calibrated)

dynamic structure factor

intensity autocorrelation function
The Lab ...
Example: $\text{B}_2\text{O}_3$

\[ f_q \approx 0.76 \]

\[ 1 + A_{coh} \]

\[ \beta \approx 0.65 \]

\[ m \approx 30 \]
Adding alkali ...

- Alters the network structure ... borate example
- diversity of structural units
- initial polymerization of network (tetraborate)
- later depolymerization (NBO)
- borate anomaly ($T_g$ maximum near 25 mol% alkali)

K. H. Mader and T. J. Loretz (1978)
Phosphorus Pentoxide

• Third most significant glass oxide after Si, B
• applications: laser media, seals, bioglass, etc.
• challenge: very hygroscopic and volatile

structural information:
• \( \text{PO}_4 \) tetrahedra in random network
• \( Q^3 \) (one oxygen is non-bridging)
Ultraphosphate Structure

- less diversity than borates
- initial depolymerization of network
- uniform conversion of Q$^3$ to Q$^2$ (network to chains)

![Graph showing fraction Q$^i$ vs. mole fraction R'O]

$Q^3$ tetrahedra

$Q^2$ tetrahedra

$Q^3$ (wet)

$x = 0$

$x = 0.5$

P$_2$O$_5$

network

NaPO$_3$

chains

History

- 1963 Cormia, etal. measure viscosity (1.5 decades) from 545°C to 655°C
- 1986 Martin & Angell measure $C_p$
  - classify as strong based on Cormia’s viscosity
  - but, intermediate based on $\Delta C_p$
- Glass transition temperature - water sensitivity
  - early literature: around 260°C
  - Martin & Angell: around 320°C
  - 1993 Hudgens & Martin: around 380°C
Experimental: P$_2$O$_5$

- P$_2$O$_5$ via Sigma (99.99%)
- handled in glovebag under dry argon
- quartz ampoules cleaned with HF wash
- P$_2$O$_5$ sublimed directly into upper region of ampoule under vacuum, then flamed sealed on each end and handle attached
- P$_2$O$_5$ fused at 900$^\circ$ C
- light scattering conducted at a fixed scattering angle (90$^\circ$) from 850$^\circ$ C to 445$^\circ$ C
Experimental: Ultraphosphates

• only for $0.4 < x \leq 0.5$ compositions
• batch with $\text{Na}_2\text{CO}_3$ and $\text{NH}_4\text{H}_2\text{PO}_4$
• quartz ampoules cleaned with HF wash
• open ampoule, fused at 900° C
• light scattering conducted at a fixed scattering angle (90°) from 600° C to near $T_g$
Ultraphosphates: Fragility

\[ (\text{Na}_2\text{O})_x \text{ (P}_2\text{O}_5)_{1-x} \]

Significant variation in fragility

\[ x = 0 \]
\[ \text{P}_2\text{O}_5 \text{ network} \]

\[ x = 0.5 \]
\[ \text{NaPO}_3 \text{ chains} \]
Ultraphosphates: KWW exponent

\[ S_q(t) = \exp\left\{-(t/\tau)^\beta\right\} \]

Considerable differences in the heterogeneity (KWW) exponent

Typical

Atypical

\( m = 20 \)

\( m = 45 \)

\( m = 57 \)

\( m = 87 \)

\( \log(\tau) \)
Ultraphosphates: Non-ergodic level

Mostly follows previous trend established for variety of liquids:

Strong -- \( f_o \approx 1 \)
Fragile -- \( f_o \approx 0.5 \)

Intuitive interpretation:

Chalcogenides

Selenium forms 2D polymer chains but can be crosslinked using either As or Ge or both to produce a 3D network.

Mixtures of certain metal elements (Se, As, Ge) produce topological changes in network structure like the oxide glasses but without the ionic byproduct.

As the **bond density**, \( <r> \), increases a **rigidity percolation** is said to occur near \( <r> = 2.4 \) at which elastic stiffening first appears.
Ultraphosphates vs. Chalcogenides

Ultraphosphates display virtually identical variation of fragility as chalcogenides when represented in terms of the bond density!

R. Boehmer and C. A. Angell, PRB 45 (1992)
Summary

• Ultraphosphates demonstrate the influence of network structure on liquid dynamics

• Decreasing bond density:
  • increases the fragility (just like chalcogenides)
  • decreases the KWW exponent
  • increases the cage effect ($\beta$ relaxation)

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