Sub-T_g glass relaxation, nucleation, and crystallization in lithium disilicate glass

A solid-state NMR and MD strategy

Henrik Bradtmüller

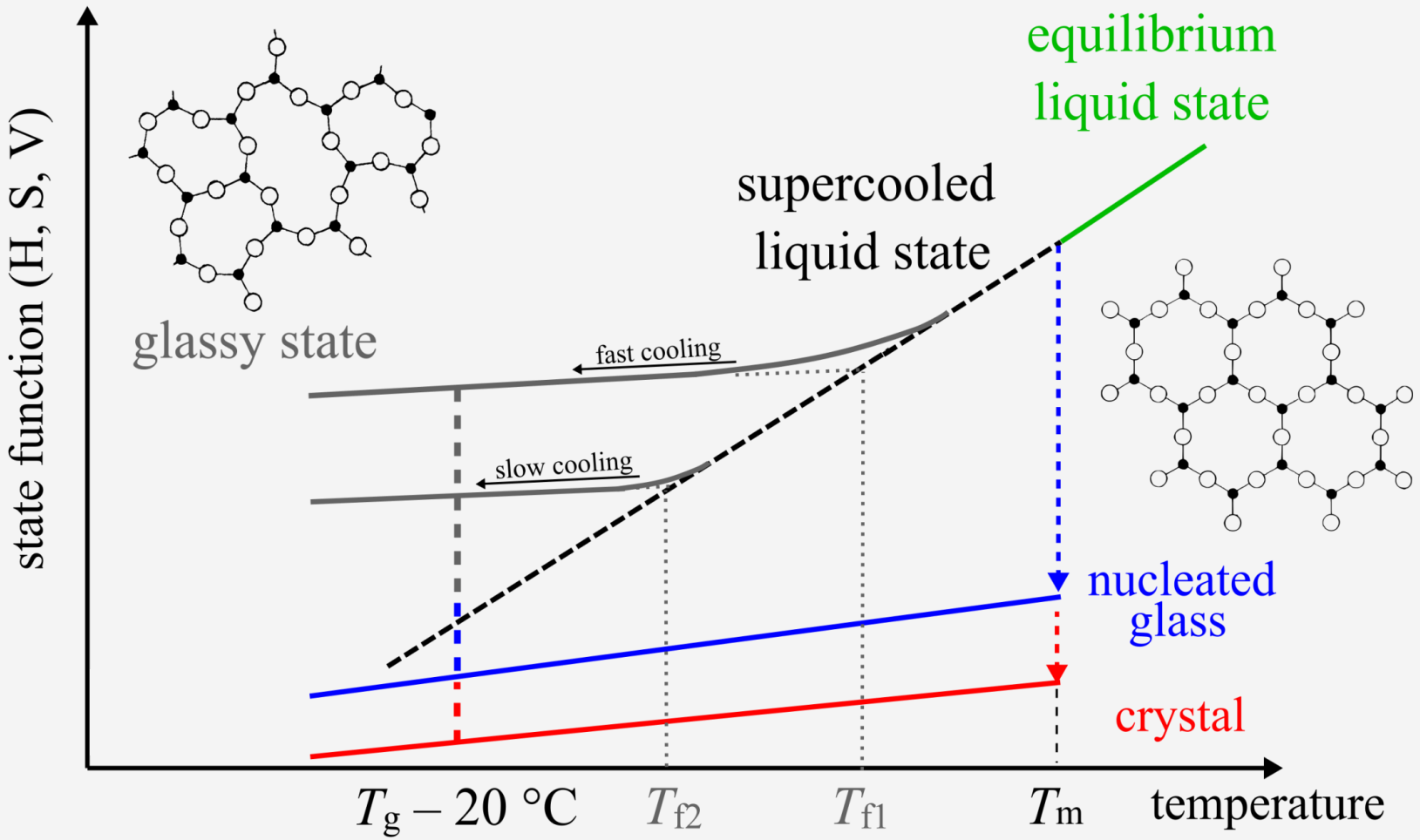
Department of Materials Engineering
Federal University of São Carlos, Brazil

LAMAV Vitreous Materials Laboratory

ufscar

FAPESP

What happens structurally when glasses head towards equilibrium?



Experimental Relaxation and Nucleation Study: $Li_2Si_2O_5$ glass

1. **Glass synthesis**

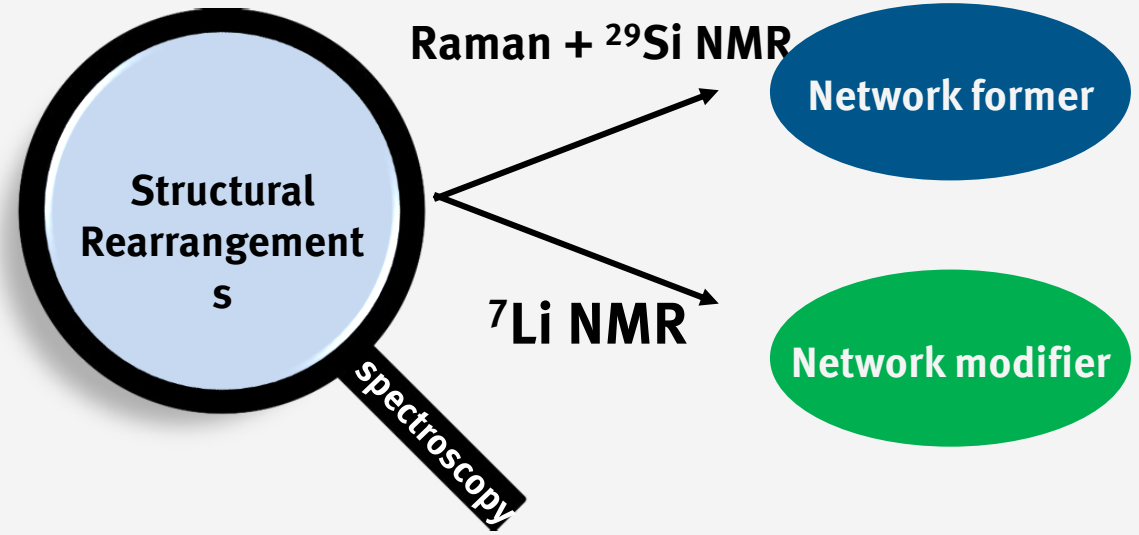
Melting at 1400 °C for 3h
Splat cooling @ RT
Repeated three times
Colorless, homogeneous glass

2. **Annealing protocol**

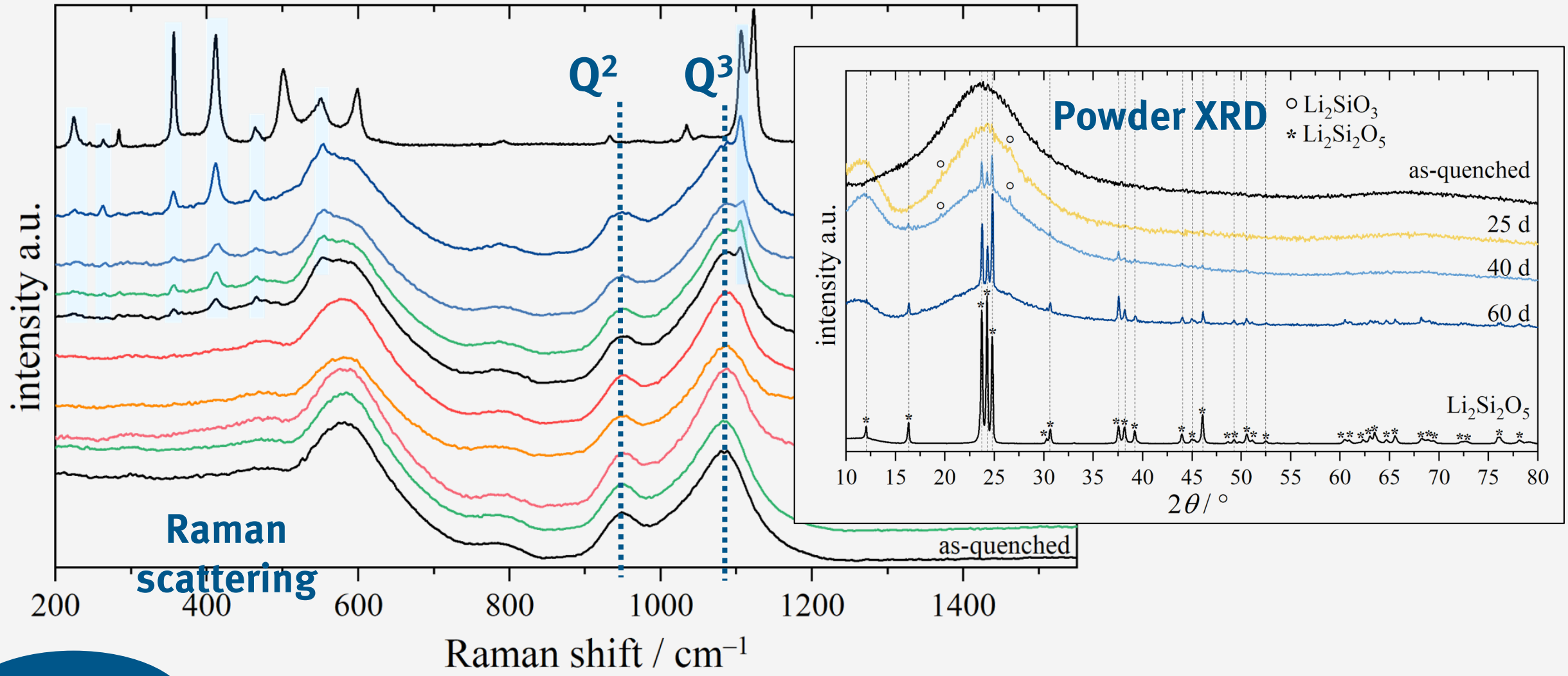
2 g pieces, vertical furnace
435 °C (ca. *T*g – 20°C)
15 min to 60 d
Cooled quickly (ambient cond.)

3. **Characterization**

DSC, XRD
Raman
NMR
MD simulations



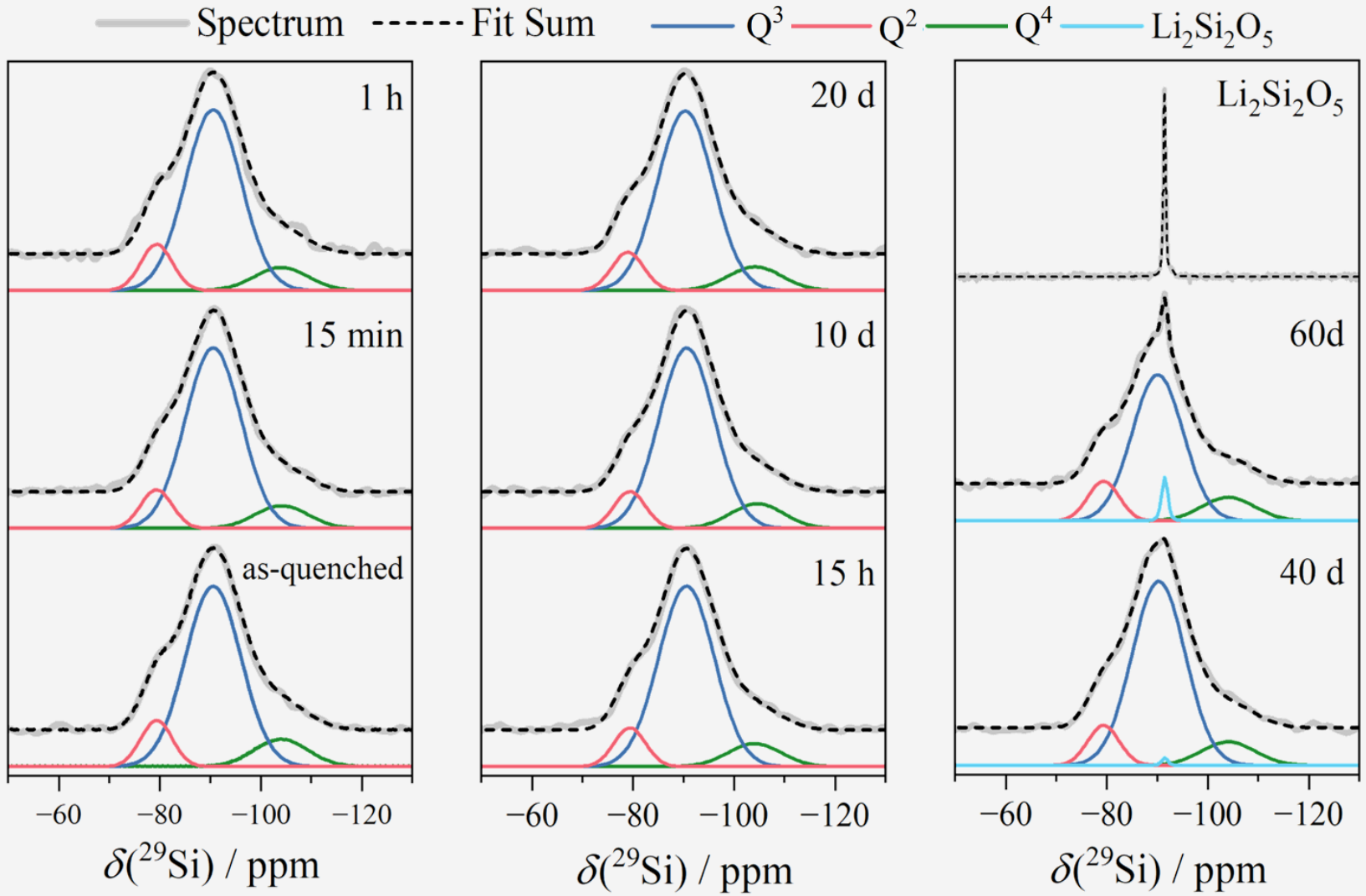
No detectable change in Q^n speciation upon annealing



Network former

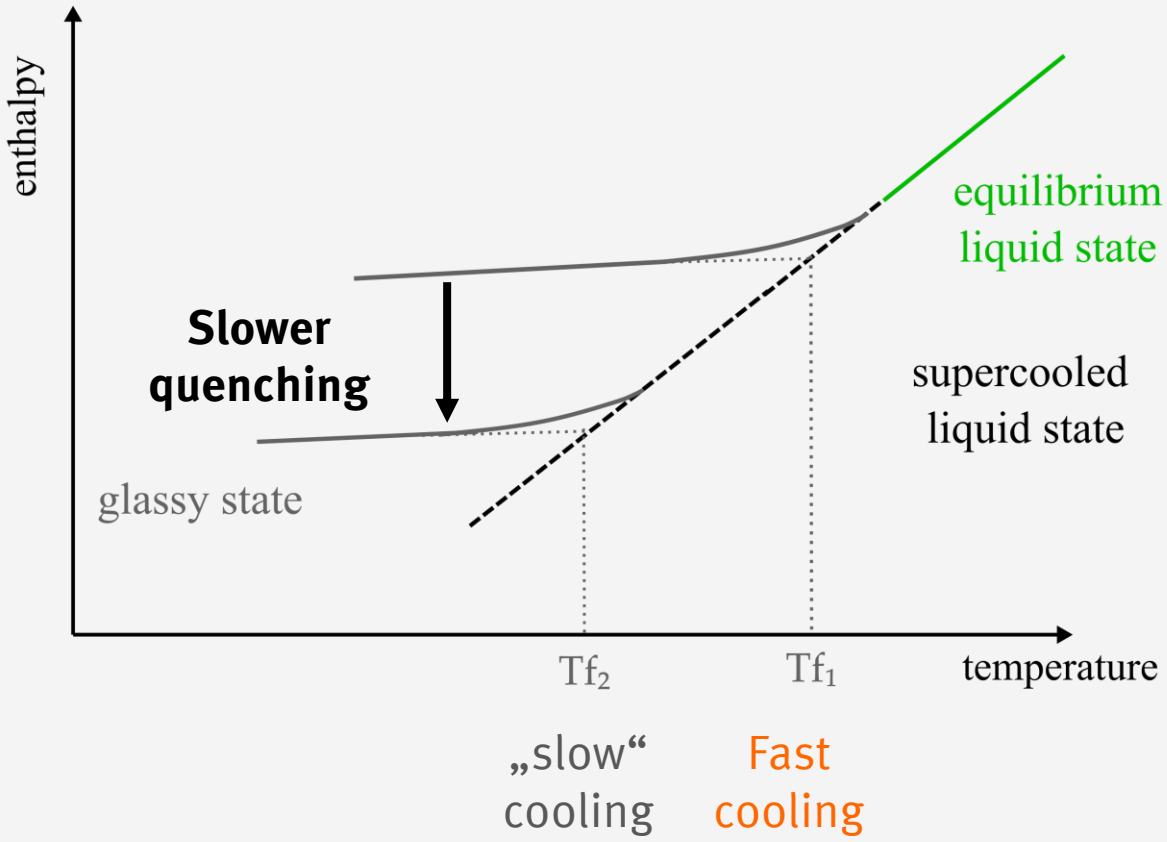
No detectable change in Q^n speciation upon annealing

^{29}Si MAS NMR

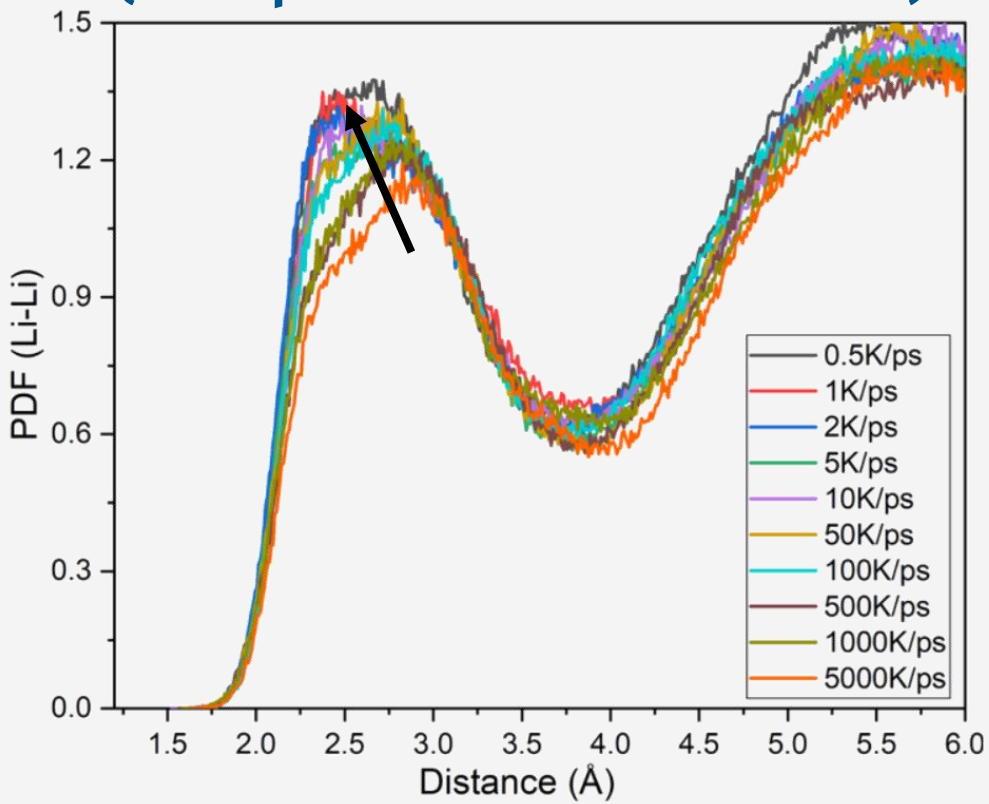


Network former

MD simulations indicate changes in network modifier distribution



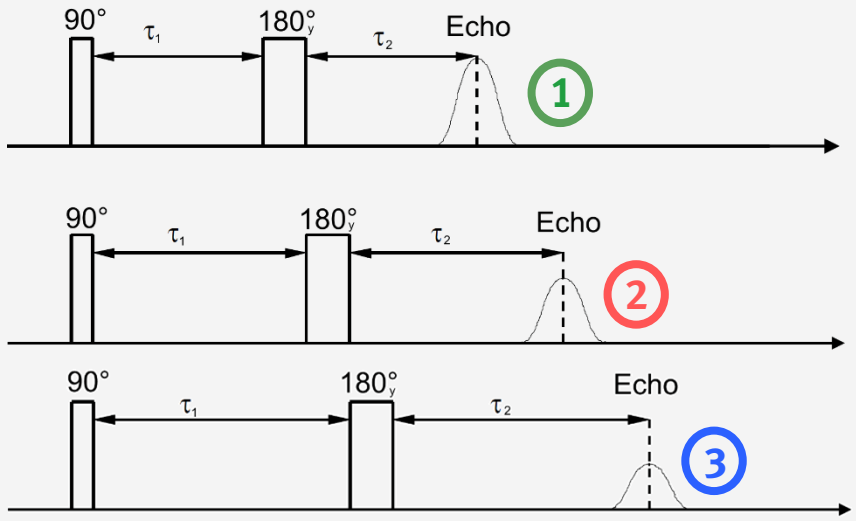
MD simulations (Li–Li pair distribution function)

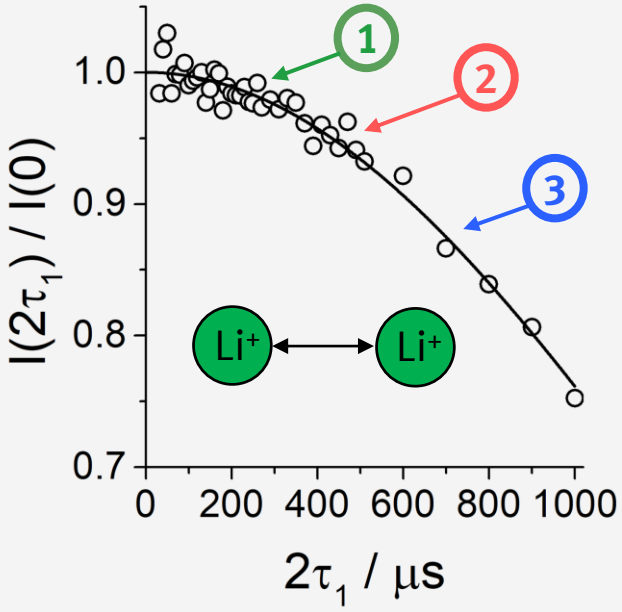


Network modifier

W. Sun, V. Dierolf, H. Jain, **J. Non. Cryst. Solids** 569 (2021) 120991.

^{7}Li dipolar NMR can measure average Li–Li distances





Experimental

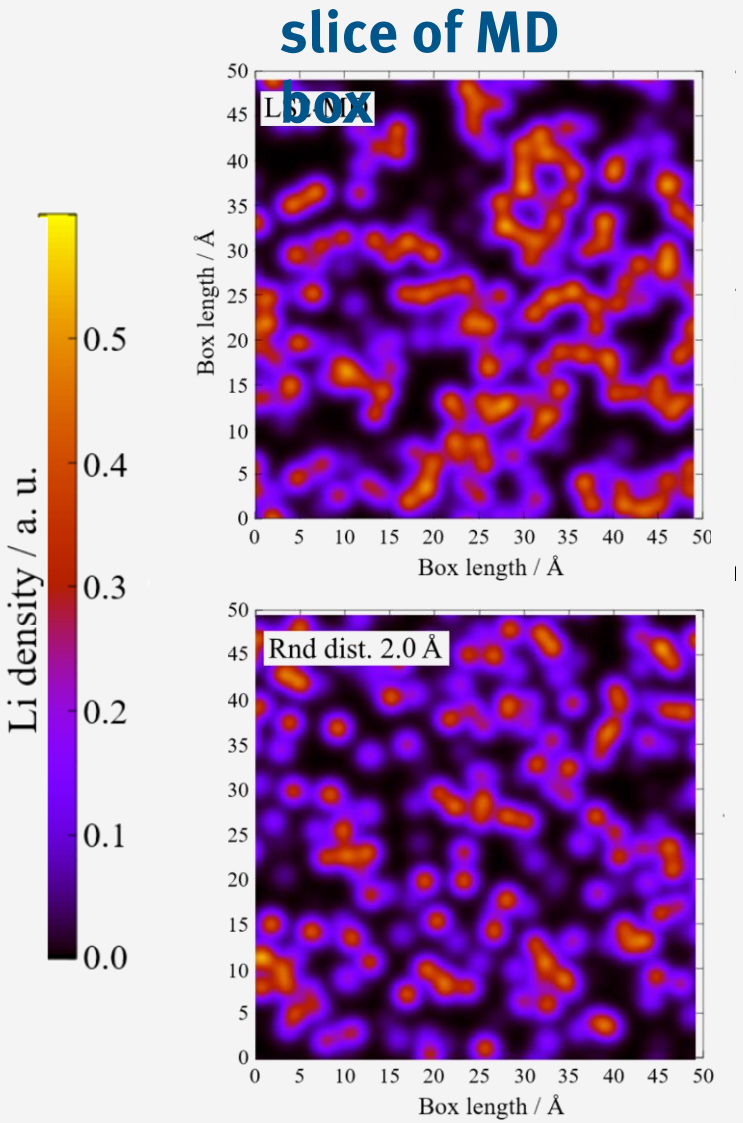
$$\frac{I(2\tau)}{I(0)} = \exp\left[-\frac{\boldsymbol{M_{2E}}}{2}(2\tau_1)^2\right]$$

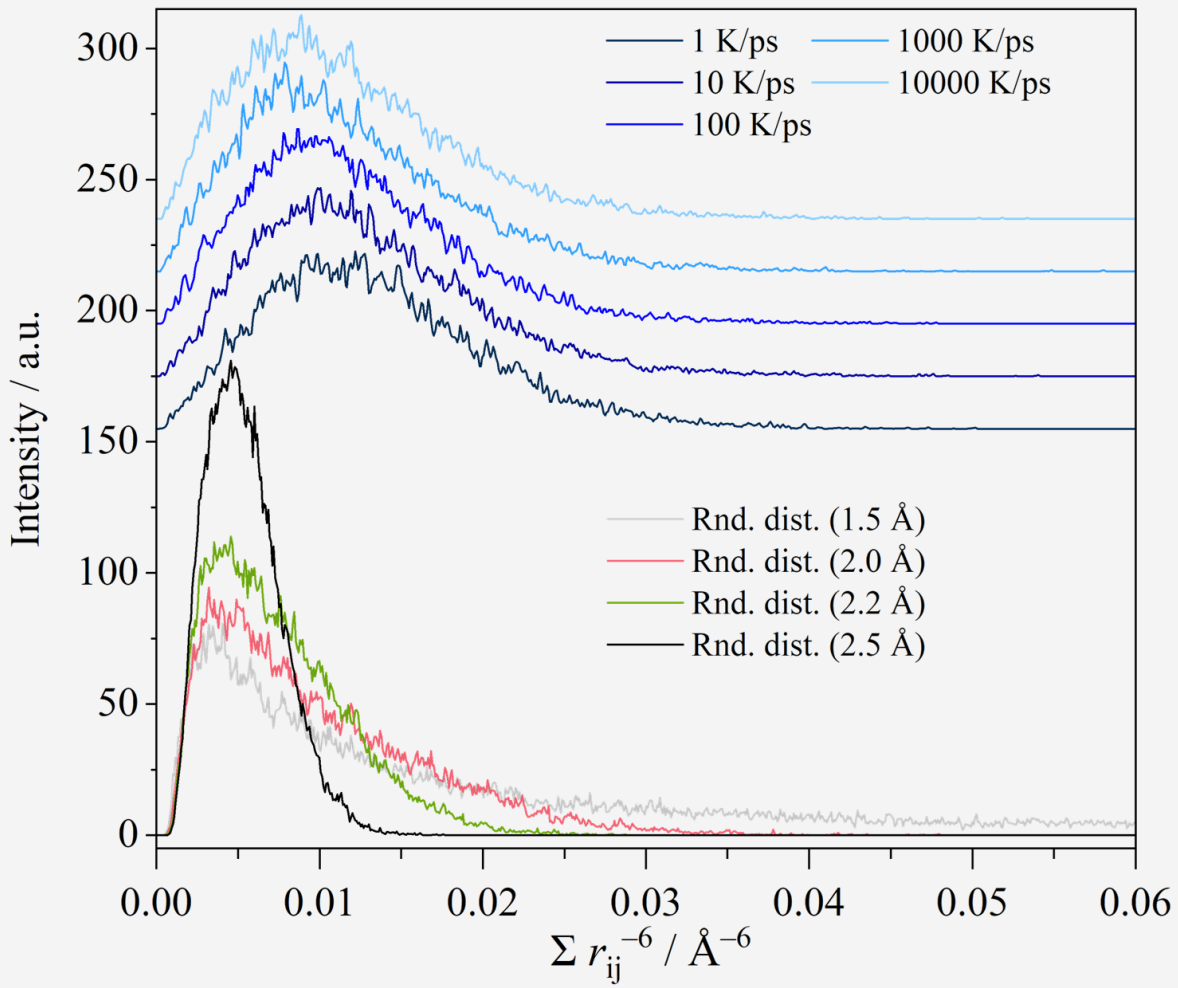
Theoretical

$$\boldsymbol{M_{2E}} = 0.9562\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_{^7\mathrm{Li}}^4 \hbar^2 \sum_{i \neq j} \frac{1}{r_{ij}^6}$$

Network modifier

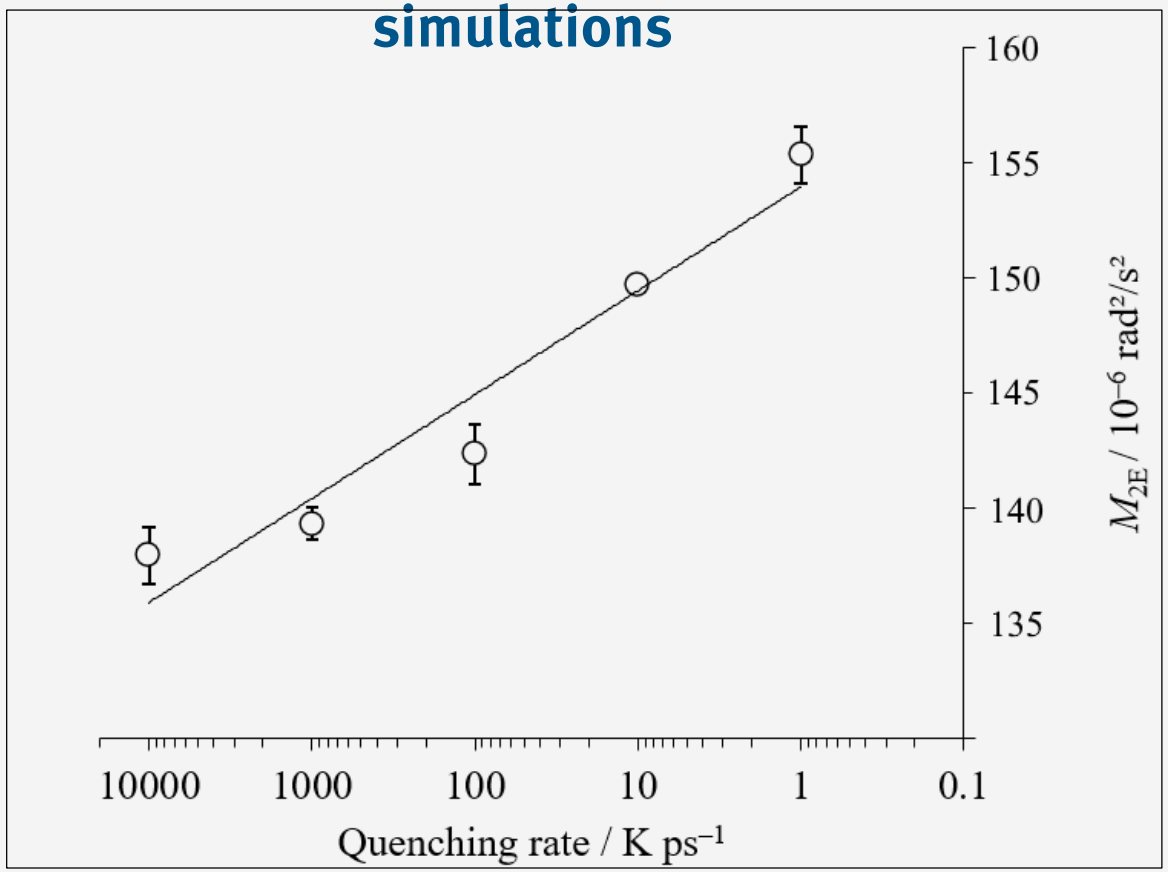
MD simulations show some Li^+ clustering for decreasing T_f



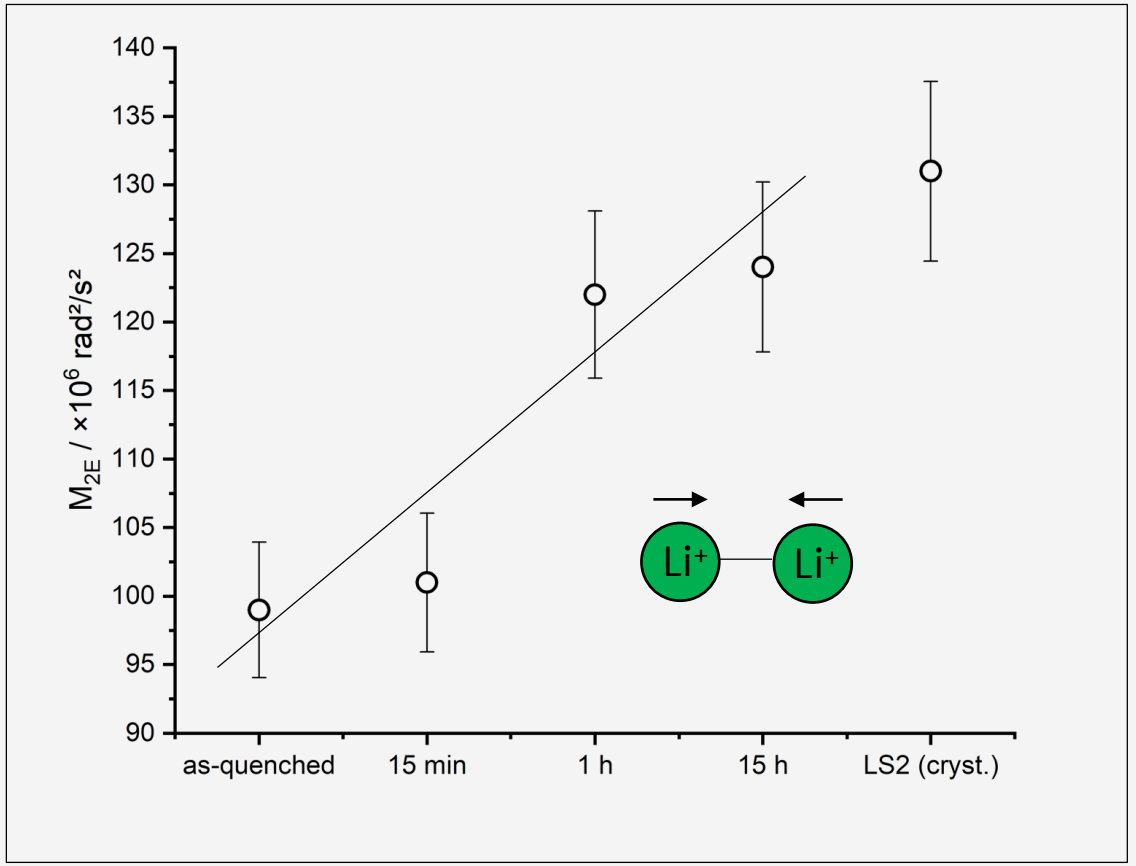


^{7}Li dipolar NMR confirms clustering with relaxation

MD simulations



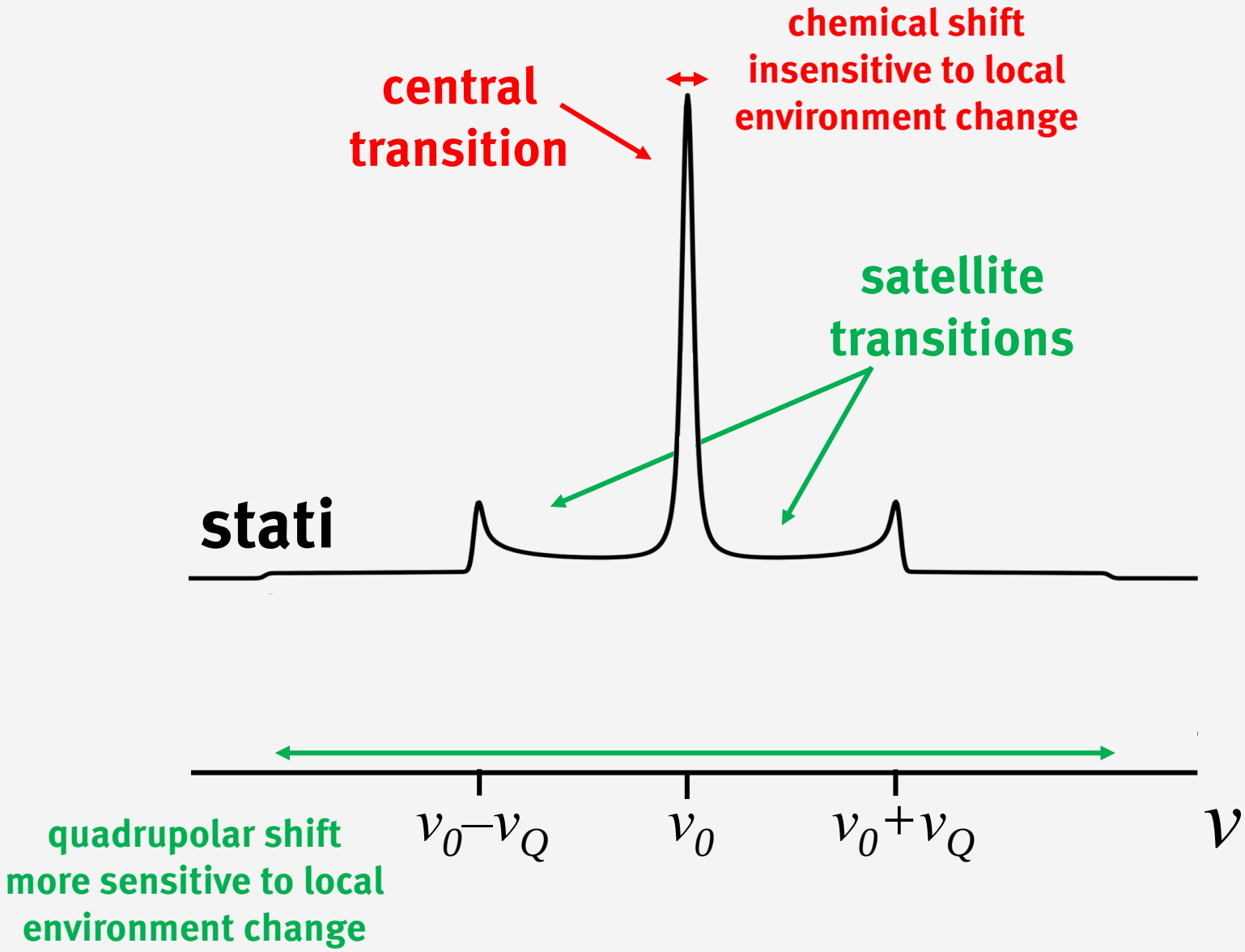
^{7}Li spin echo decay NMR



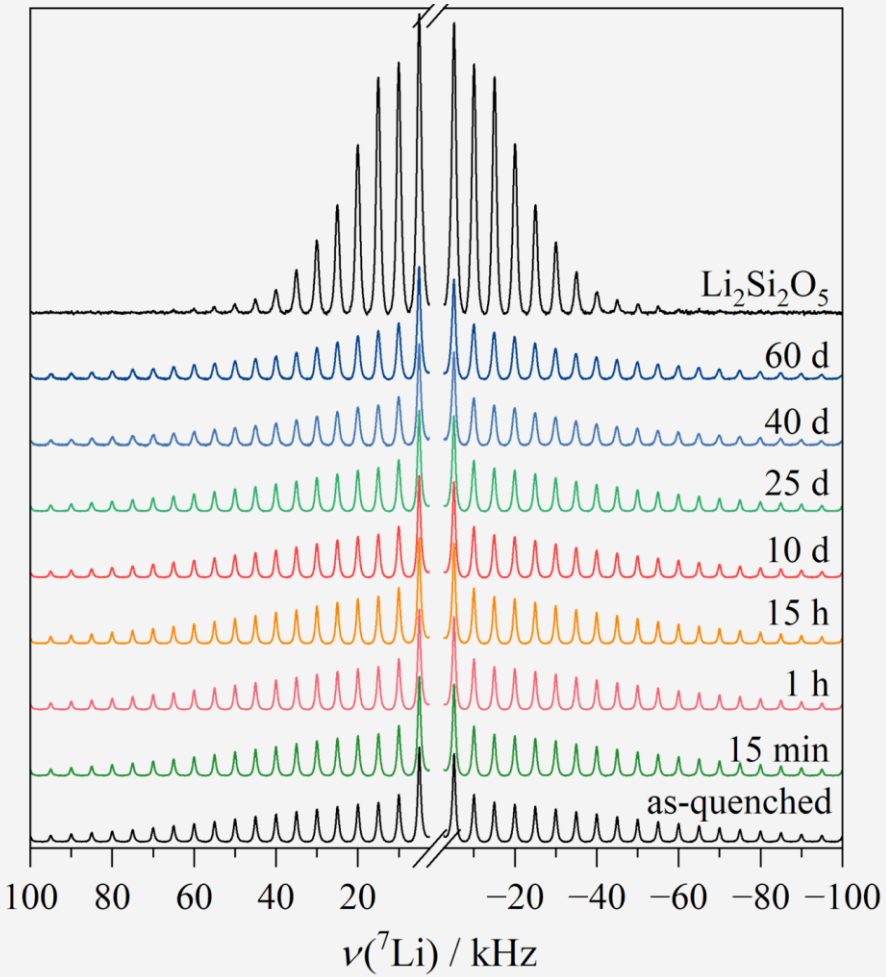
← fictive temperature

glass relaxation →

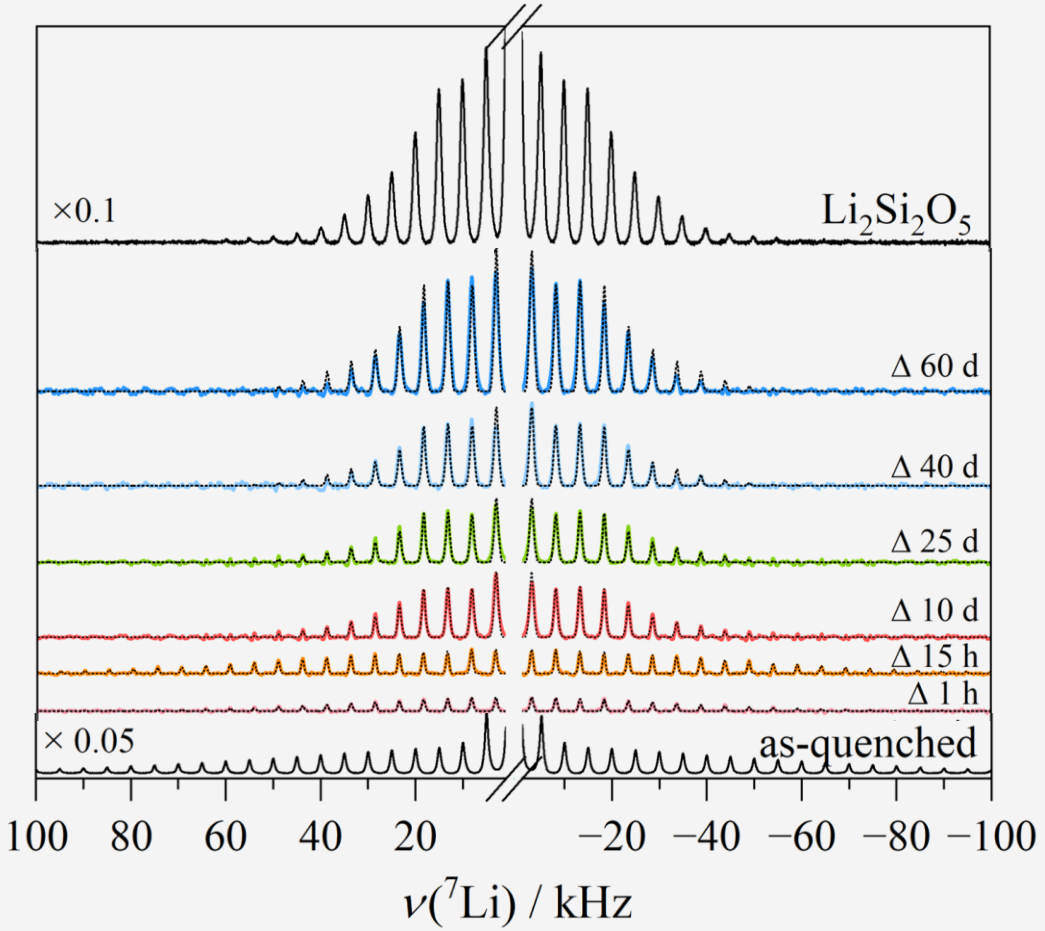
^{7}Li spin is also sensitive to changes in its local environment



^{7}Li difference spectroscopy exposes glass nucleation



SATRAS NMR



Difference spectra

Network modifier

Sub T_g annealing of LS2 glass

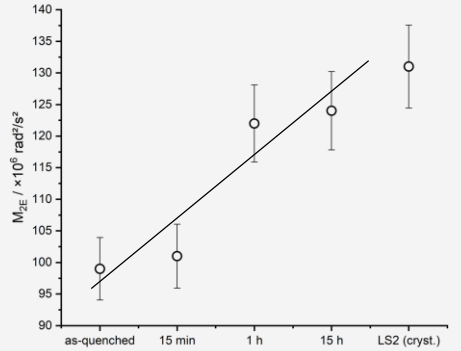
Relaxation: reorganization of spatial Lithium ion distribution towards more clustering

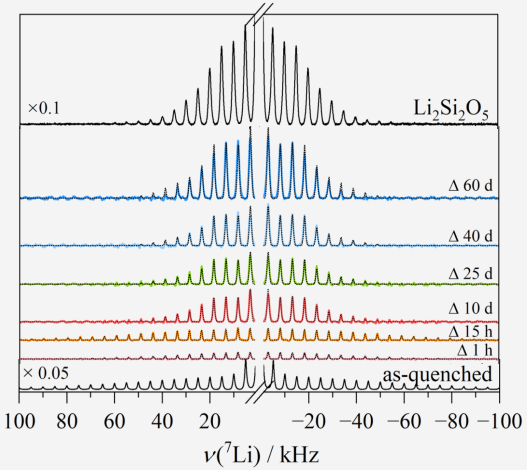
^{7}Li spin echo decay spectroscopy

5

Nucleation: profound change in electric field gradient distribution

^{7}Li SATRAS difference spectroscopy





Most relevant: Changes in electrostatic interactions network modifier ‹-› NBOs. Q^n redistribution effects minor

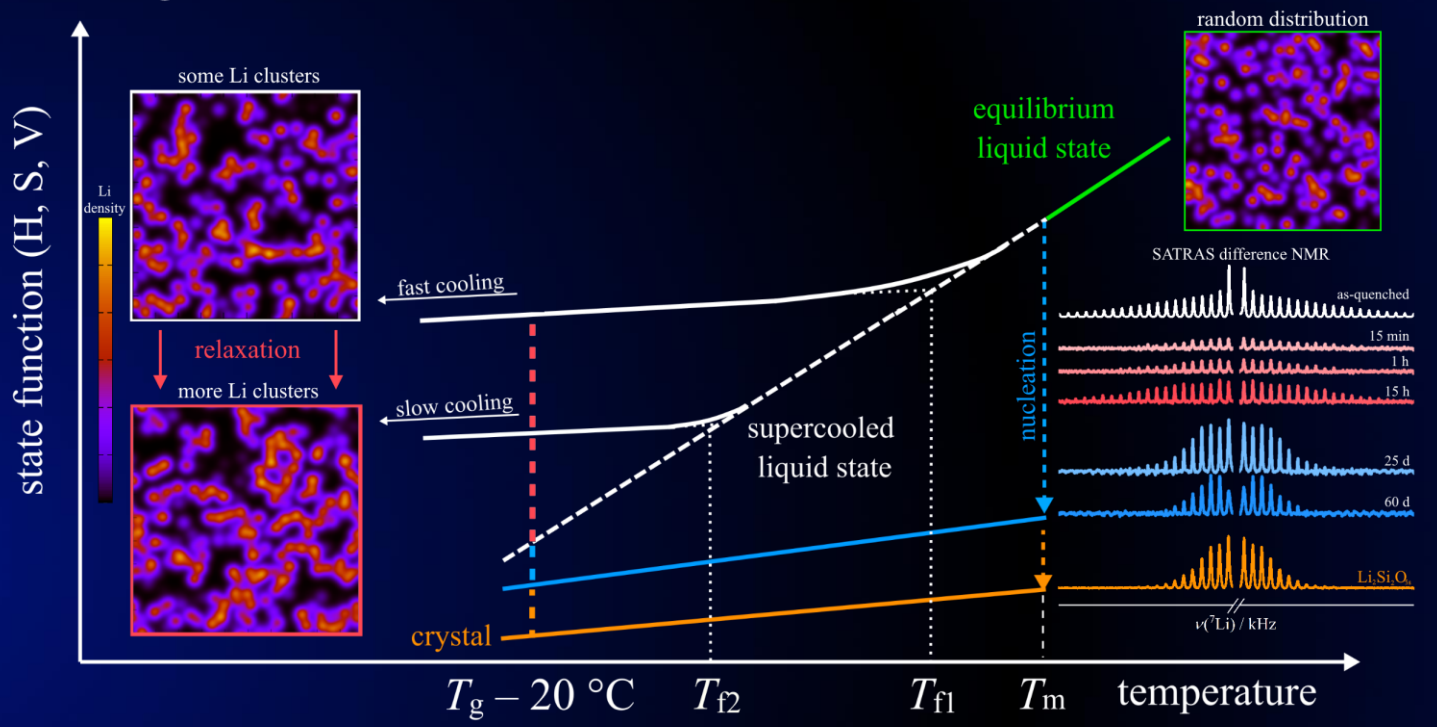
Acknowledgements

Dr. Anuraag Gaddam(MD)
USP – IFSC

Dr. Silvia H. Santagnelli(Raman)
UNESP - IQ

Prof. Hellmut Eckert
USP - IFSC

Prof. Edgar D. Zanotto
UFSCAR - DEMA

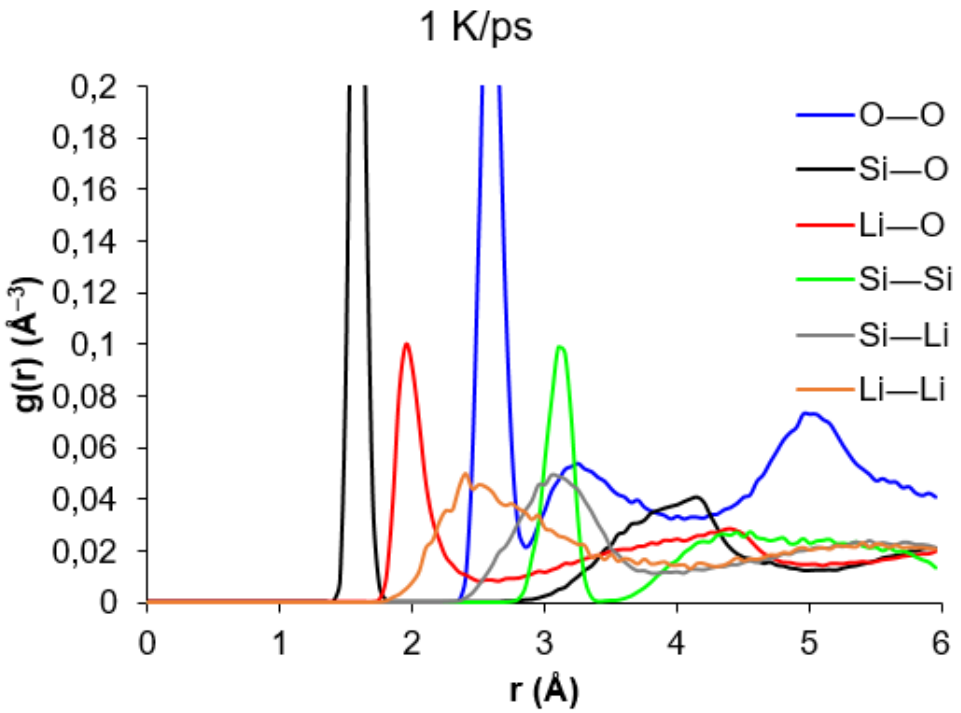


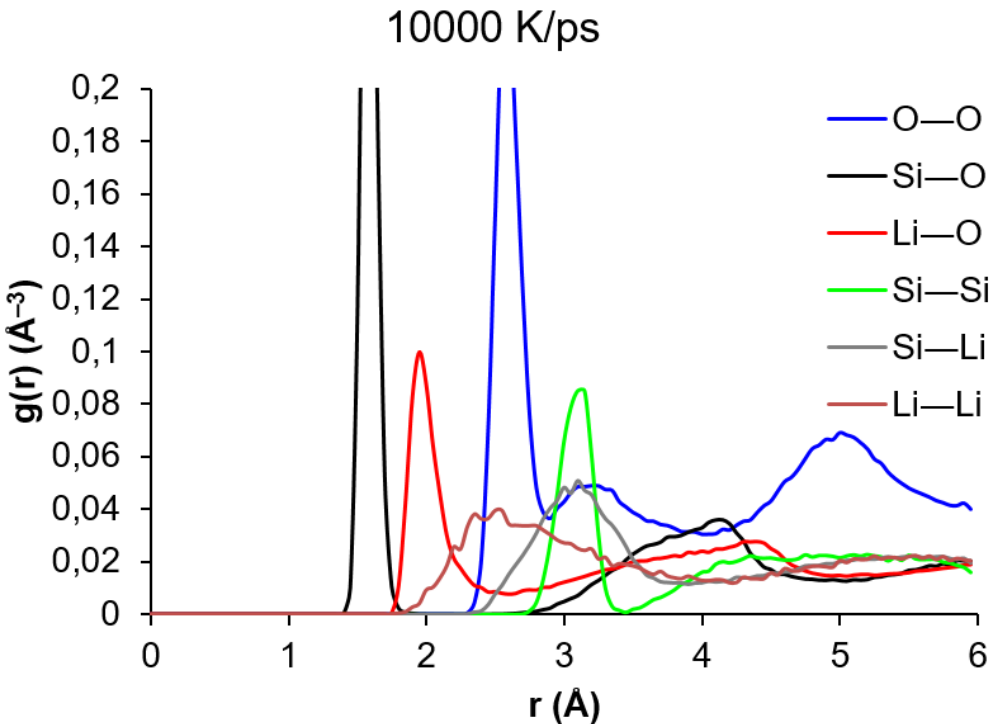
H.B. https://hbrmn.github.io
mail@bradtmueller.net

Backup Slides

MD Simulations: effect of quenching rate

$$U(r) = \frac{z_i z_j e^2}{r} + D_{ij}\left\{\left(1 - e^{-a_{ij}(r-r_0)}\right)^2 - 1\right\} + \frac{C_{ij}}{r^{12}}$$





Pair	D_{ij} (eV)	a_{ij} (Å^{-2})	r_0 (Å)	C_{ij} (eV Å^{12})
$Li^{0.6}$—$O^{-1.2}$	0.001114	3.429506	2.681360	1.0
$Si^{2.4}$—$O^{-1.2}$	0.340554	2.006700	2.100000	1.0
$O^{-1.2}$—$O^{-1.2}$	0.042395	1.379316	3.618701	22.0