EXAFS-SAXS-WAXS

G.N. Greaves
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Aberystwyth University,
Aberystwyth SY23 3BZ, UK

GN Greaves and S Sen,
Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids,
Advances in Physics, 2007, 56, 1-166

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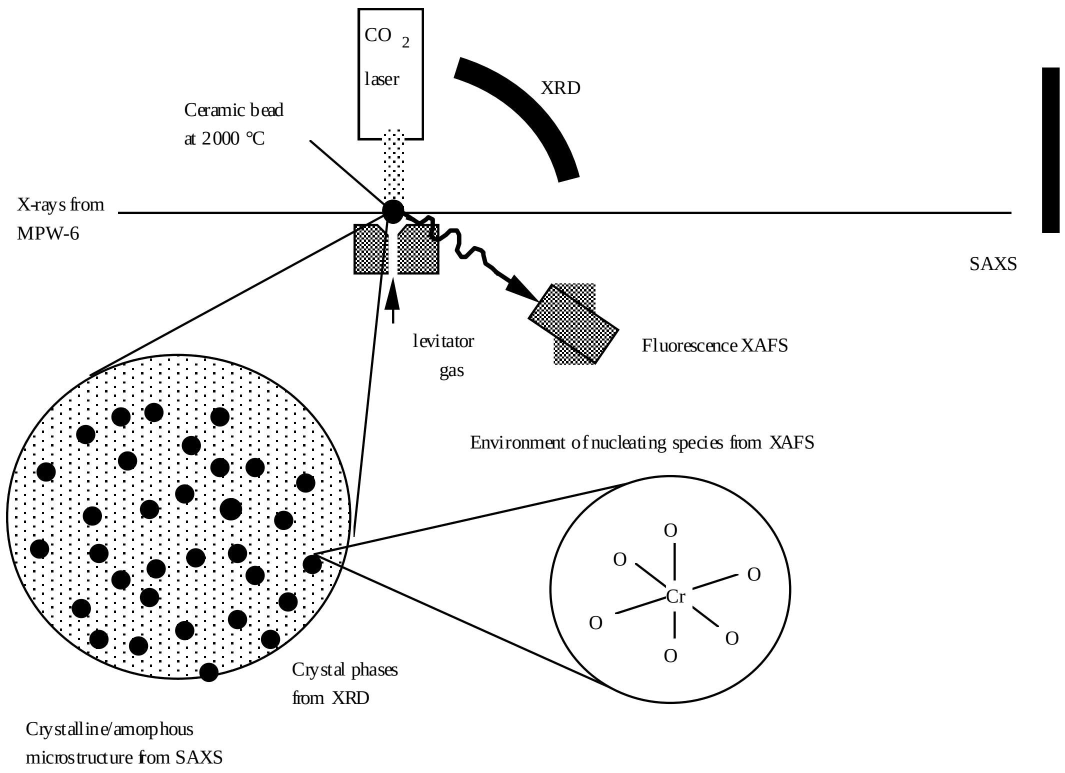
- Combining x-ray techniques
- EXAFS – modifier channels and MRN
- SAXS – IRO and diffusion
- WAXS – amorphisation
- EXAFS-SAXS-WAXS–formation of glass ceramics

Combining x-ray techniques

SAXS/WAXS
Bras W, Derbyshire G E, Ryan AJ, Mant G R, Felton A, Lewis R A, Hall C J and Greaves G N
Nucl. Instr. and Methods. A326, 587-591 (1993)

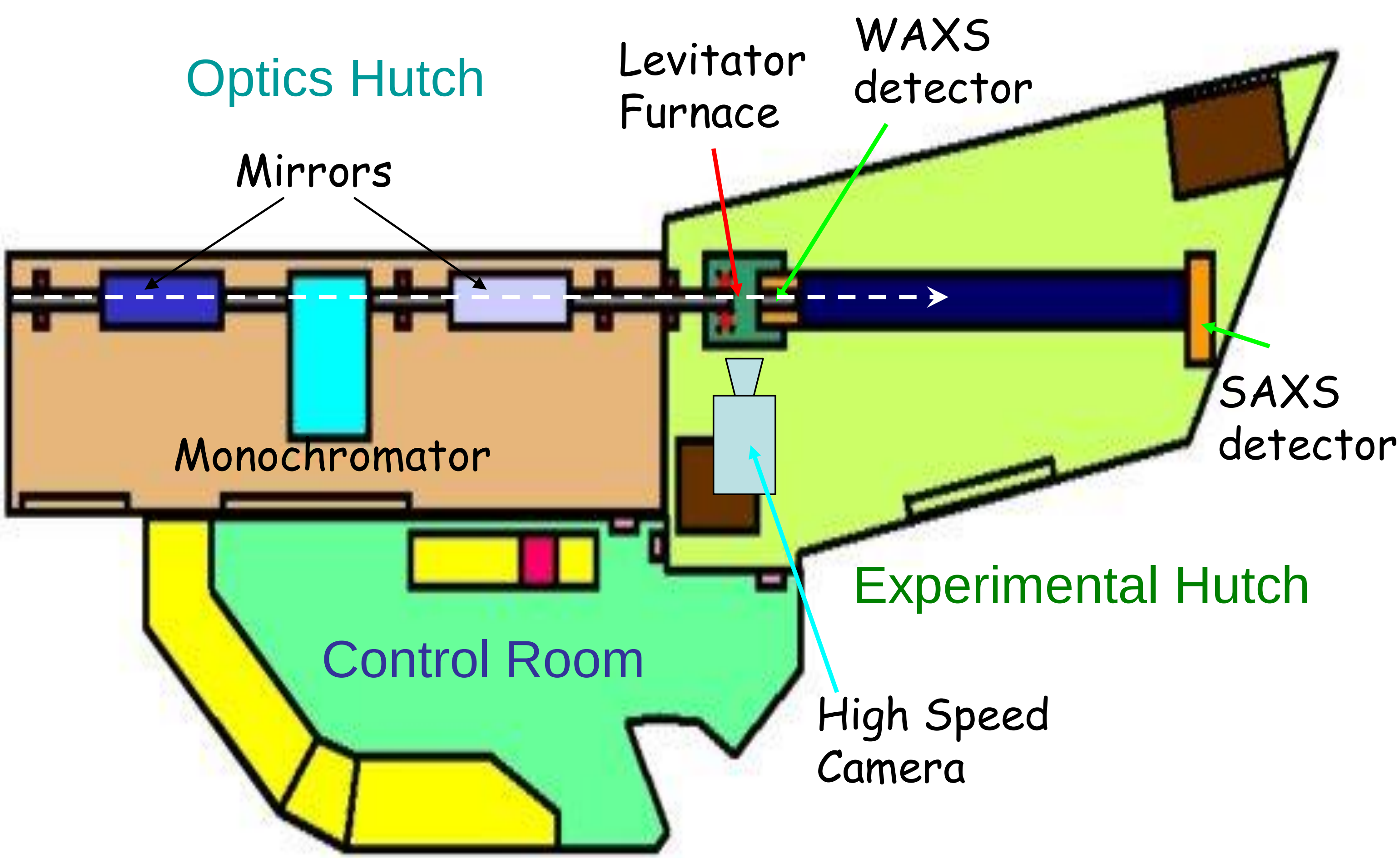
EXAFS/WAXS
Sankar G, Wright P A, Srinivasa N, Thomas J M, Greaves G N, Dent A J, Dobson B R, Ramsdale C A and Jones R H,
J. Phys. Chem. 97, 9550-9554 (1993)

combined x-ray techniques



Beamline 6.2 at Synchrotron Radiation Source

now moving to I22 at Diaampond Light Source



SAXS/WAXS

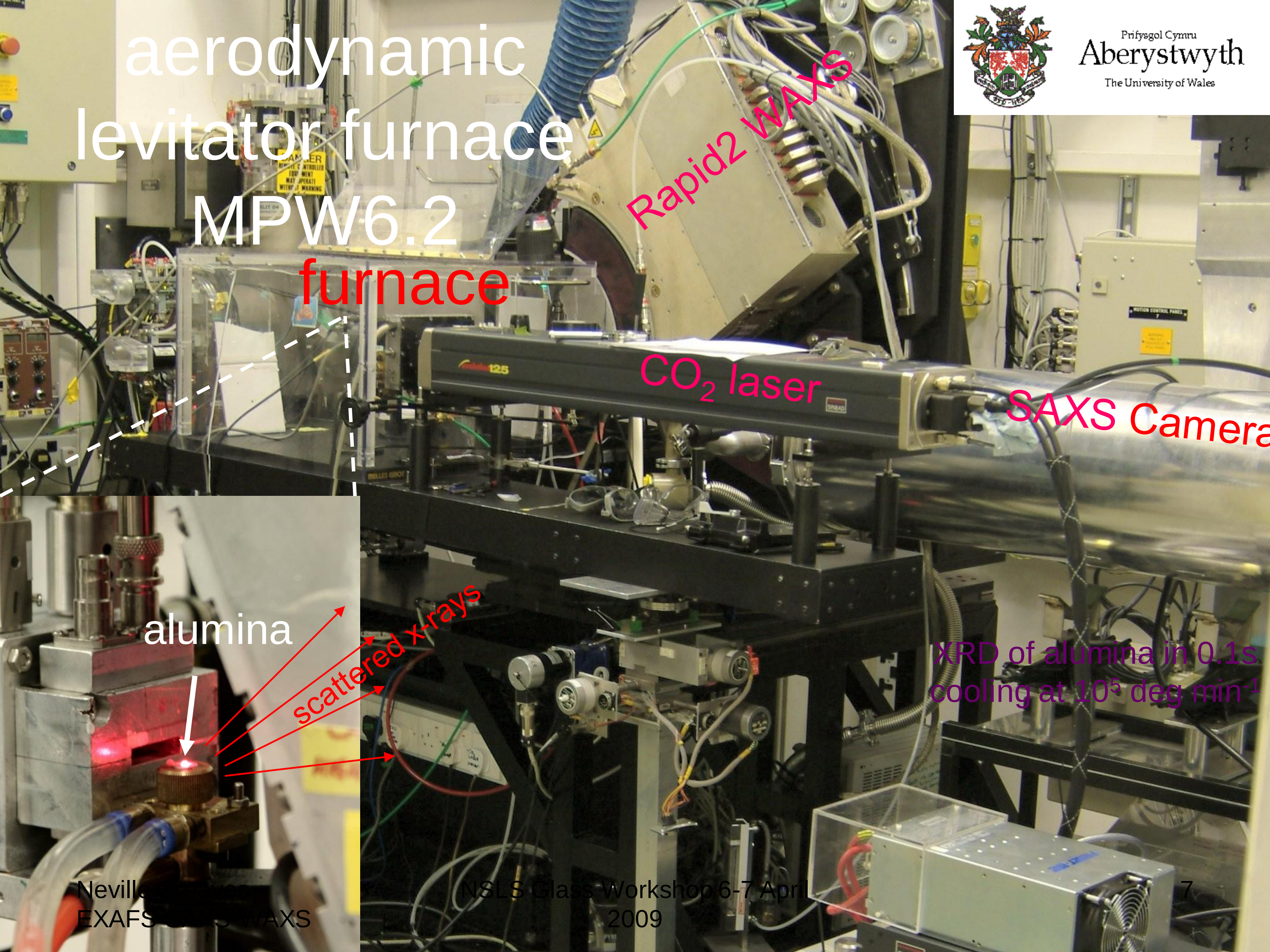
Combined small angle scattering and XRD

SRS 6.2, ESRF DUBBLE, I22 Diamond Light Source

W. Bras, G.E. Derbyshire, A.J. Ryan, G.R. Mant, A. Felton, R.A. Lewis, C.J. Hall and G.N. Greaves, *Nucl. Instr. and Methods.* 1993, **A326**, 587

W Bras, IP Dolbnya, D Detollenaere, R van Tol, M Malfois, GN Greaves, AJ Ryan and E Heeley J Appl. Cryst. **36**, 791-794 (2003)

aerodynamic levitator furnace MPW6.2



EXAFS

Modifier channels and MRN

The Local Structure of Silicate Glasses
Greaves G N, Fontaine A, Lagarde P, Raoux D and Gurman S J
Nature, <u>293</u>, p611-616 (1981)

Cation Microsegregation and Ionic Mobility in Mixed Alkali Glasses
Vessal B, Greaves G N, Marten P T, Chadwick A V, Mole R, Houde-Walter S
Nature <u>356</u>, 504-507 (1992)

EXAFS - basics

Element specific:

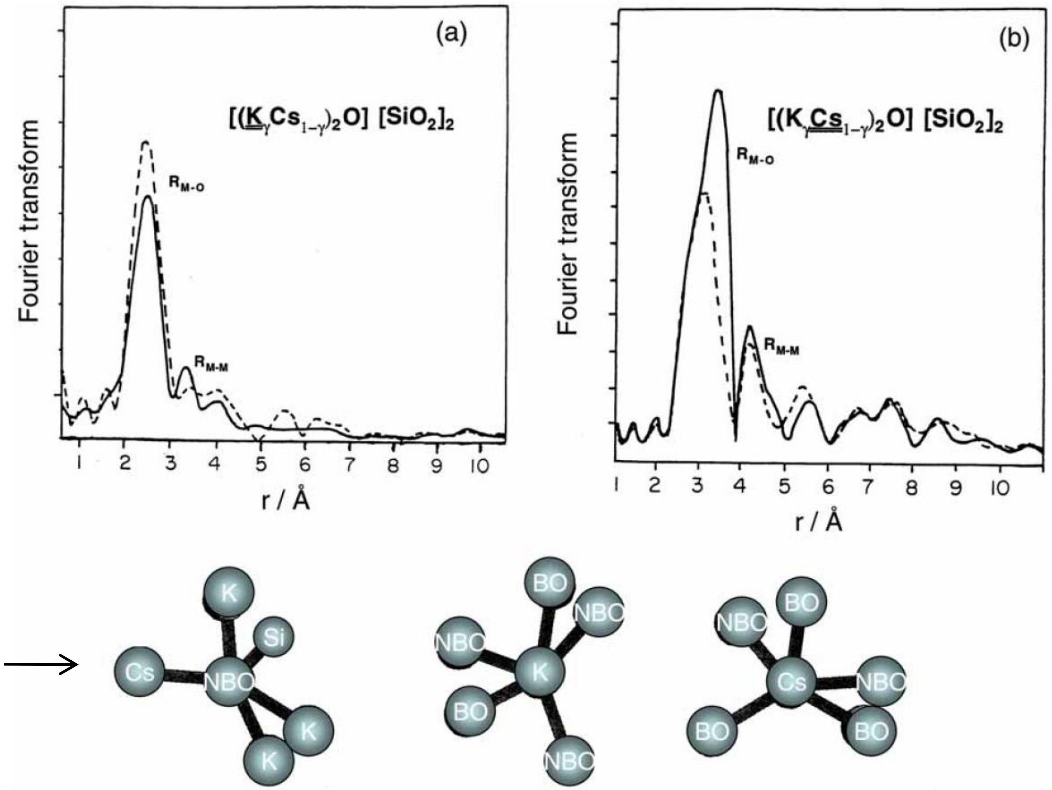
Coordination Number, N   Inter-atomic Distance, R   Debye-Waller Factor , σ

$$\chi(Q) = \sum_{\beta} \frac{-A(Q)}{Q} \frac{N}{R_{\beta}^{2}} \left| f_{\beta}(Q,\pi) \right| \exp\left(\frac{-2R_{\beta}}{\lambda} \right) \exp\left(-2\sigma^{2}Q^{2}\right) \sin\left(2QR_{\beta} + 2\delta + \phi\right)$$

N and R

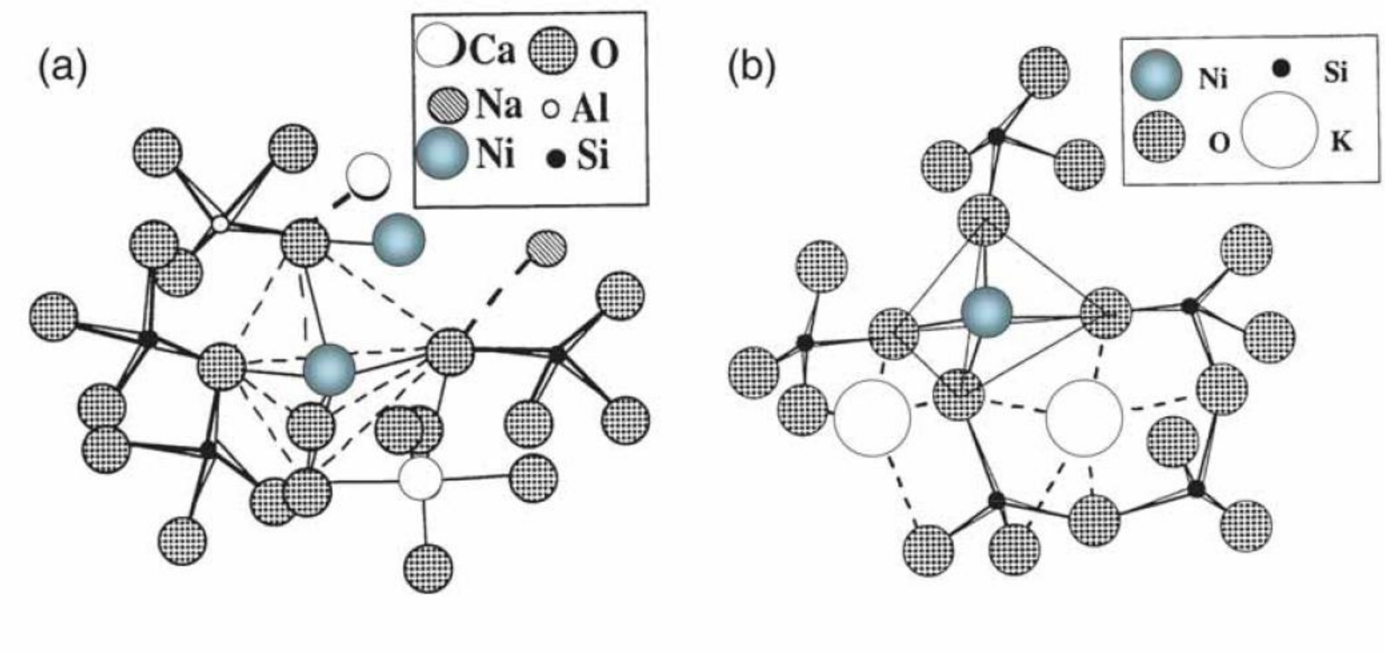
Modifiers adopt well-defined sites in oxide glass networks

modifier polyhedra →



A Structural Basis for Ionic Diffusion in Oxide Glasses
Greaves G N, Gurman S J, Catlow C R A, Chadwick A V, Houde-Walter S, Dobson B R and Henderson C M B
Phil. Mag. A65, 1059-1072 (1991)

N and R
Environments of intermediates in silicates



L. Galoisy and G. Calas, Geochimica et Cosmochimica **57** 3613 (1993); ibid **57** 3627.

modified random network

Molecular Dynamics

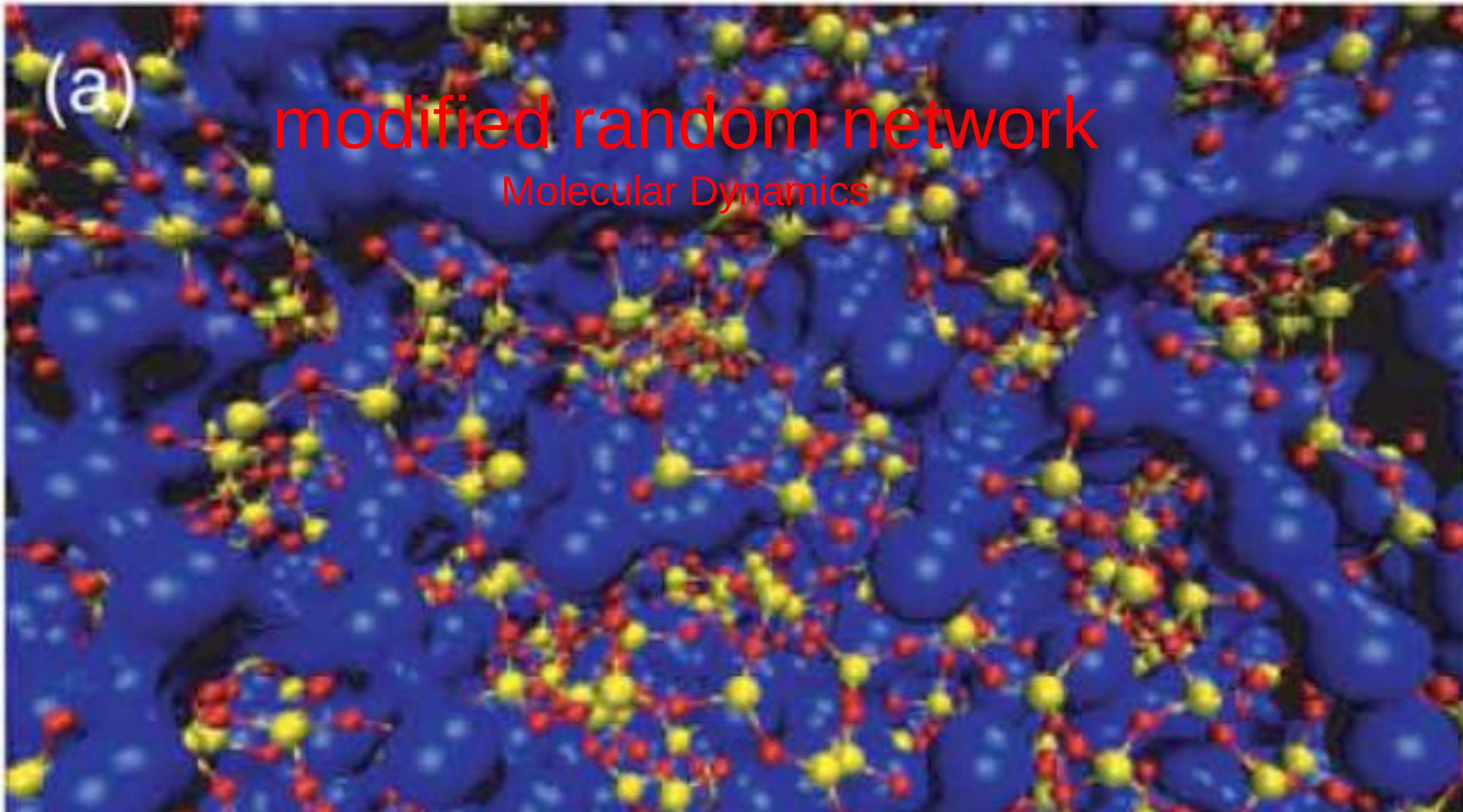
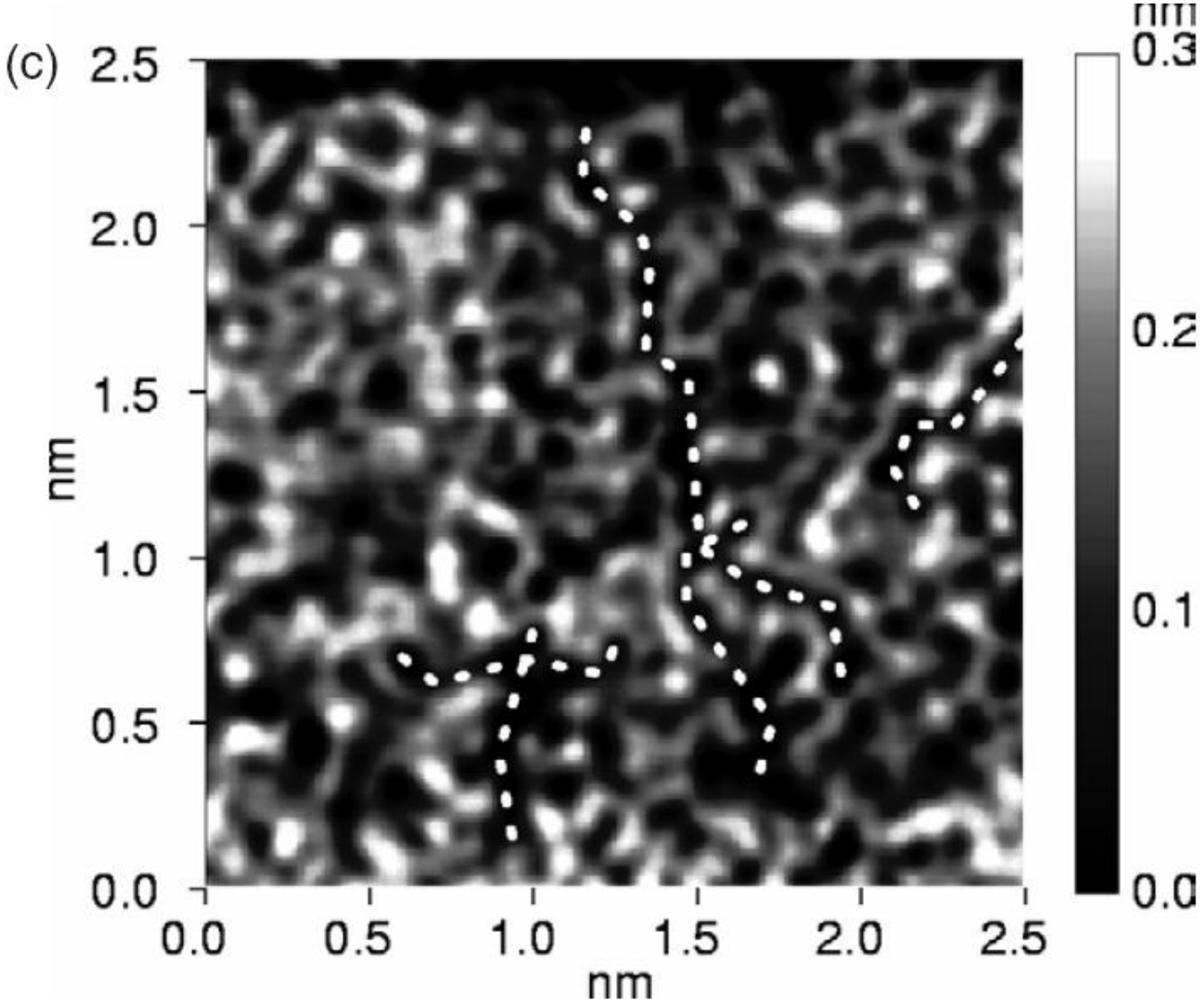


Figure 19. Static alkali channels modelled with molecular dynamics in alkali silicate glasses. (a) ‘Snapshot’ of the structure of the $Na_2Si_3O_7$ glass silicate with the Na atoms (blue) emphasized with an enlarged equipotential isosurface. Reproduced with permission from Meyer *et al*.

Meyer, J. Horbach, W. Kob, F. Kargl and H. Schobler, Phys. Rev. Lett. **93** 027801,1–4 (2004).

AFM

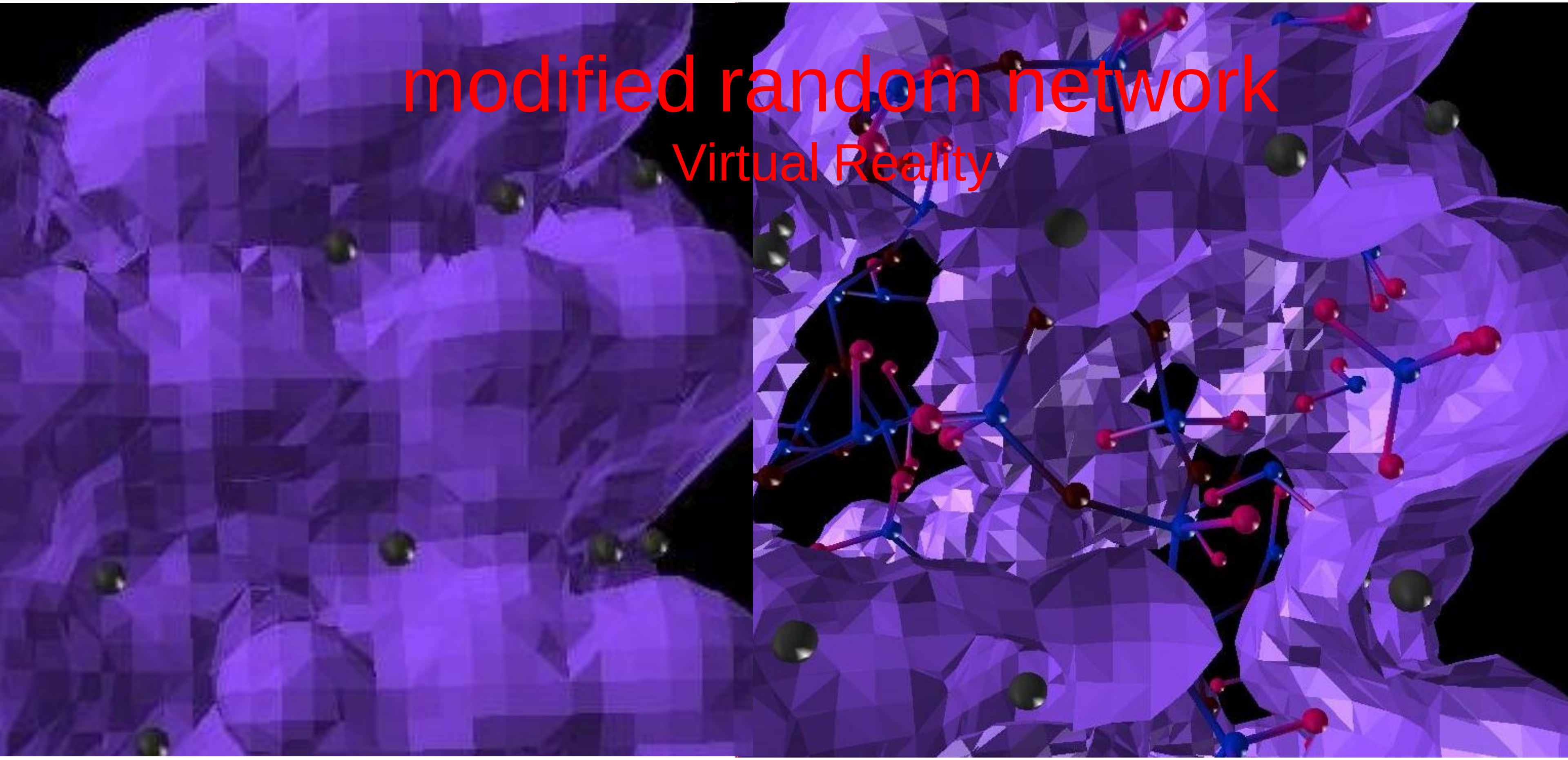
modified random network



G.H. Frischat, J.-F. Poggemann and E. Heide, J. Non-Cryst. Solids **345–346** 197 (2004).

modified random network

Virtual Reality



network isosurface and cutaway for $Na_2Si_2O_5$

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SAXS

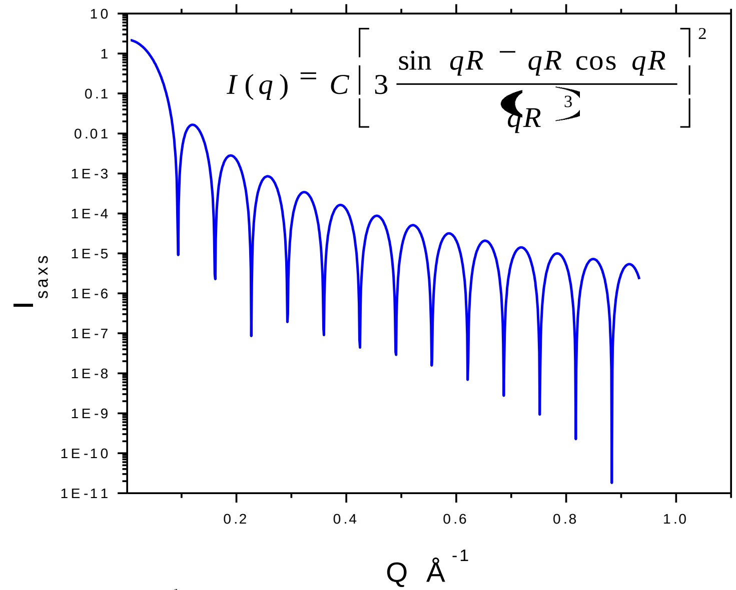
Intermdiate range order and diffusion
Long Range order and LL Transitions

Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids,
GN Greaves and S Sen,
***Advances in Physics*, 2007, 56, 1-166**

G.N. Greaves, M.C. Wilding, S. Fearn, D. Langstaff, F. Kargl, S. Cox, Q. Vu Van, O. Majérus, C.J. Benmore, R. Weber, C.M. Martin, L. Hennet ***Science* 2008, 322, 566-570.**

SAXS - basics

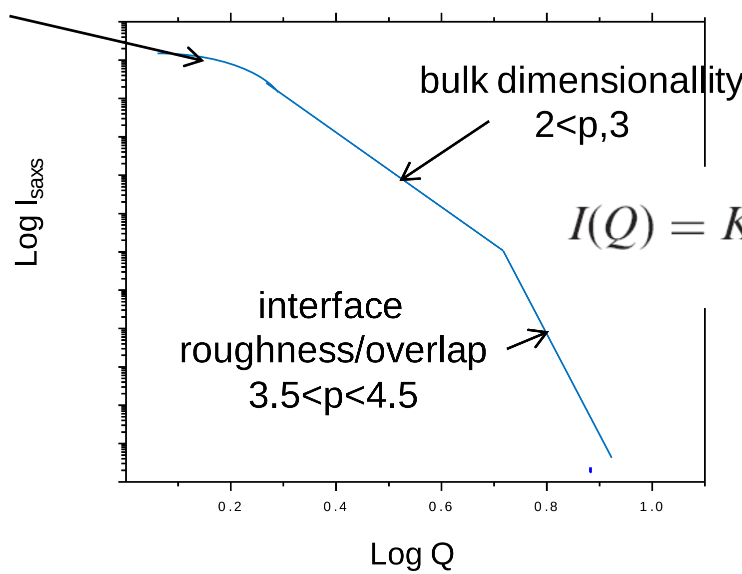
monodispersed particles



Guinier

$$I(Q) = I(0)e^{-R_{R_g}^2 Q^2/3}$$

fractal structures



Porod

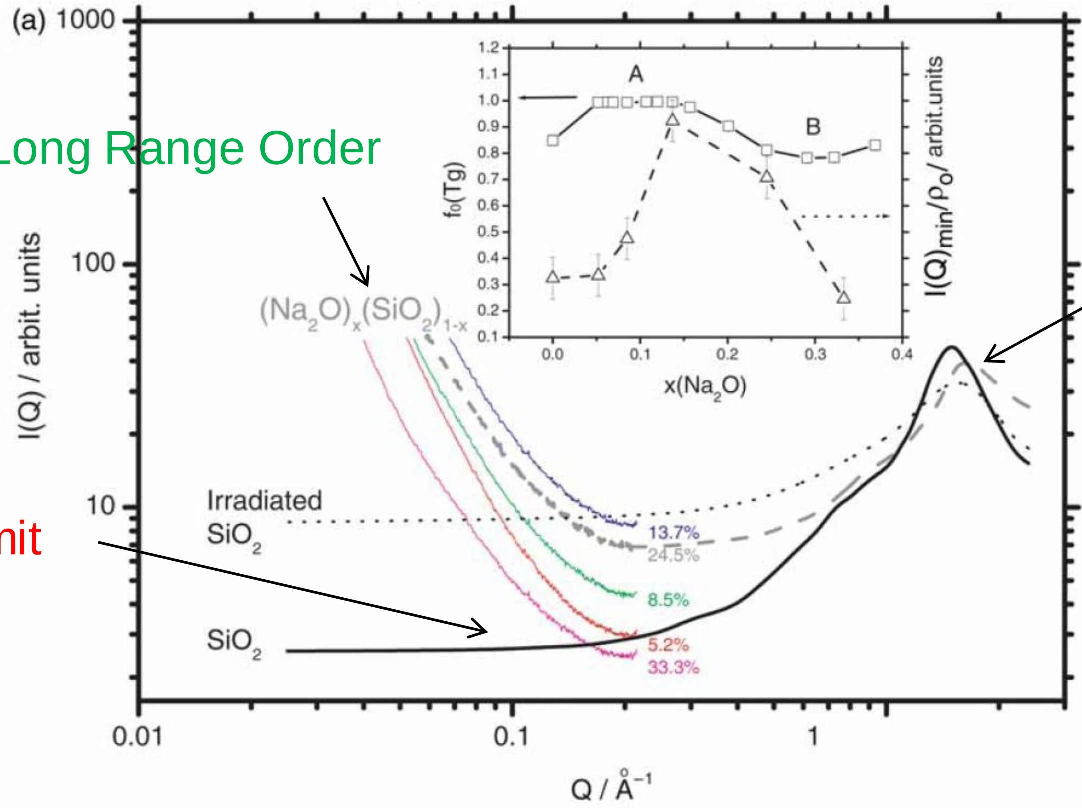
$$I(Q) = K_1 + \frac{K_2}{Q^p} \quad Q > \frac{1}{R_g}$$

SAXS and the Structure Factor, S(Q)

Long Range Order

First Sharp Diffraction Peak FSDP

Thermal Limit



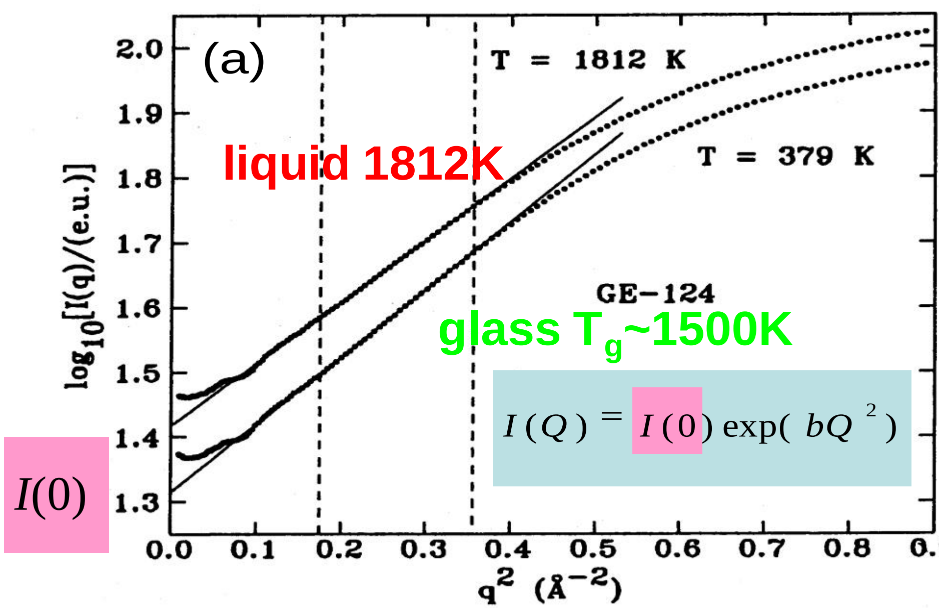
$$V < \Delta\rho^2 > / \rho_0^2 = S(0)/\rho_0 = I(0)/(\rho_0 \sum_{\alpha}^{N} W_{\alpha\beta\ldots}^2) = k_B T K_T$$

density fluctuations & compressibility

SAXS from **liquid** and **glassy** SiO_2

Q independent

$$V < \Delta\rho^2 > / \rho_0^2 = S(0)/\rho_0 = I(0)/(\rho_0 \sum_{\alpha}^{N} W_{\alpha\beta\ldots}^2) = k_B T K_T$$



K_T, compressibility

R. Bruning, C. Levelut, A. Faivre, R. LeParc, J.-P. Simon, F. Bley, and J.-L. Hazemann: Europhys. Lett. Vol. 70, (2005), p.211.

V.V. Golubkov, J. Non-Cryst. Solids **192–193** 463 (1995).

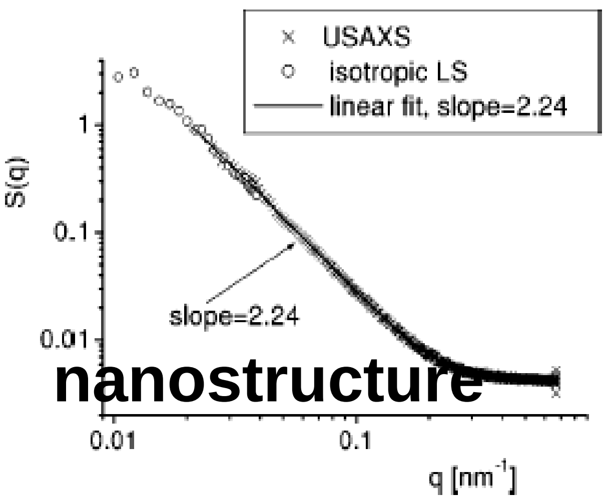
nanostructure & long range fluctuations in OTP

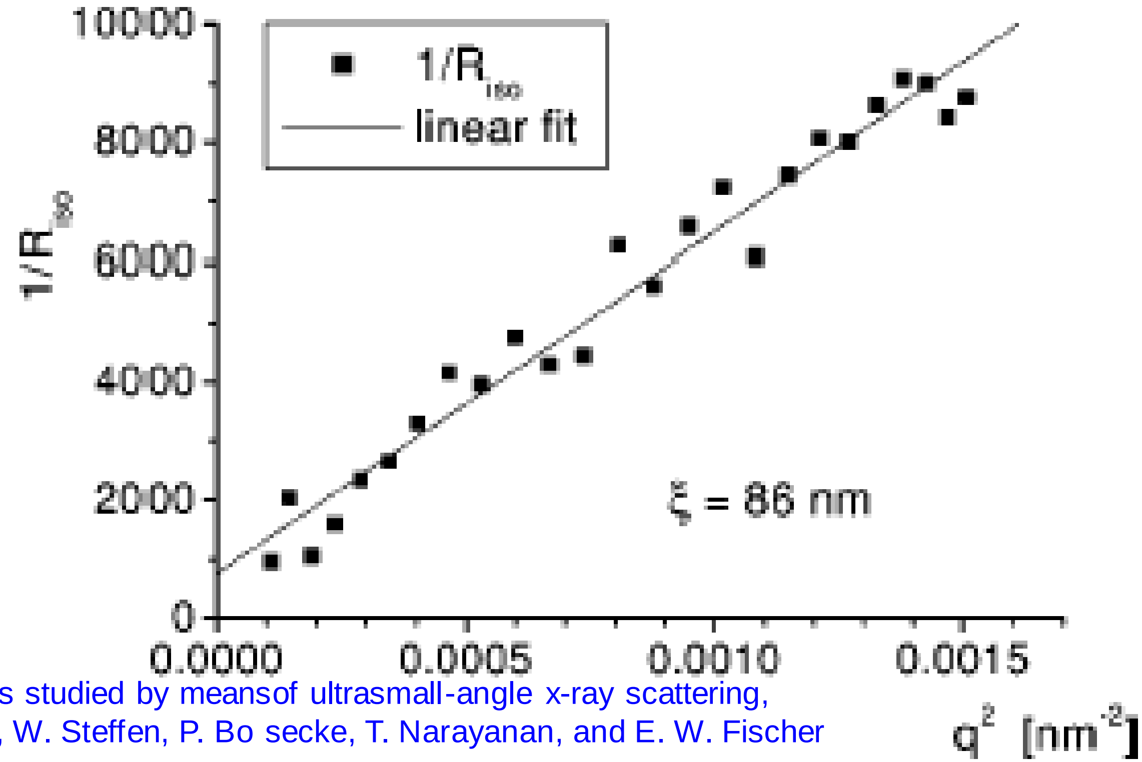
Ornstein-Zernike approximation

$$I(Q) = \frac{I_0}{1 + Q^2 \xi^2}$$

H.E. Stanley, Introduction to phase transitions and critical phenomena, Oxford University press Oxford, 1971

ξ correlation length





Long-range density fluctuations in orthoterphenyl as studied by meansof ultrasmall-angle x-ray scattering, A. Patkowski, Th. Thurn-Albrecht, E. Banachowicz, W. Steffen, P. Bo secke, T. Narayanan, and E. W. Fischer (2000) Phys Rev E, 61, 6909-6912

Yttria-alumina liquids & L-L Transitions

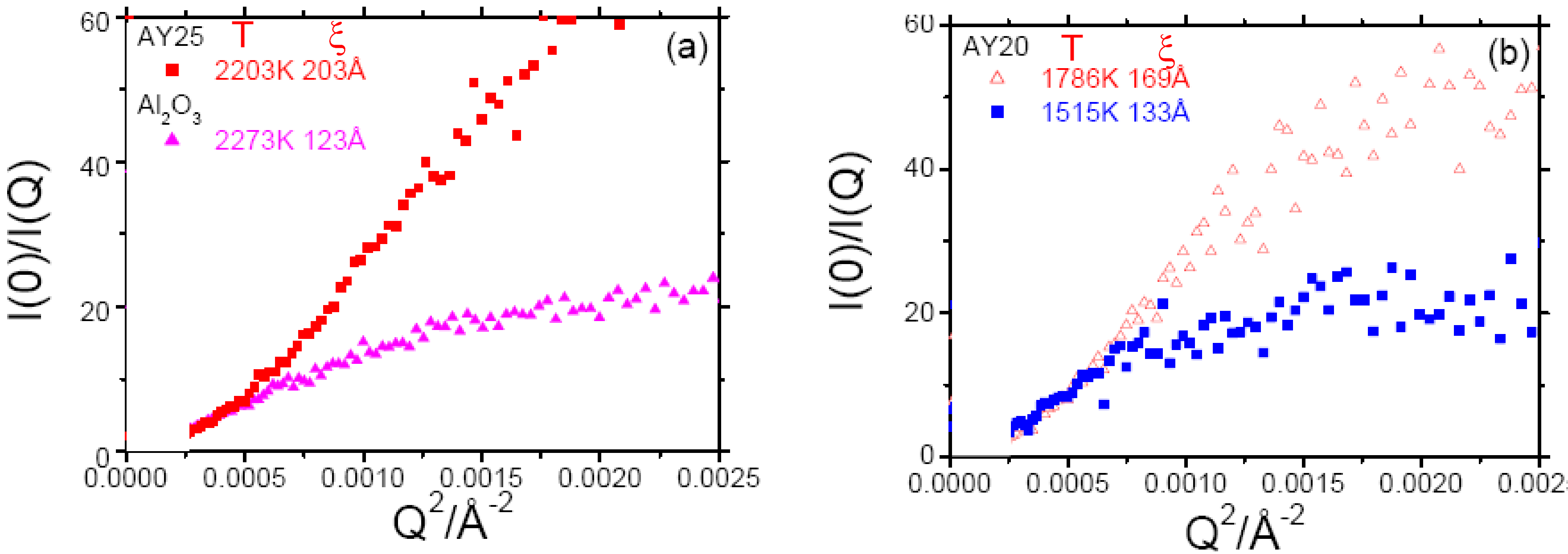


Fig. 6 Ornstein-Zernike plots of SAXS data $I(0)/I(Q)$ v Q^2, including the correlation lengths ξ of long range fluctuations analysed from the slopes at low Q for different temperatures. (a) SAXS data for liquid Al_2O_3 and AY25 at temperatures above T_m taken from Fig. 3(a) and the very different ξ values for these liquids of different strength. (b) AY20 data from Fig. 3(b), showing the increase in ξ at the liquid-liquid transition around 1788K (Fig. 4(a)) and the shift in the maximum to larger wavevectors.

$$I(Q) = \frac{I_0}{1 + Q^2\xi^2}$$

ξ correlation length

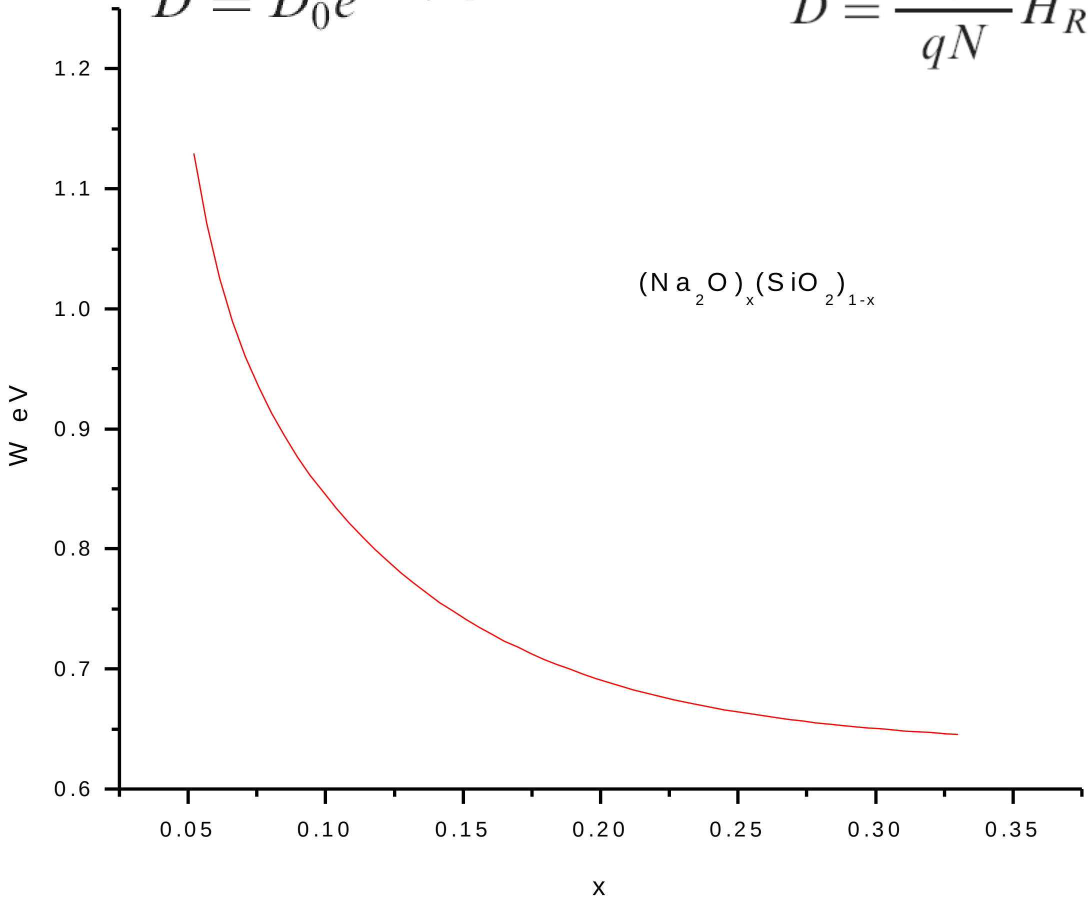
Liquid-liquid transitions, crystallisation and long range fluctuations in supercooled yttrium oxide-aluminium oxide.
G.N. Greaves, M.C. Wilding, L. Hennet, W. Bras, O. Majérus, S. Fearn, F. Kargl
Journal of Non-Crystalline Solids (2009), doi:10.1016/j.jnoncrysol.2009.01.030

ionic diffusion/electrical conductivity

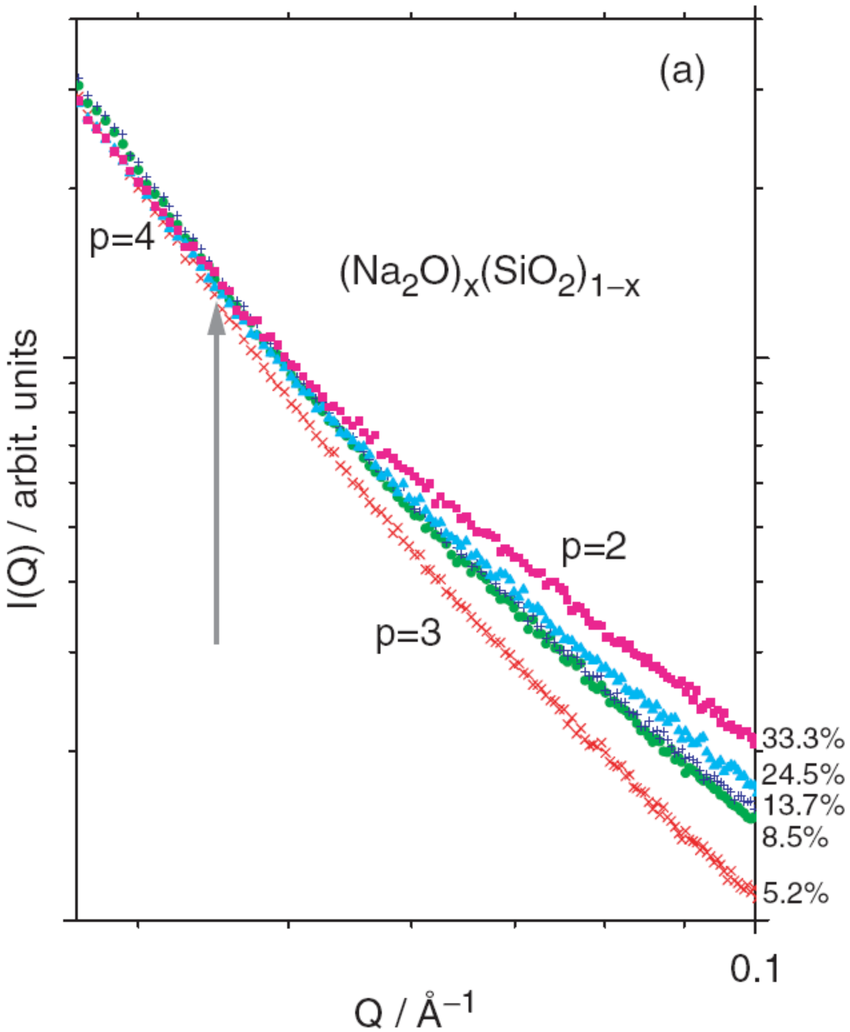
Single alkalis

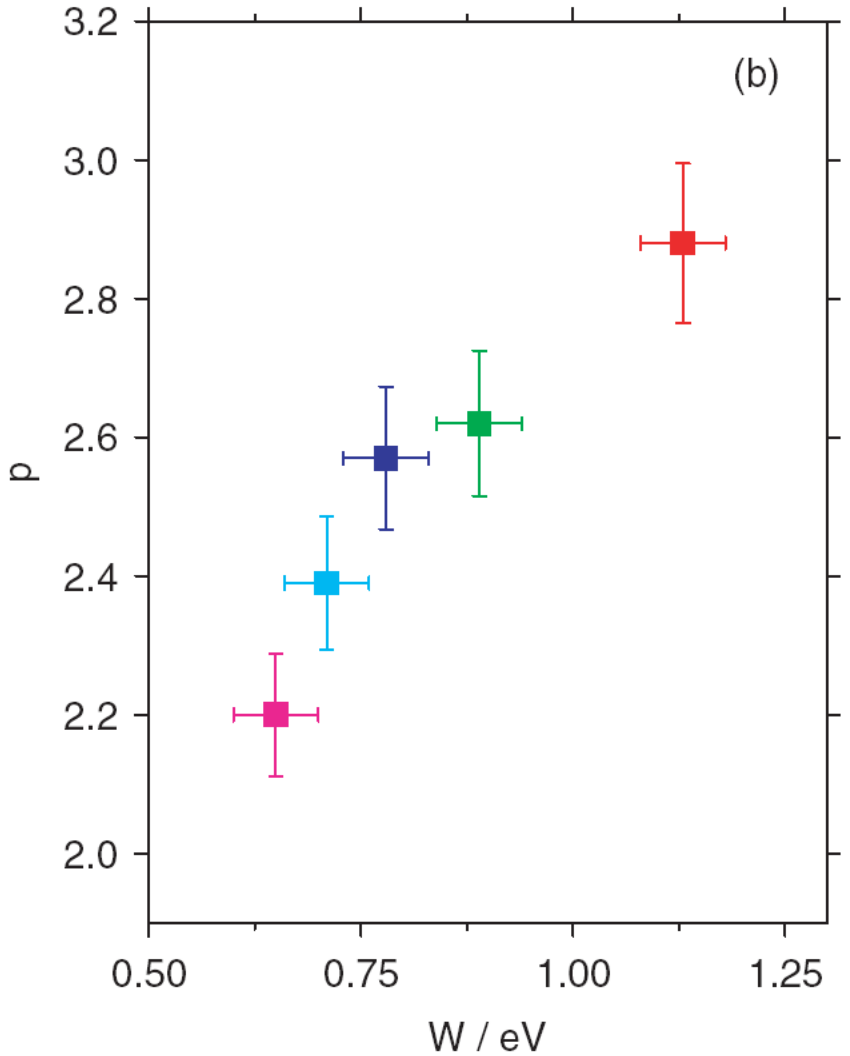
$$D = D_0 e^{-W/k_B T}$$

$$D = \frac{\sigma k_B T}{qN} H_R$$



SAXS and dimensionality and ionic diffusion





Solids,

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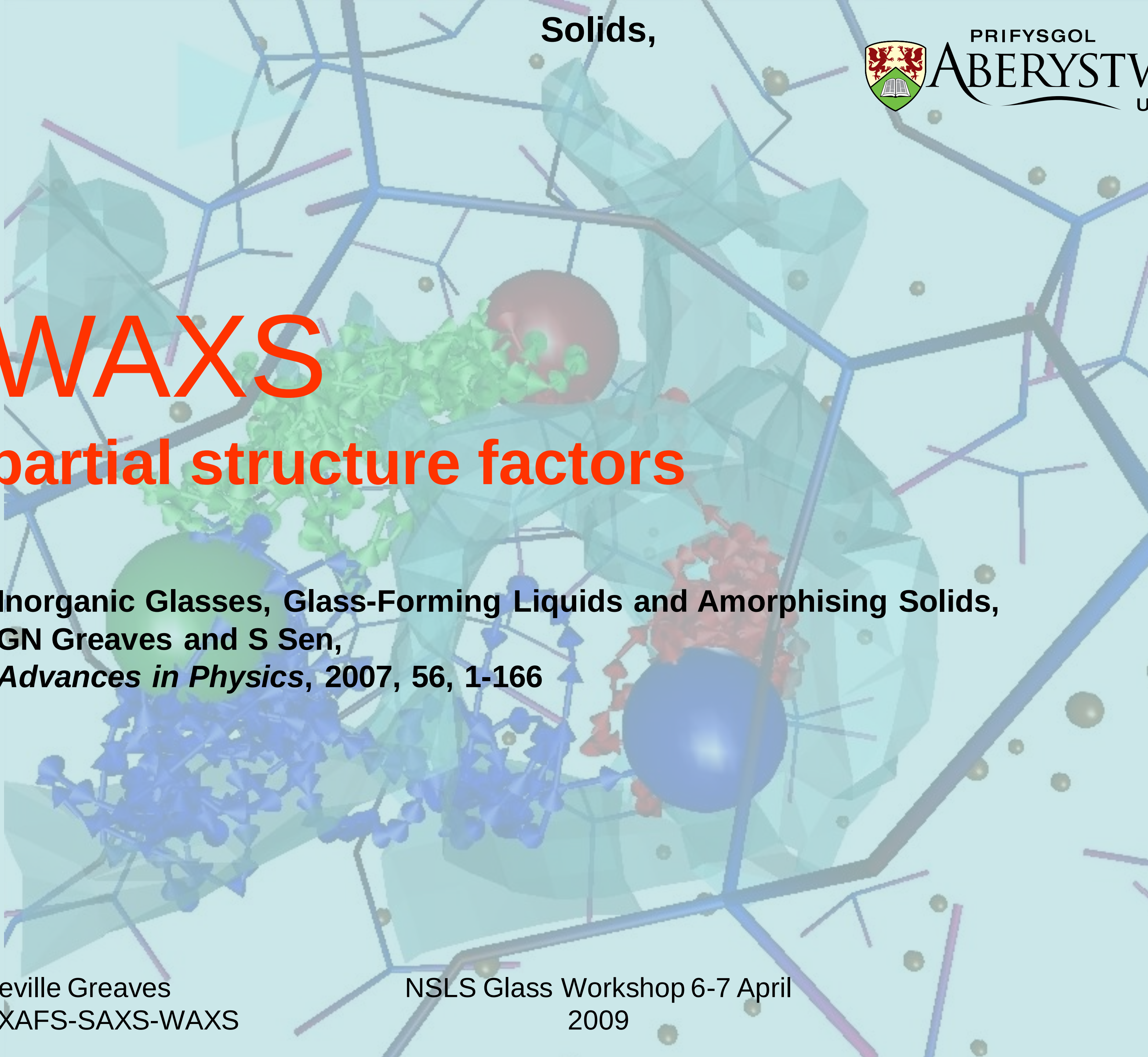


WAXS

partial structure factors

Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids,
GN Greaves and S Sen,
***Advances in Physics*, 2007, 56, 1-166**

WAXS - basics

Element specific:

Structure Factor, $S(Q)$ — Partial Structure Factors, $S_{\alpha\beta}(Q)$ — Radial Distribution Factor, $J(r)$

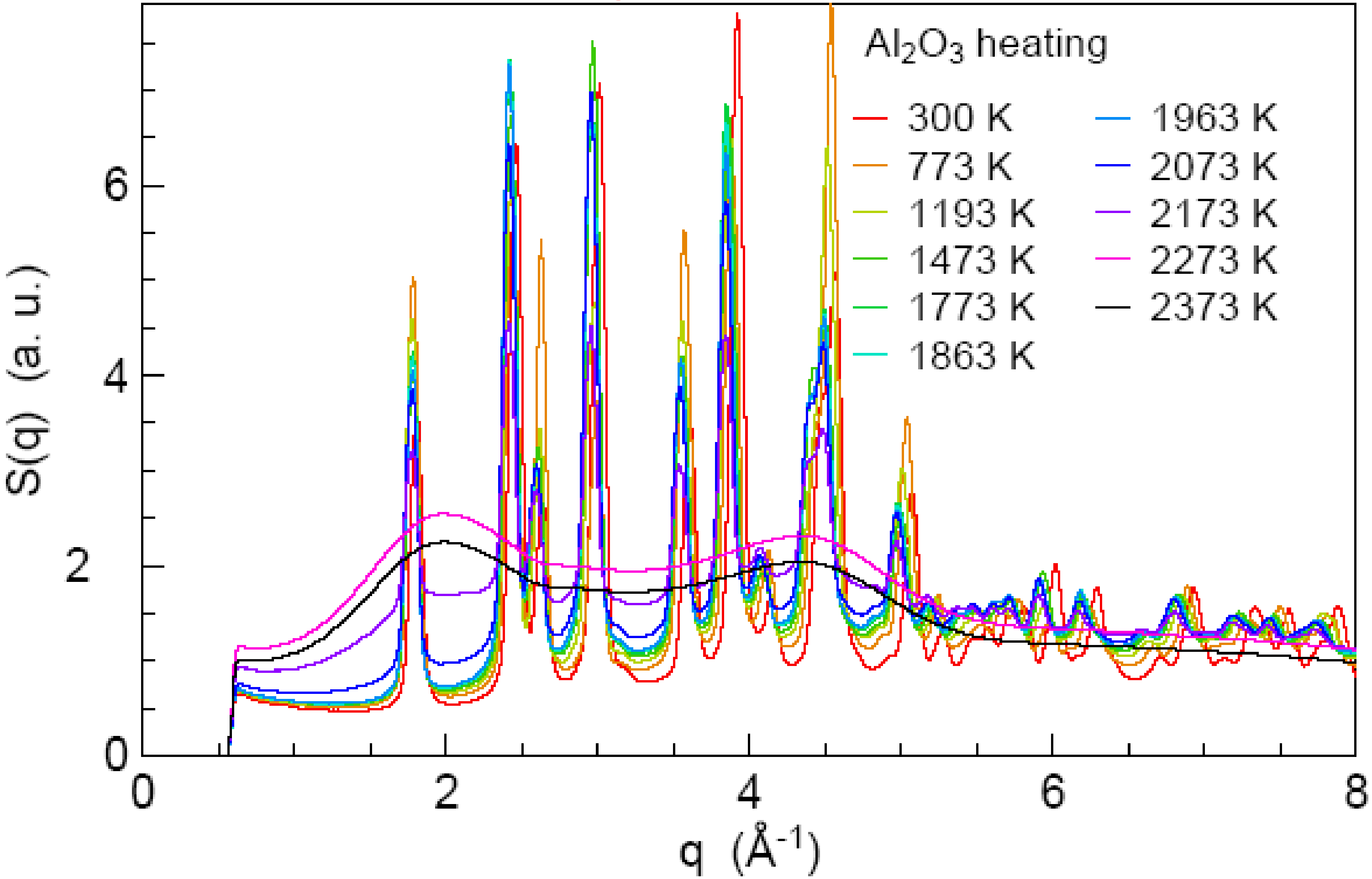
$$S(Q) = \sum_{\alpha}^{N} \sum_{\beta}^{N} W_{\alpha} W_{\beta} S_{\alpha\beta}(Q)$$

$$S_{\alpha\beta}(Q) = \frac{\sin Qr_{\alpha\beta}}{Qr_{\alpha\beta}}$$

$$J(r) = \frac{2r}{\pi} \int_0^{\infty} [Q\{S(Q) - 1\} \sin Qr]\, dQ + 4\pi\rho_0 r^2$$

In situ X-ray Scattering and Diffraction

melting alumina ID16 ESRF



In situ structural studies of alumina during melting and freezing, G. N. Greaves, M. C. Wilding, S. Fearn, D. Langstaff, F. Kargl, Q. Vu Van, L.Hennet, I. Pozdnyakova, O. Majérus, *Advances in Synchrotron Radiation* (in press 2009)

Partial structure factors in silica glass - RMC from XRD and ND

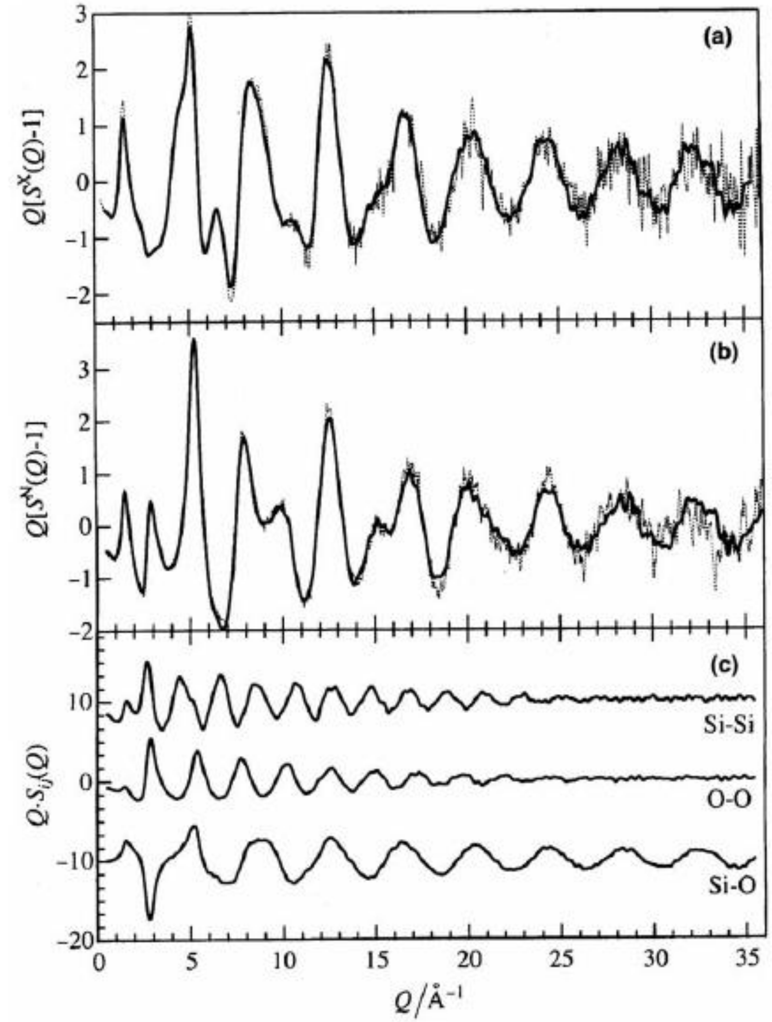


Figure 6. Reverse Monte Carlo simulation of silica glass compared to high-energy X-ray scattering (a) and neutron scattering (b). The interference functions, $Q(S(Q)-1)$ differ because of the different cross-section weightings. Dashed lines are experimental and solid lines the result of RMC modelling. The partial structure factors for Si–Si, O–O and Si–O obtained from RMC modelling are given in (c), displaced vertically. Reproduced with permission from [60] © 2001 Elsevier.

H. Ohno, S. Kahara, N. Umesaki and K. Suzuya, J. Non-Cryst. Solids **293–295** 125 (2001).

Polyhedra in silicate glasses

EXAFS, ND and Molecular Dynamics

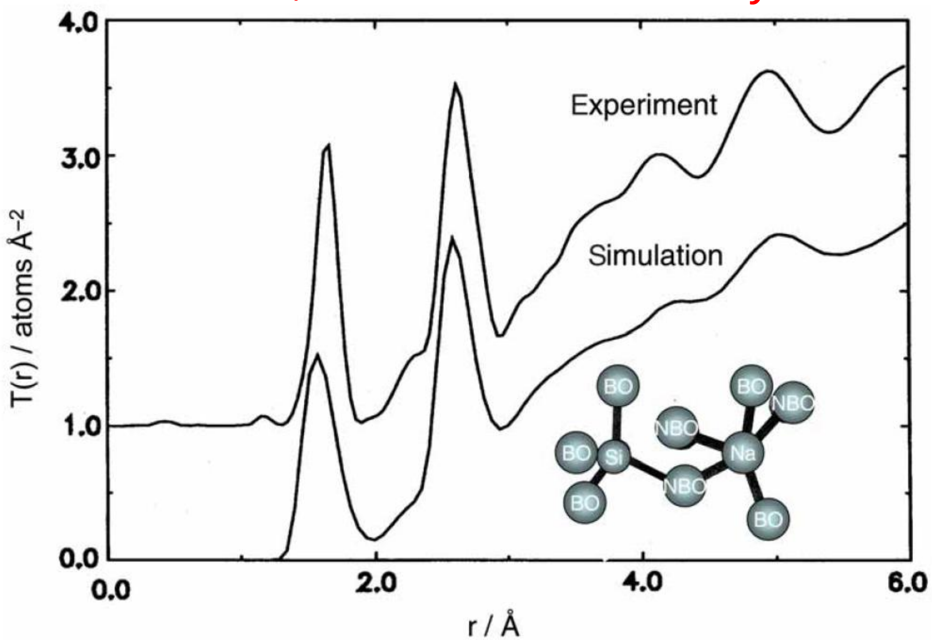


Figure 10. The total RDF $T(r) = J(r)/r$ (a) for $Na_2Si_2O_5$ glass obtained from neutron scattering (Exp) [132] compared to the predictions from an MD model (Sim) at 1000 K [125, 126]. A Si, Na, BO and NBO configuration is illustrated. Reproduced with permission from [126]

A Structural Basis for Ionic Diffusion in Oxide Glasses
Greaves G N, Gurman S J, Catlow C R A, Chadwick A V, Houde-Walter S, Dobson B Rand Henderson CMB
Phil. Mag. A65, 1059-1072 (1991)

Computer Simulation of Sodium Disilicate Glass
Smith W, Greaves GN and Gillan MJ
J. Chem. Phys. 103, 3091-3097 (1995)

Cation Microsegregation and Ionic Mobility in Mixed Alkali Glasses
Vessal B, Greaves G N, Marten P T, Chadwick A V, Mole R, Houde-Walter S
Nature 356, 504-507 (1992)

Solids,

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EXAFS-SAXS-WAXS

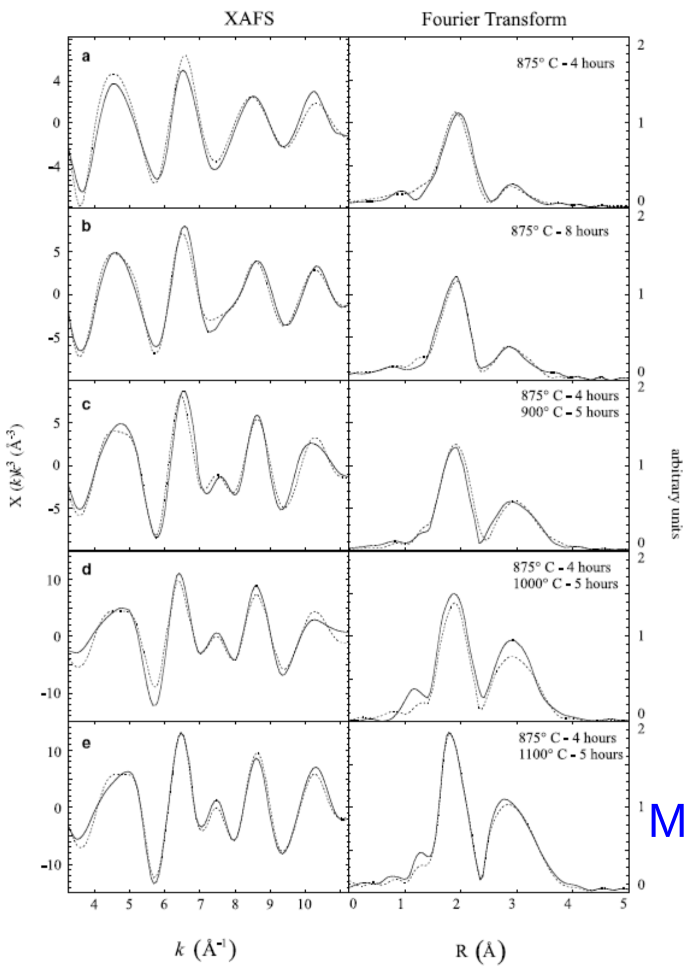
processing of glass ceramics

Bras, W.; Greaves, G. N.; Oversluizen, M.; Clark, S. M.; Eeckhaut, G. The development of monodispersed alumino-chromate spinel nanoparticles in doped cordierite glass, studied by in situ X-ray small and wide angle scattering, and chromium X-ray spectroscopy. *J. Non-Cryst. Solids* **2005**, *351* (27−29), 2178–2193.

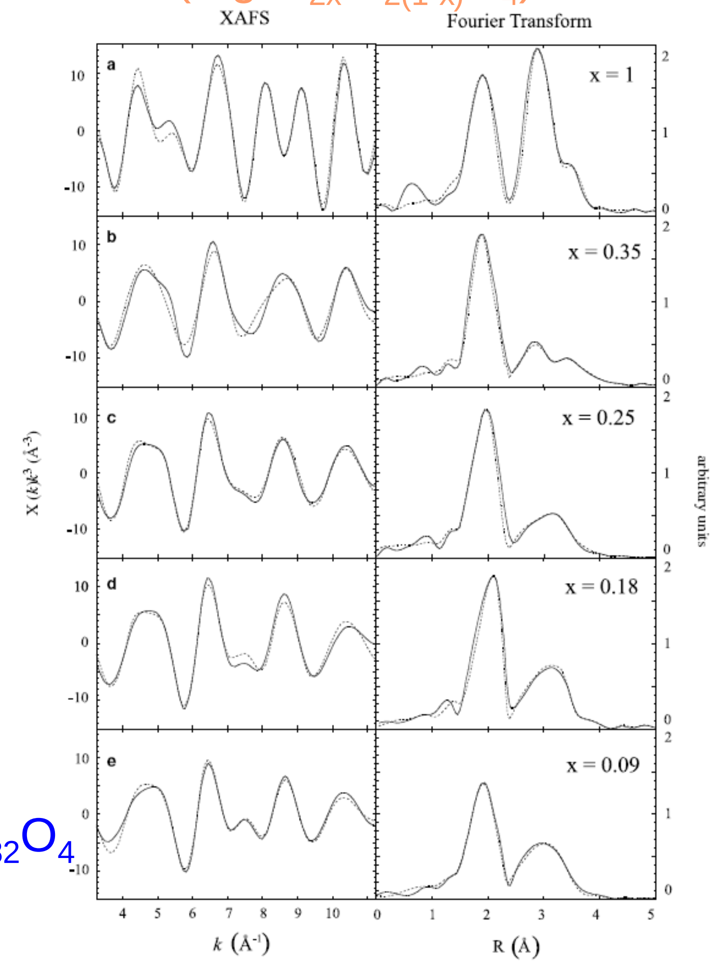
Bras, W, Clark, SM, Greaves, GN, Kunz, M, van Beek, W, Radmilovic, V, Nanocrystal growth in cordierite glass ceramics studied with x-ray scattering *Crystal Growth and Design*, **doi: 10.1021/cg07056v** (in press 2009)

Cr EXAFS

cordierite ($Mg_2Al_4Si_5O_{18}$) glass doped with 0.34 mol% Cr_2O_3



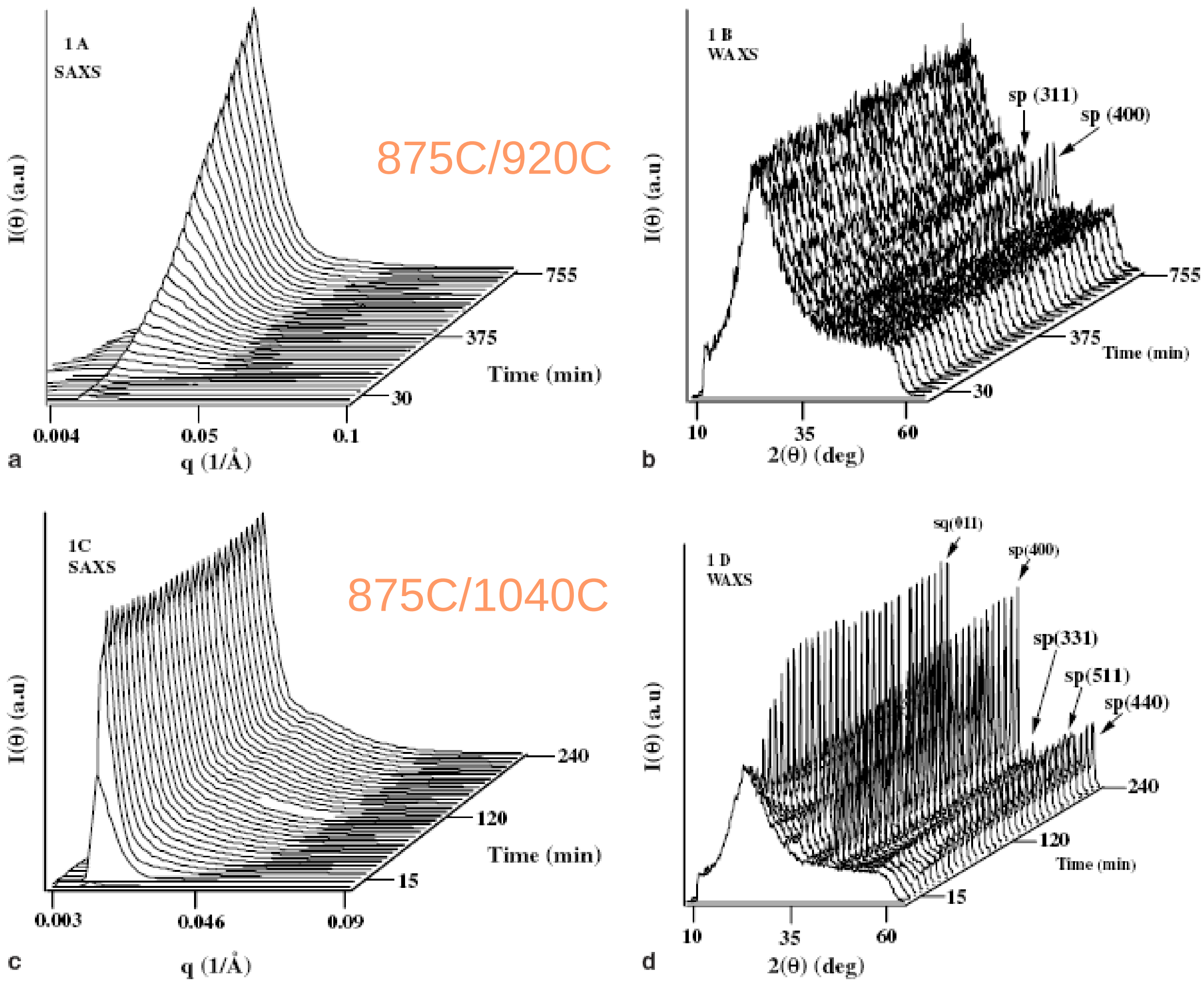
chromo-aluminate spinels ($MgCr_{2x}Al_{2(1-x)}O_4$)



$MgCr_{0.18}Al_{1.82}O_4$

cordierite ($Mg_2Al_4Si_5O_{18}$)
glass heat treated
at different temperatures

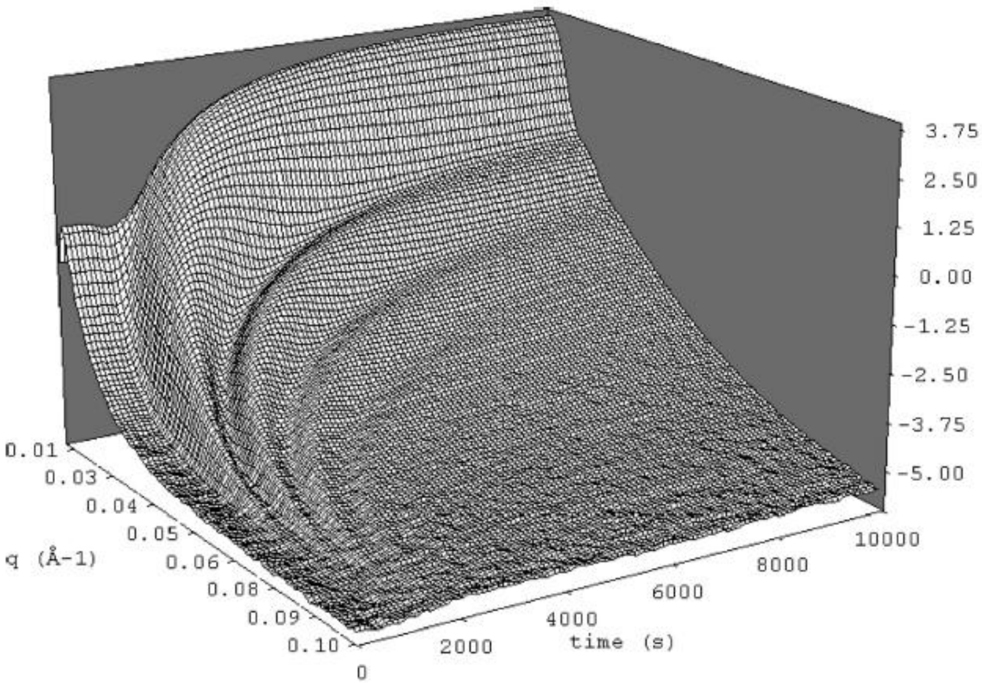
In situ SAXS/WAXS



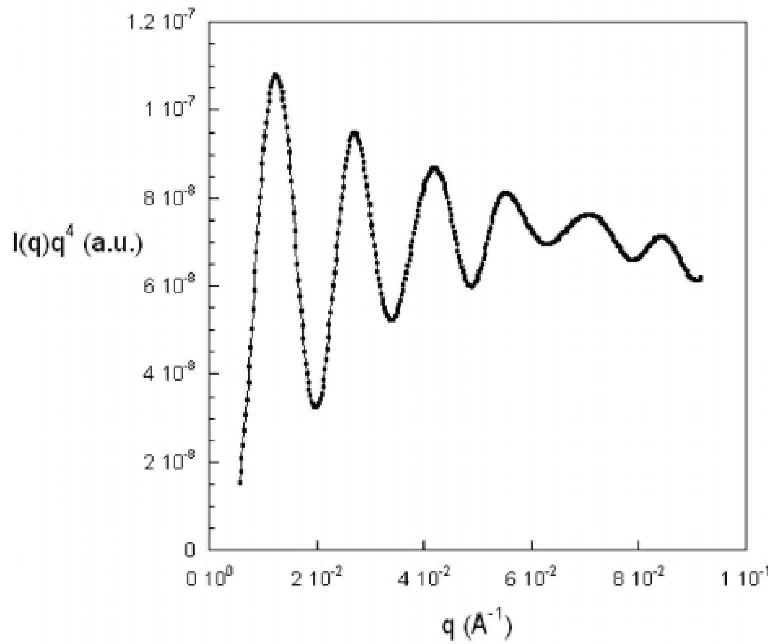
cordierite/Cr glass
875C/925C

SAXS and form factor

ln I_{saxs} v Q



I_{saxs} Q^4 v Q
i.e with thermal fluctuations removed

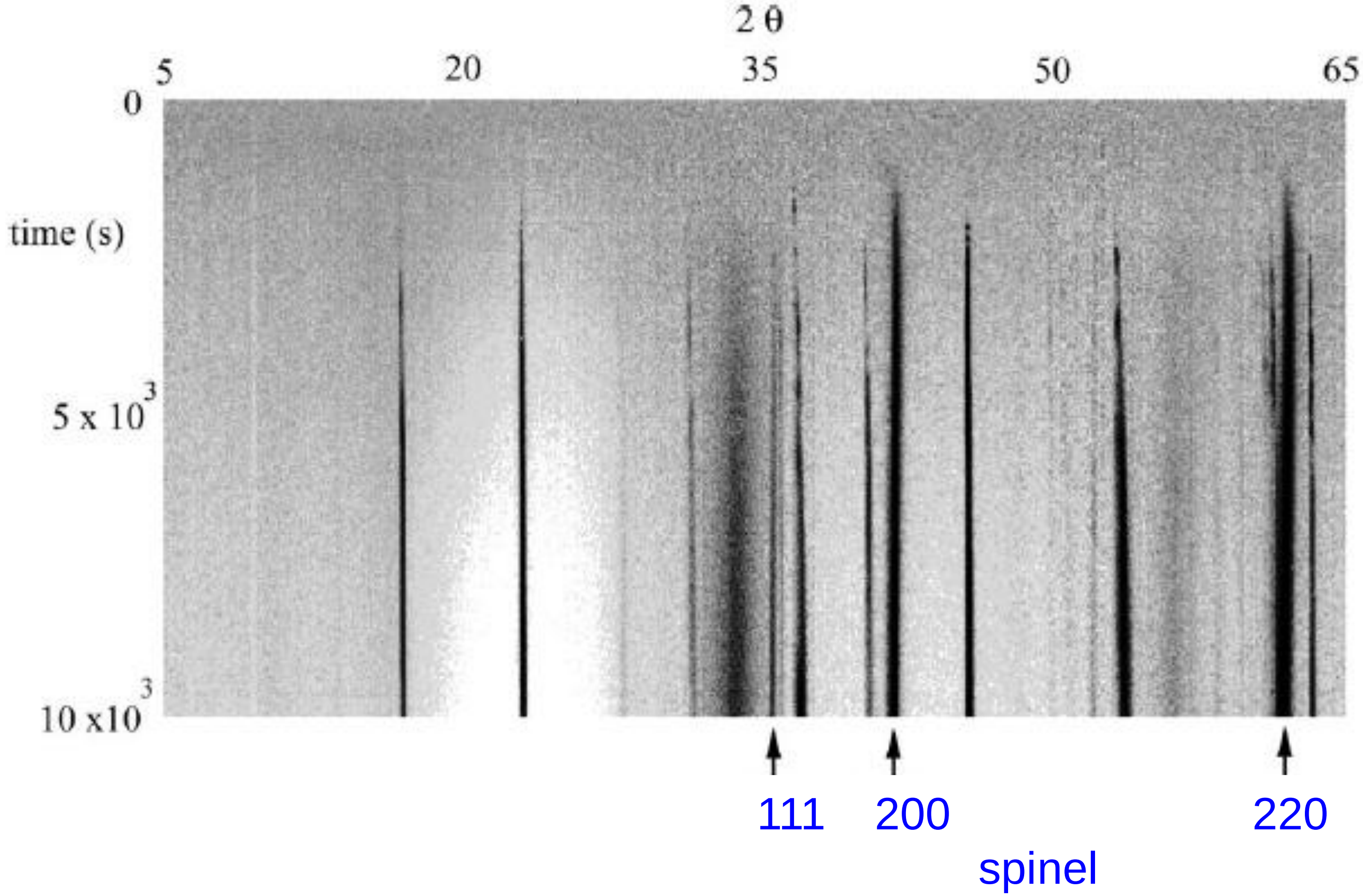


20nm crystallites highly monodispersed

$MgCr_{0.18}Al_{1.82}O_4$

distinguishing nanocrystalline phases

spinel ($MgCr_{0.18}Al_{1.82}O_4$) in bulk & stuffed quartz (μ- cordierite) at surface



in situ spinel particle growth and internal strain

Guinier radius

$$R_g = \sqrt{\frac{3}{5}}\, R$$

Particle radius

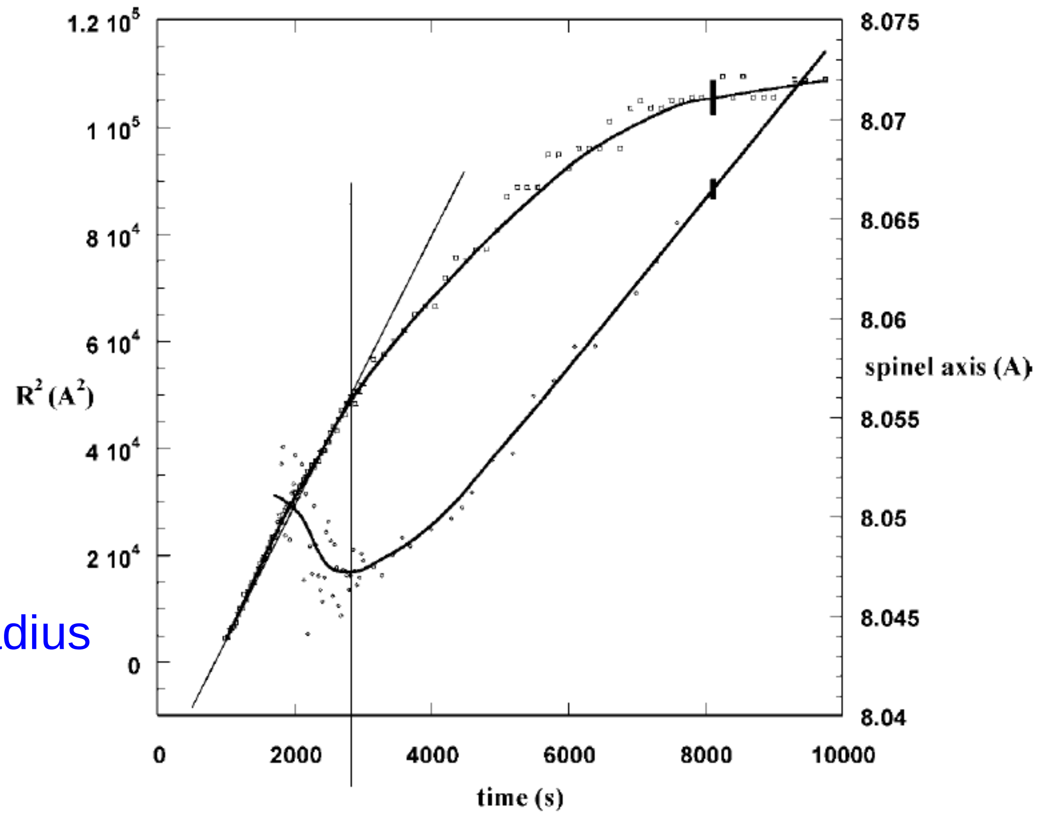


Figure 7. The correlation between the R^2 of the particle and time (□). The vertical bar at time = 8000 s indicates the error margin at the later stages of development. At the early stages, a linear fit can be made to the R^2 data. This confirms the predictions that we are dealing with a diffusion-limited growth process. The development of the spinel unit cell volume as function of time (◇). The changeover from shrinking to growing coincides with the moment when the particle size leaves the $(t)^{1/2}$ growth regime. Also noteworthy is that this is the moment when the noise is much reduced.

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- Combining x-ray techniques
- EXAFS – modifier channels and MRN
- SAXS – IRO and diffusion
- WAXS – amorphisation
- EXAFS-SAXS-WAXS–formation of glass ceramics