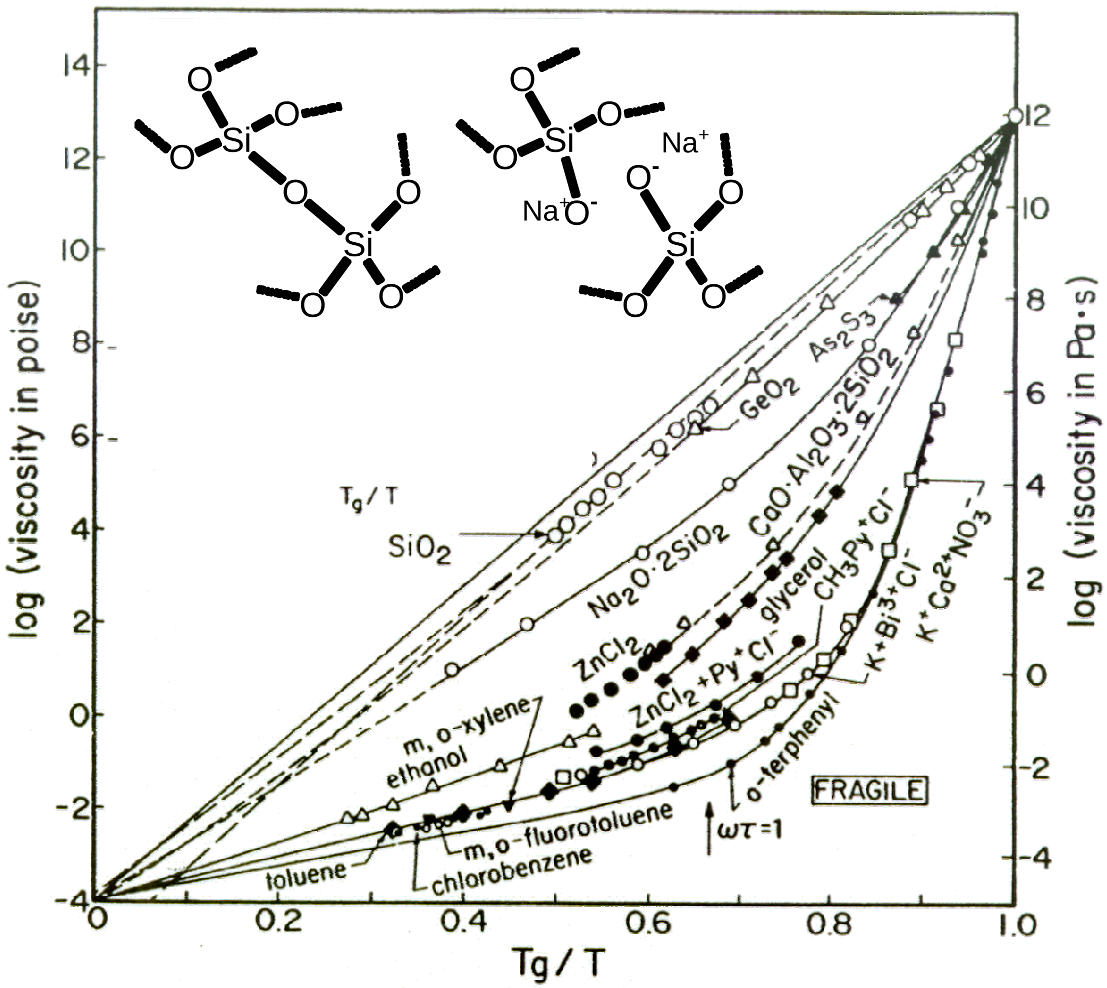
Dynamic Light Scattering in Glassforming Ultraphosphate Liquids

R. Fabian, J. Changstrom,
D. Sidebottom*
Creighton University

Creighton
UNIVERSITY

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*?



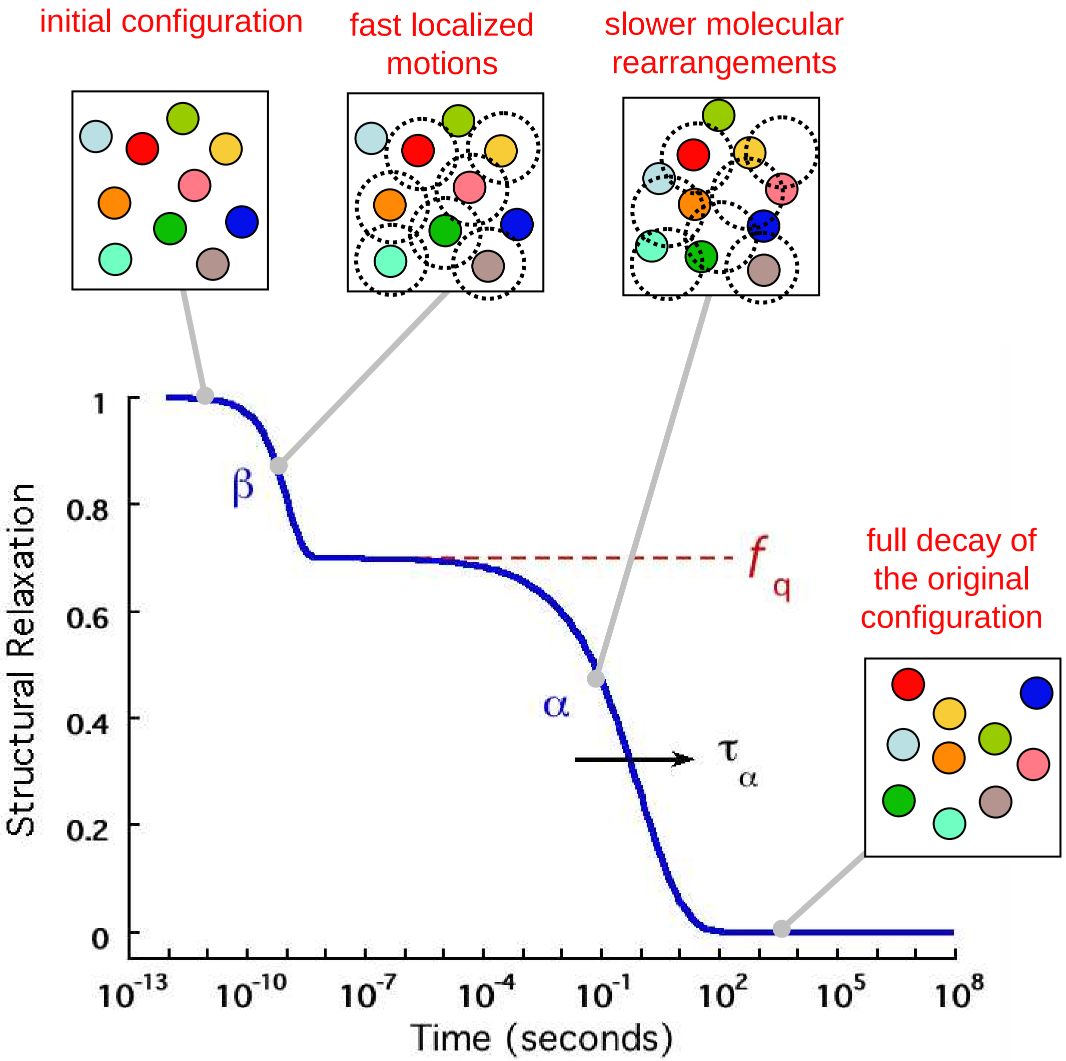
Structural Relaxation in Liquids

Two step decay:

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

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

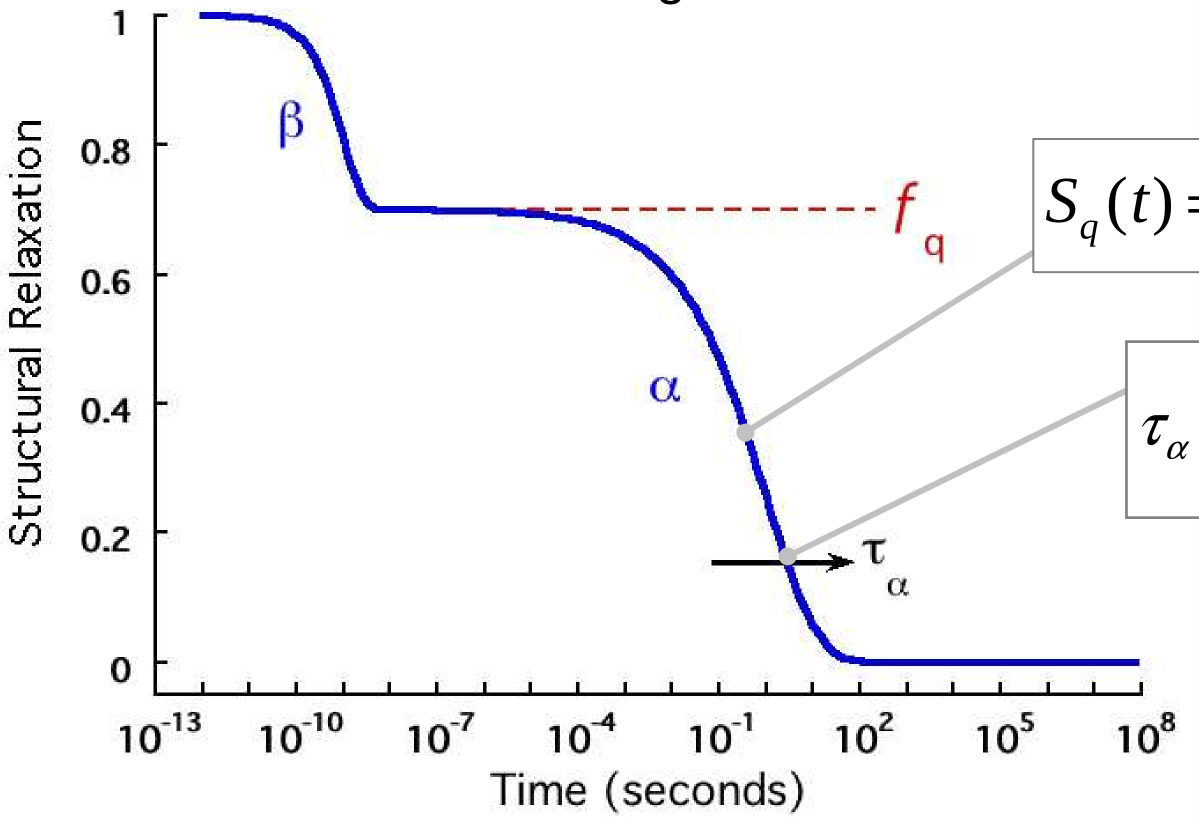
– ***nonergodic level***
  - plateau, f_q



Creighton University

Viscoelastic (α) Relaxation

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



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

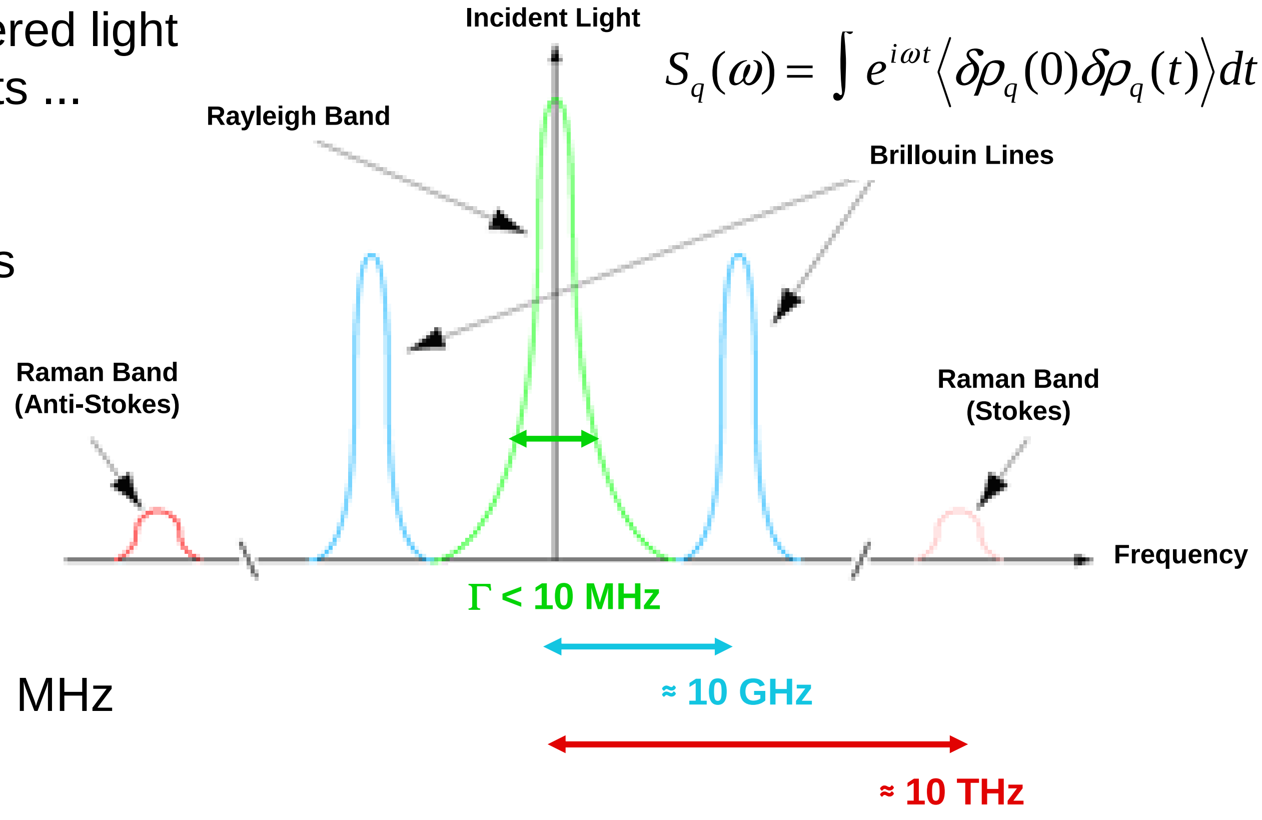
$$\tau_\alpha = \tau_o \exp\left\{\frac{DT_o}{T - T_o}\right\}$$

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*

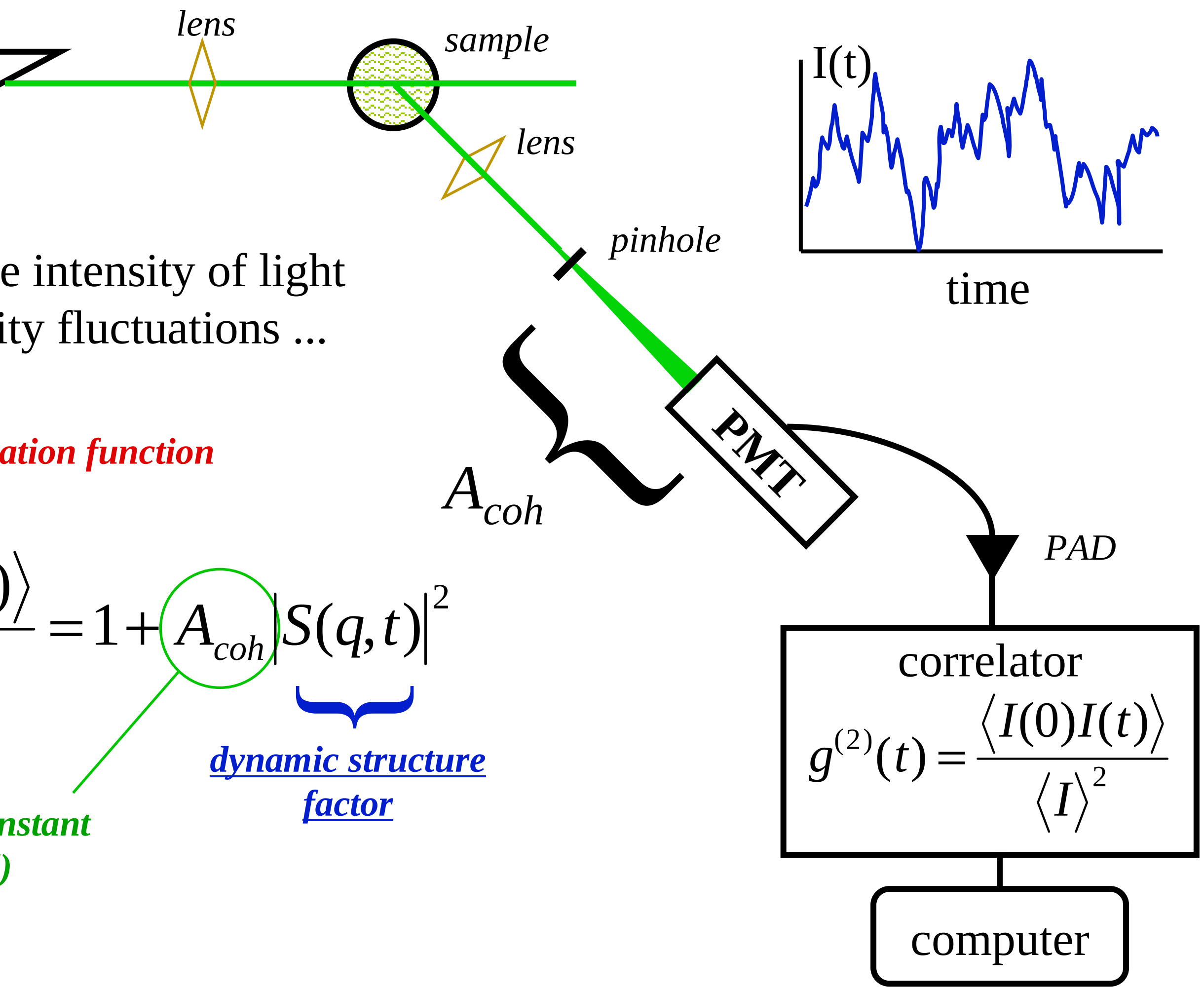
$$S_q(\omega) = \int e^{i\omega t} \left\langle \delta\rho_q(0)\delta\rho_q(t) \right\rangle dt$$



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

Creighton University

Photon Correlation Spectroscopy



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

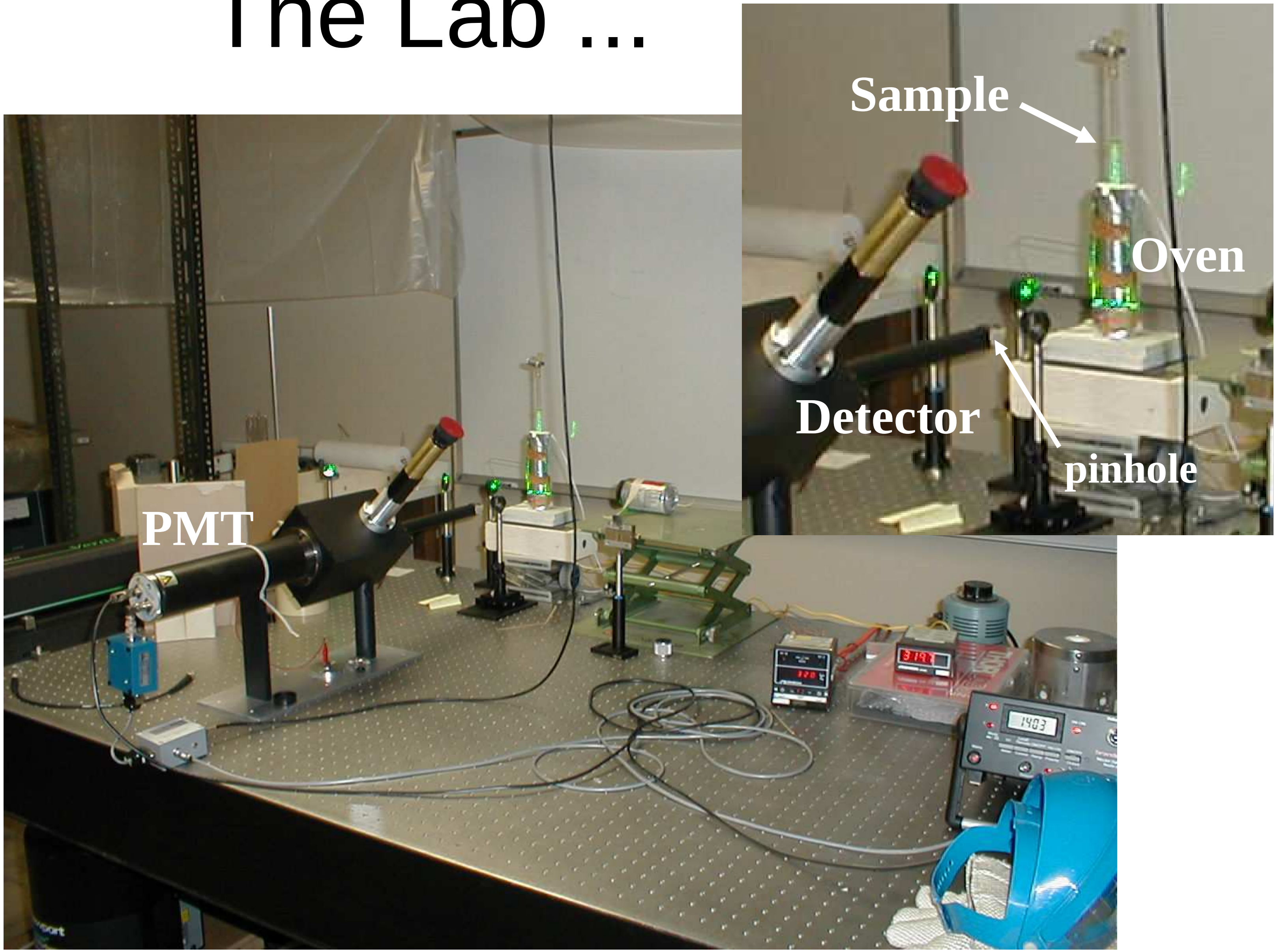
intensity autocorrelation function

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

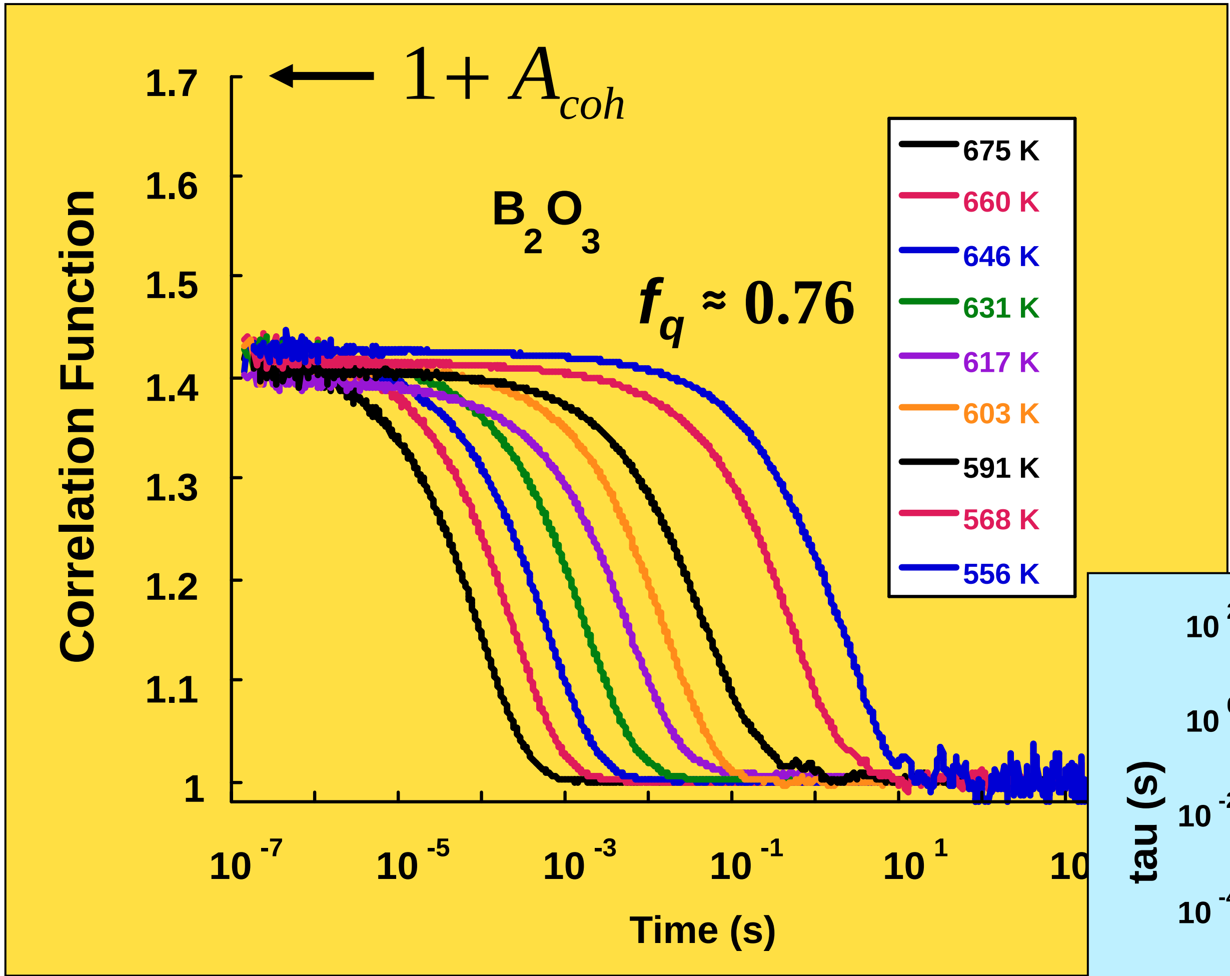
dynamic structure factor

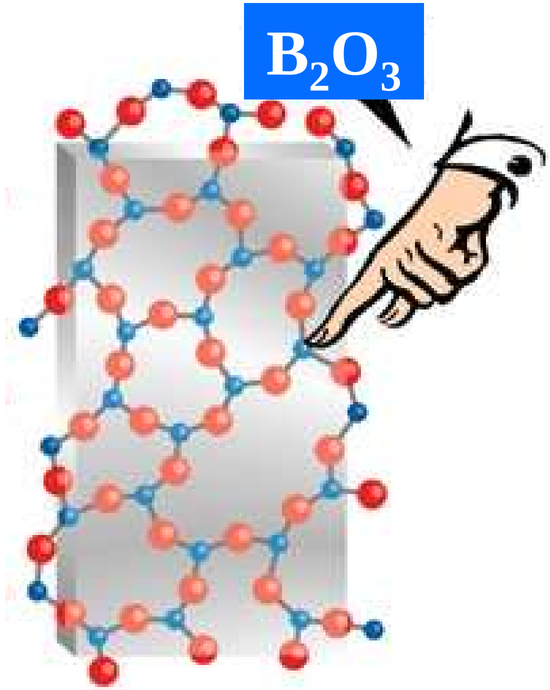
instrumental constant (calibrated)

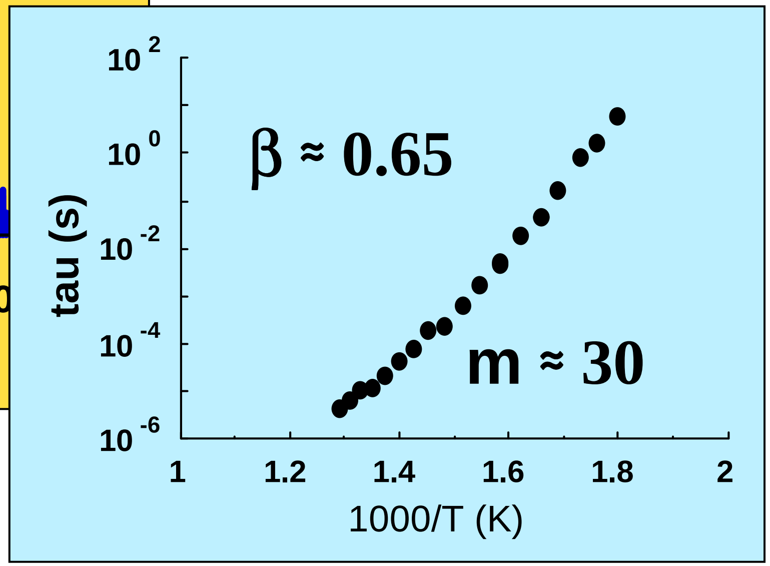
The Lab ...



Example: B_2O_3



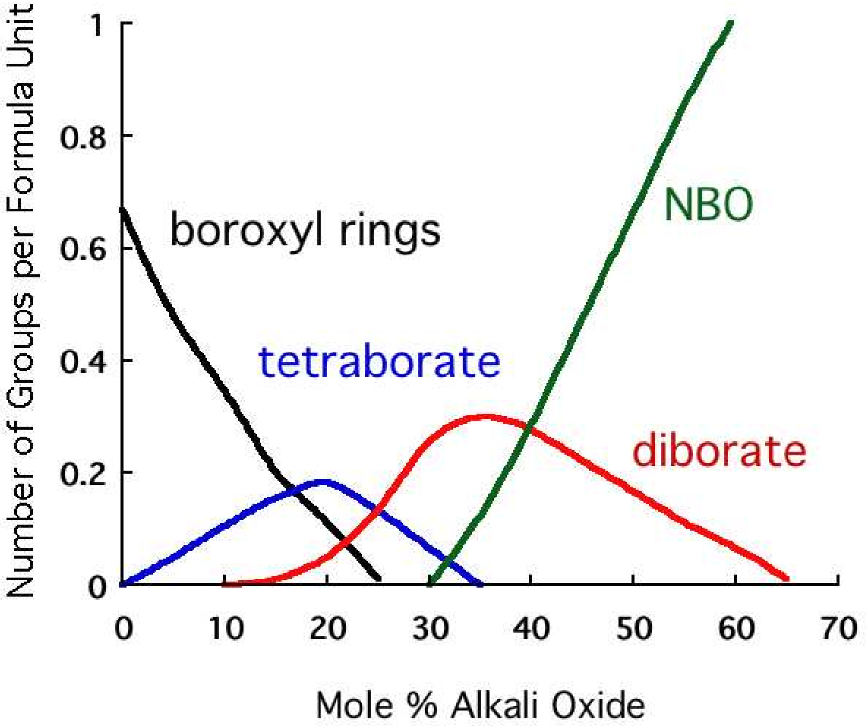




Creighton
UNIVERSITY

Adding alkali ...

- Alters the network structure ... borate example



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

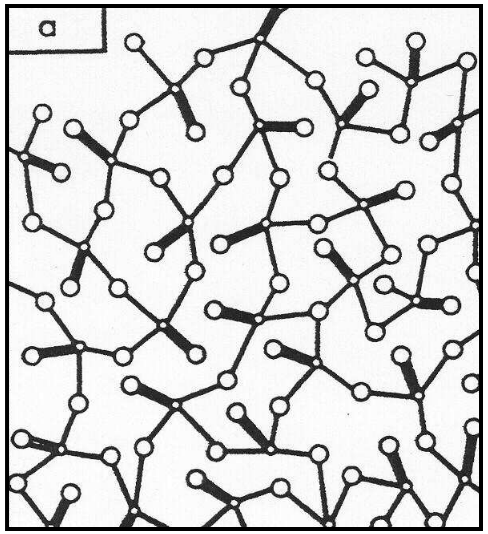
- diversity of structural units
- initial *polymerization* of network (tetraborate)
- later *depolymerization* (NBO)
- *borate anomaly* (T_g maximum near 25 mol% alkali)

Phosphorus Pentoxide

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

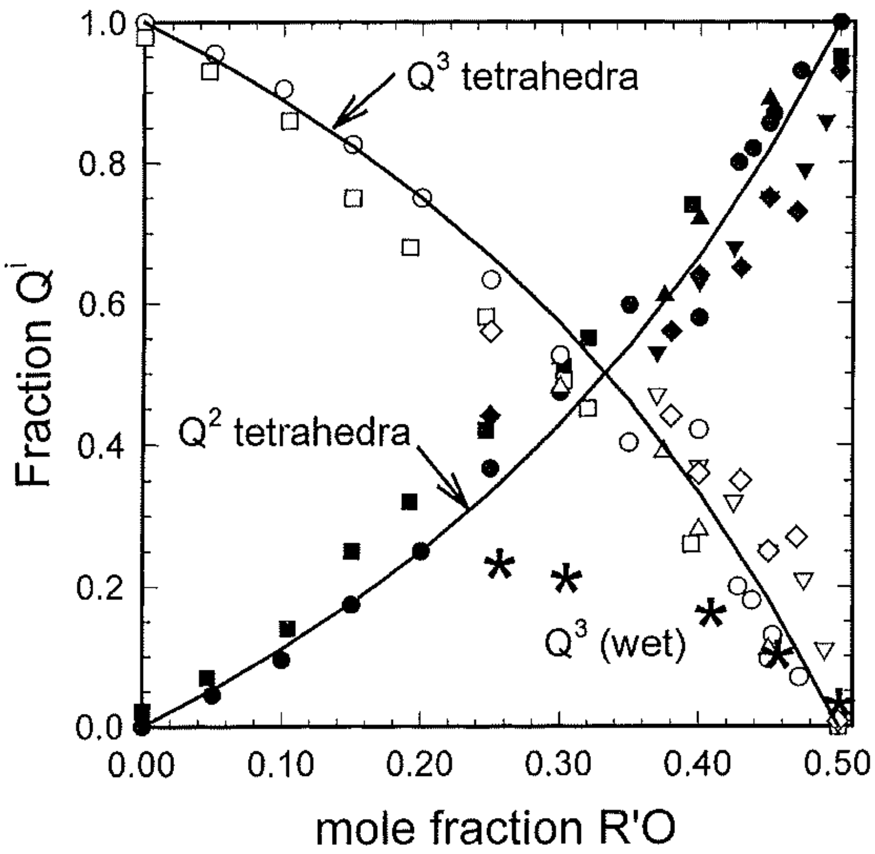
structural information:

- PO_4 tetrahedra in random network
- Q^3 (one oxygen is non-bridging)



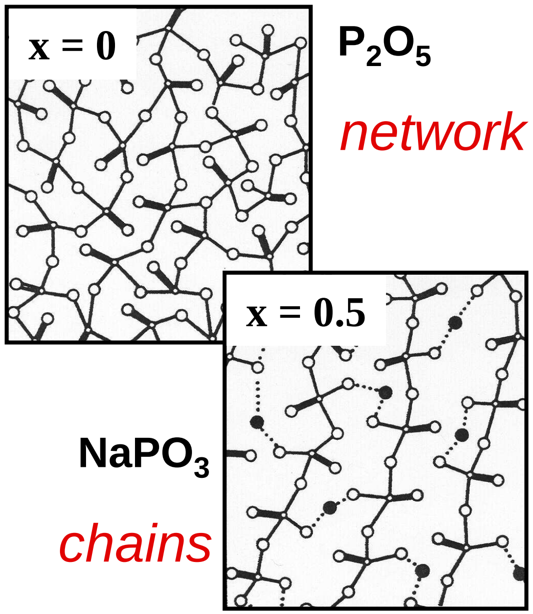
Creighton UNIVERSITY

Ultraphosphate Structure



*R. K. Brow, JNCS **263&264** (2000)*

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



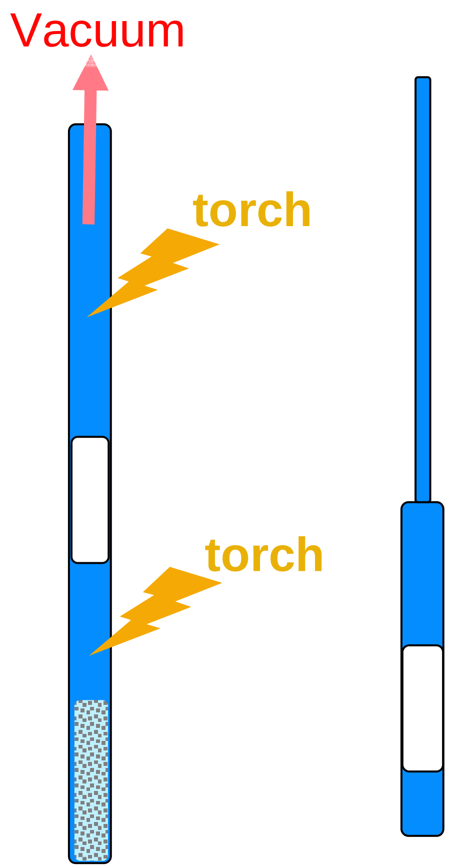
History

- 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 ΔC_p
- Glass transition temperature - water sensitivity
  - early literature: around 260° C
  - Martin & Angell: around 320° C
  - 1993 Hudgens & Martin: around 380° C

Creighton UNIVERSITY

Experimental: P_2O_5

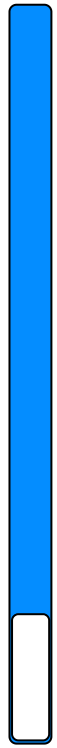
- P_2O_5 via Sigma (99.99%)
- handled in glovebag under dry argon
- quartz ampoules cleaned with HF wash
- P_2O_5 sublimed directly into upper region of ampoule under vacuum, then flamed sealed on each end and handle attached
- P_2O_5 fused at 900° C
- light scattering conducted at a fixed scattering angle (90°) from 850° C to 445° C



Creighton University

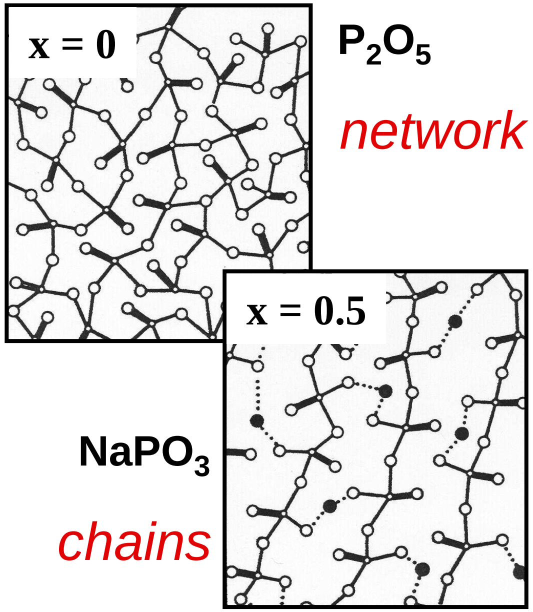
Experimental: Ultraphosphates

- only for $0.4 < x \leq 0.5$ compositions
- batch with Na_2CO_3 and $NH_4H_2PO_4$
- 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



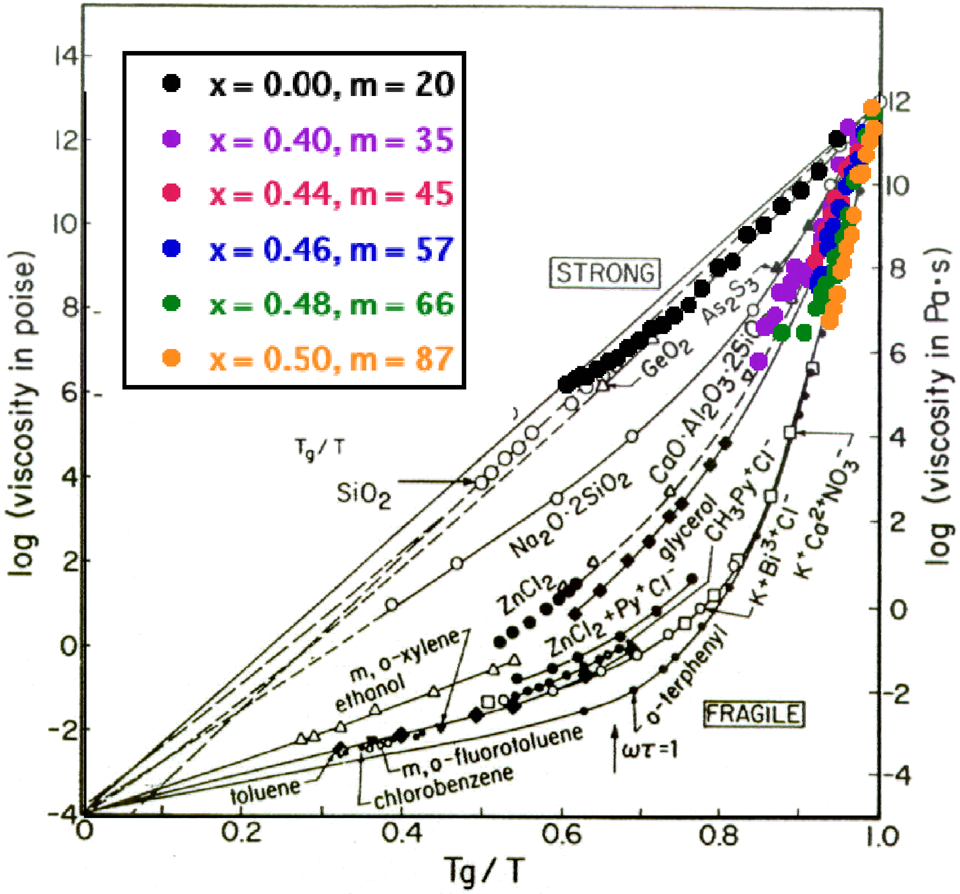
Creighton
UNIVERSITY

Ultraphosphates: Fragility



$(Na_2O)_x\ (P_2O_5)_{1-x}$

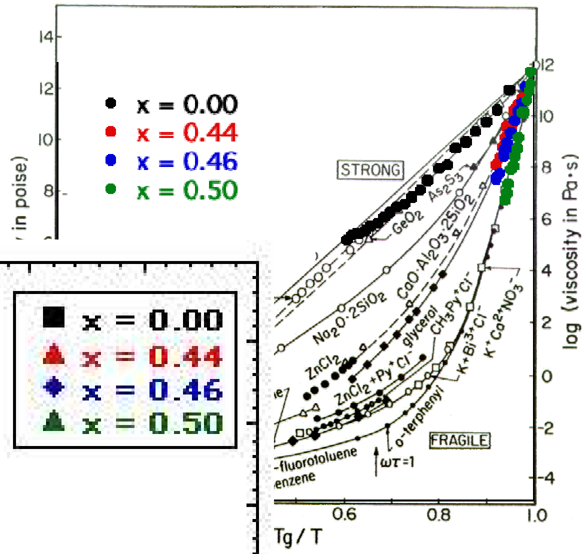
Significant variation in fragility

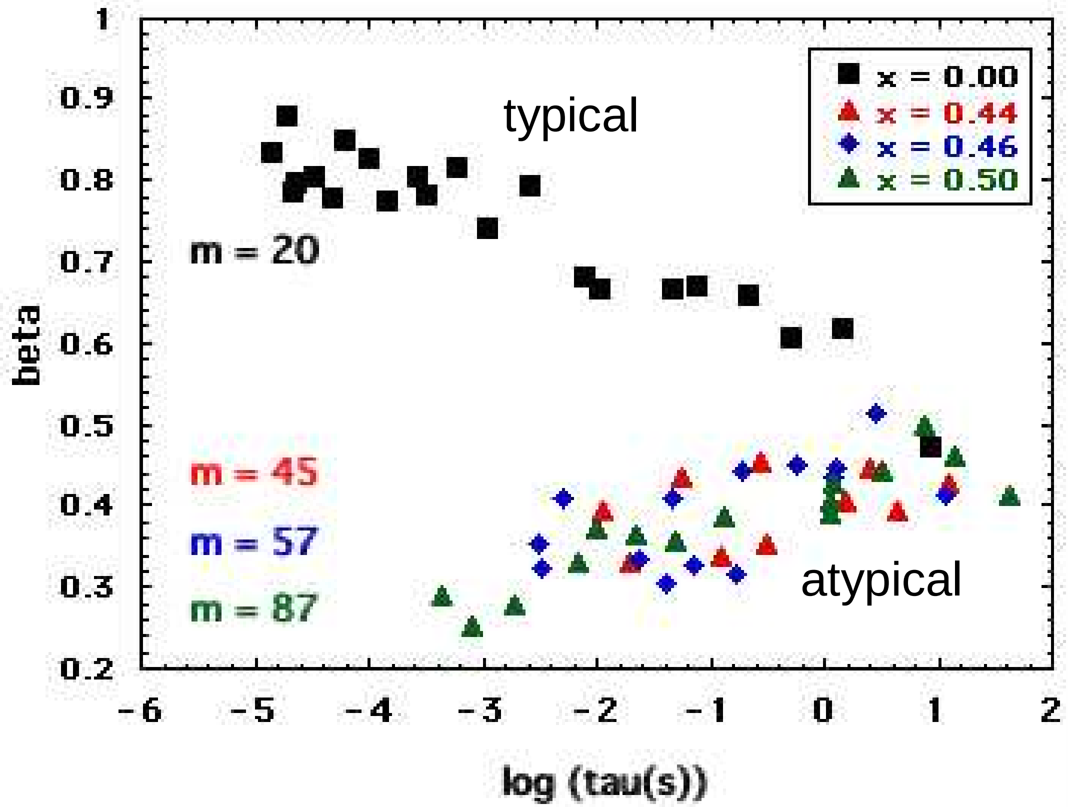


Creighton UNIVERSITY

Ultraphosphates: KWW exponent

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

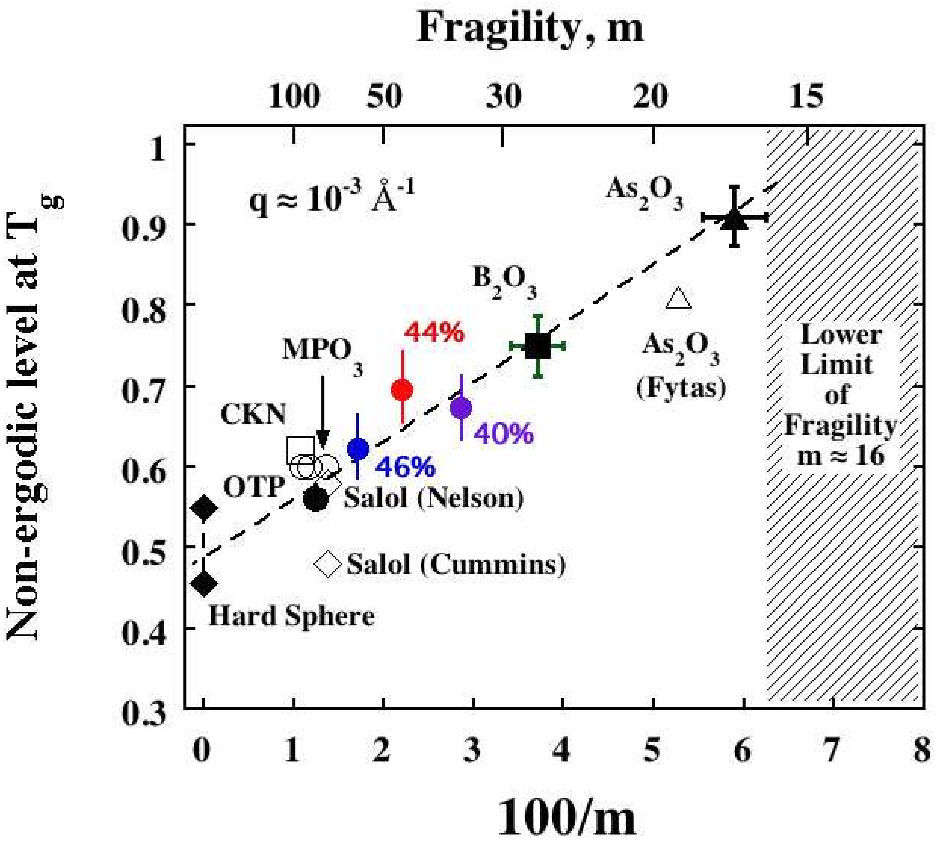




Considerable differences in the heterogeneity (KWW) exponent

Creighton UNIVERSITY

Ultraphosphates: Non-ergodic level



*D. L. Sidebottom etal, PRB **75** (2007)*

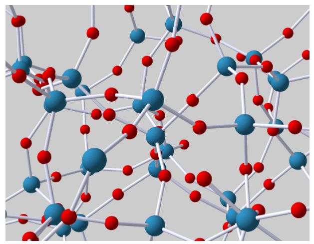
Mostly follows previous trend established for variety of liquids:

Strong -- $f_o \approx 1$

Fragile -- $f_o \approx 0.5$

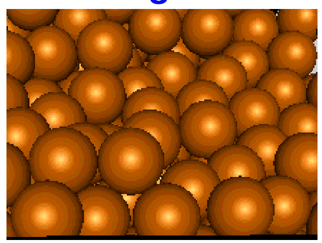
Intuitive interpretation:

Strong



discrete bonding limits 'cage rattle'

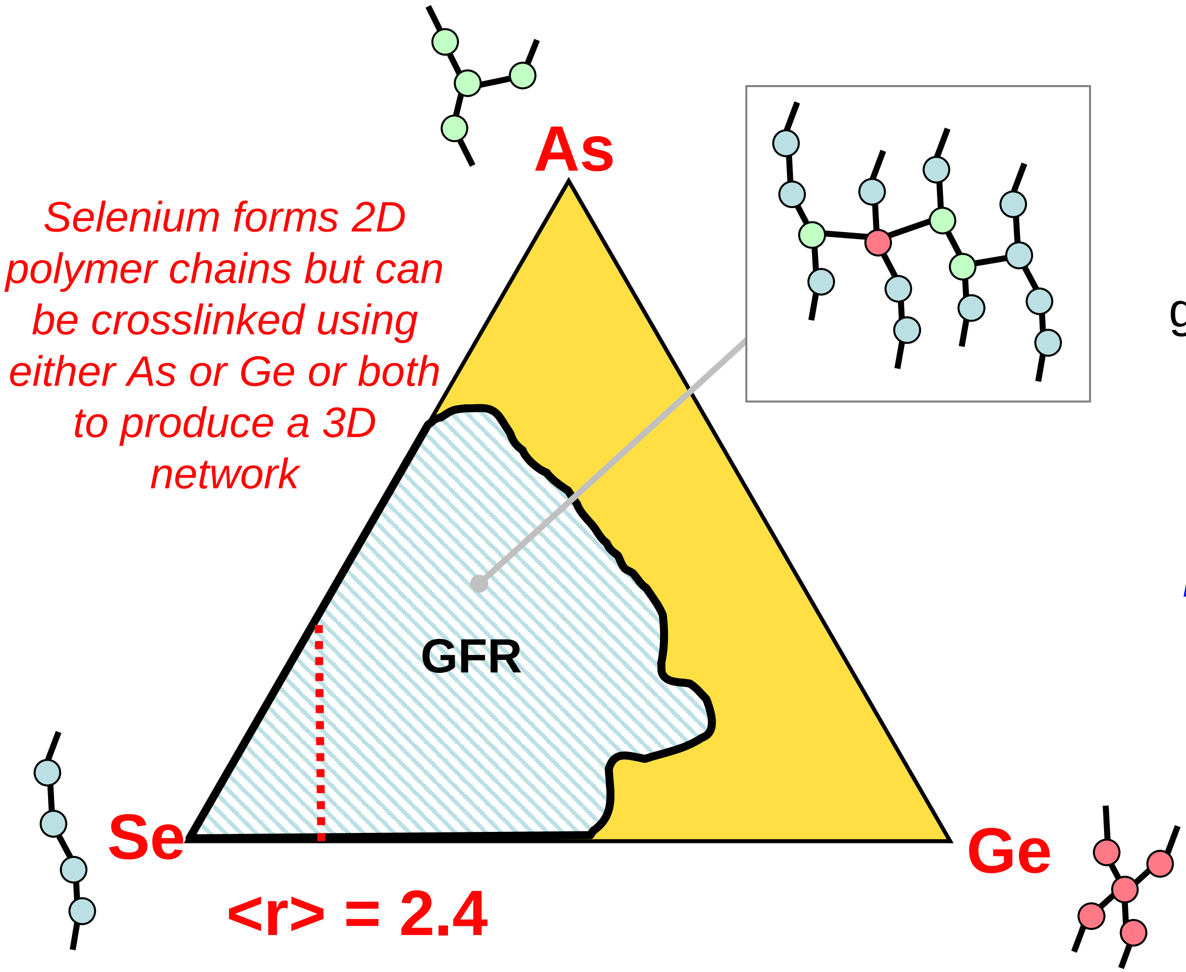
Fragile



continuous bonding promotes 'cage rattle'

Creighton UNIVERSITY

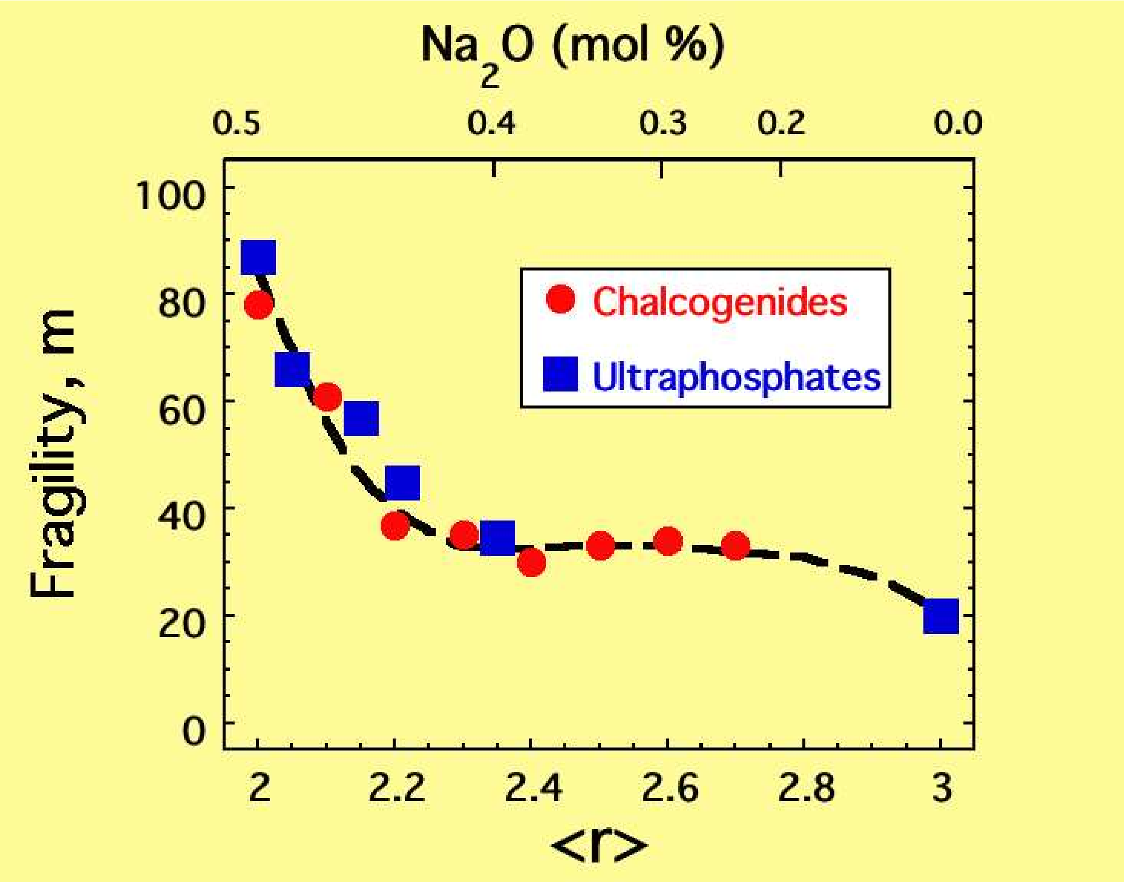
Chalcogenides



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)*

Creighton UNIVERSITY

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 (β relaxation)

Thanks to funding by the Petroleum Research Fund (#43743-GB10) and by Research Corporation (#CC6641)

and to Dr. S. W. Martin for his help

Creighton UNIVERSITY