Solid-state NMR of relaxation and crystallization of lithium disilicate glass

FAPESP – Baylat Workshop

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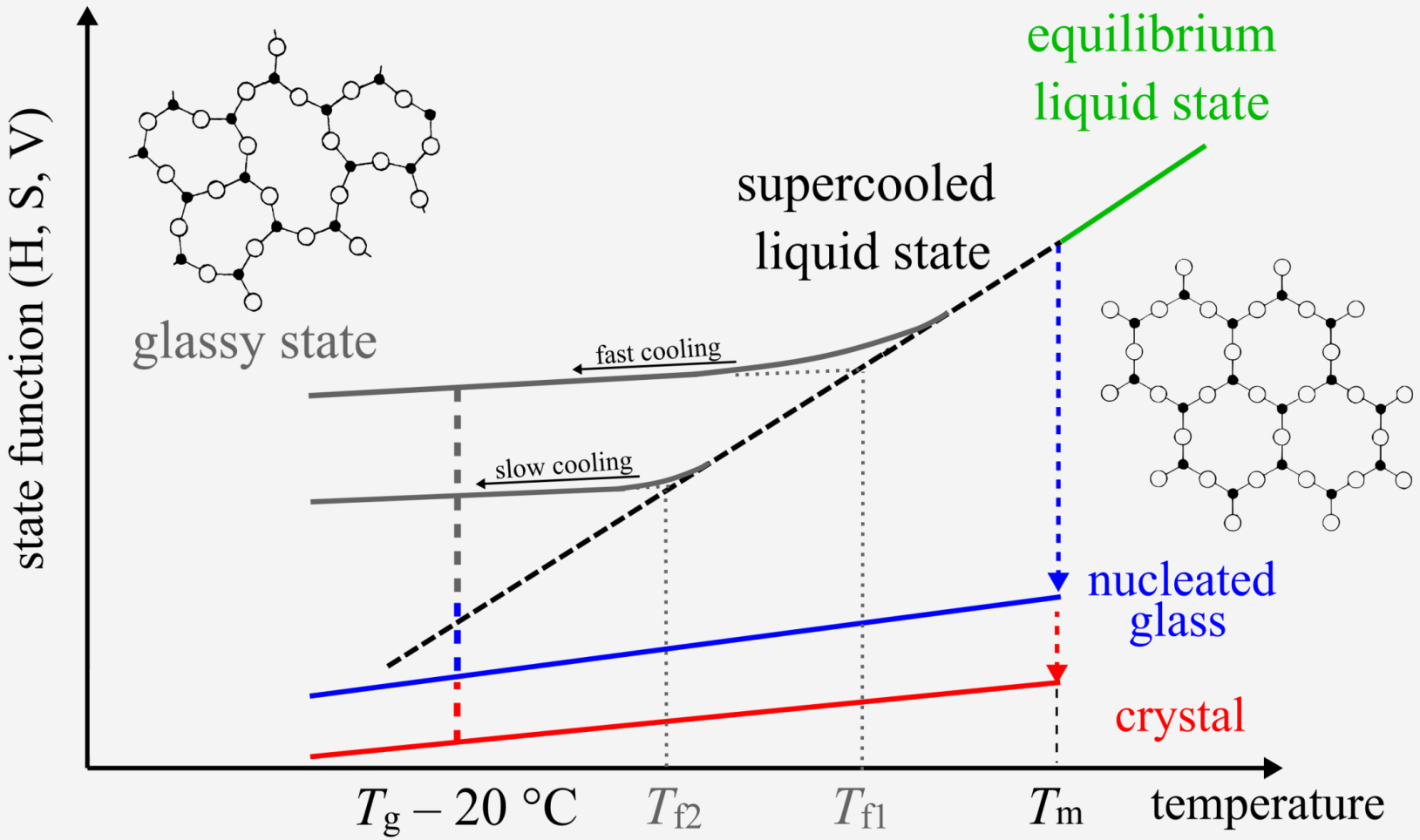
What happens structurally when glasses head towards equilibrium?



Experimental Relaxation and Nucleation Study: $Li_2Si_2O_5$ glass

1. **Glass synthesis**

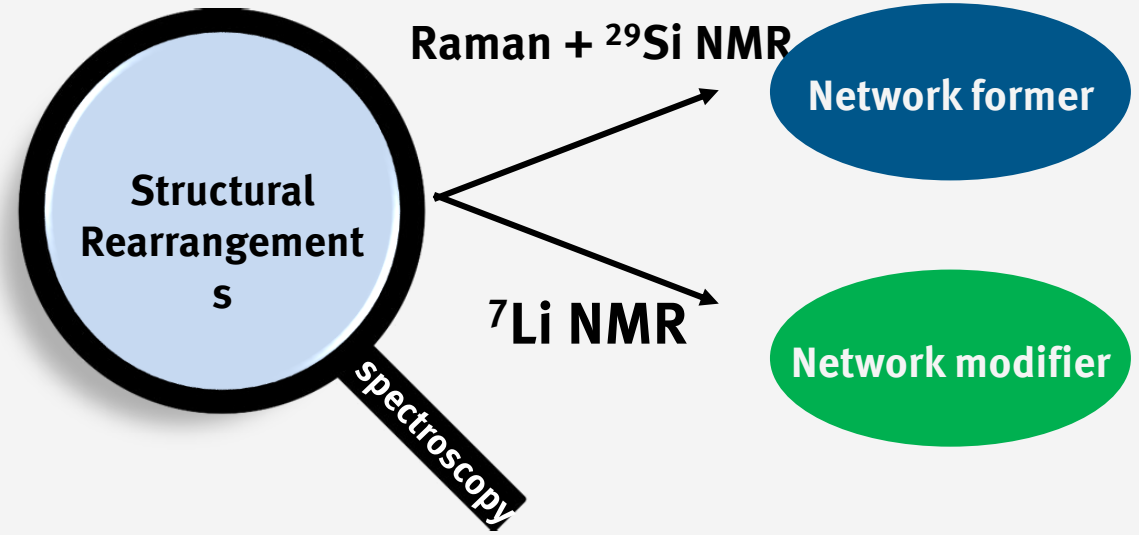
Melting at 1400 °C for 3h
Splat cooling @ RT
Repeated three times
Colorless, homogeneous glass

2. **Annealing protocol**

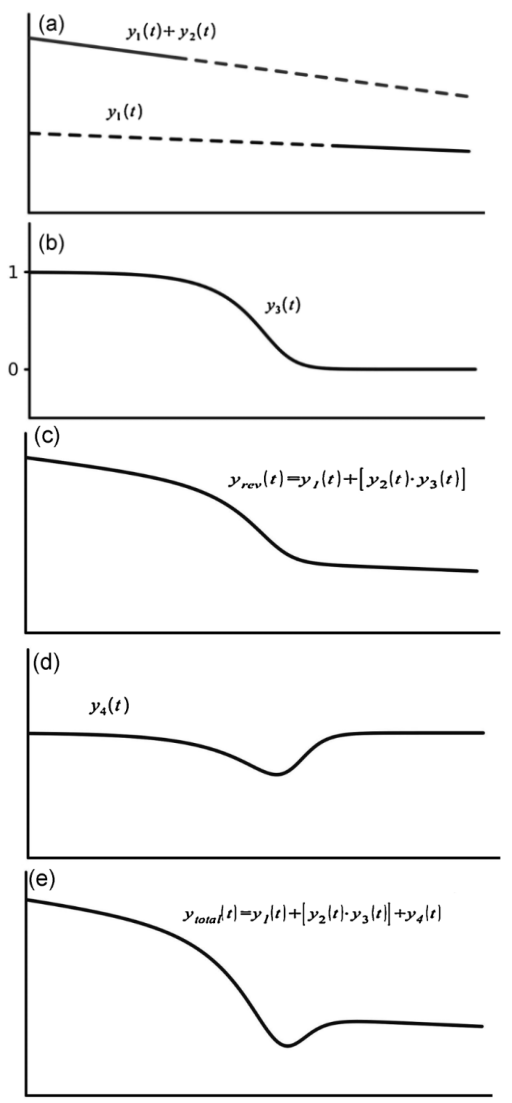
2 g pieces, vertical furnace
435 °C (ca. T_g – 20°C)
15 min to 60 d
Cooled quickly (ambient cond.)

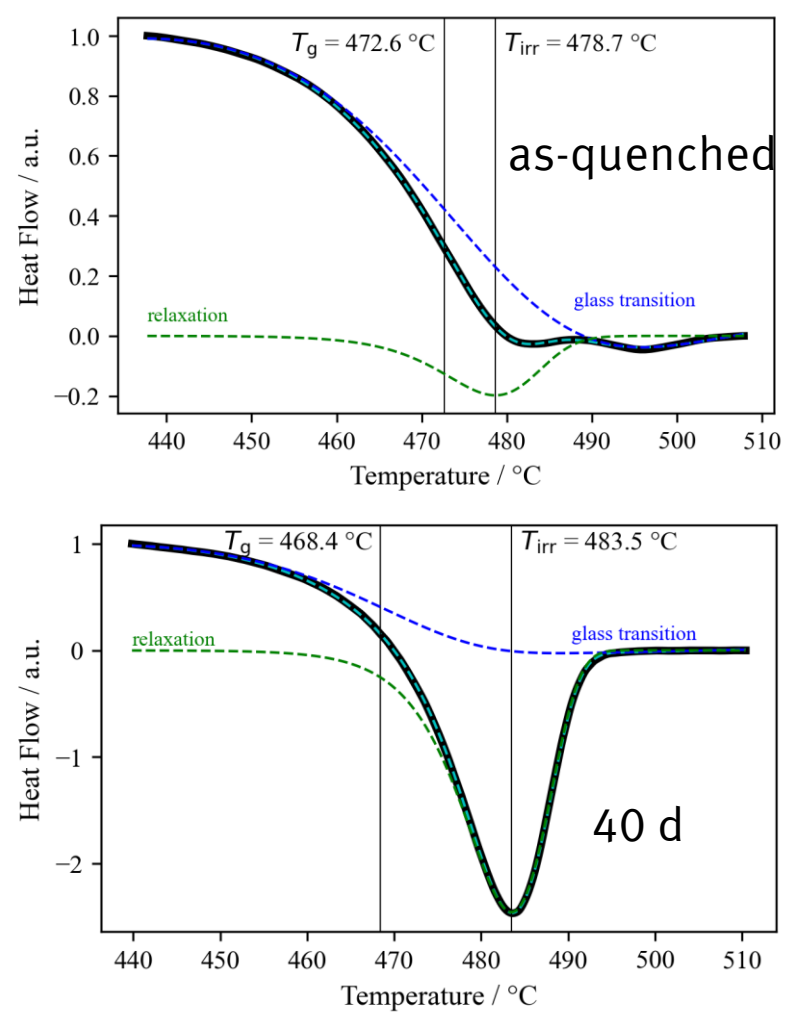
3. **Characterization**

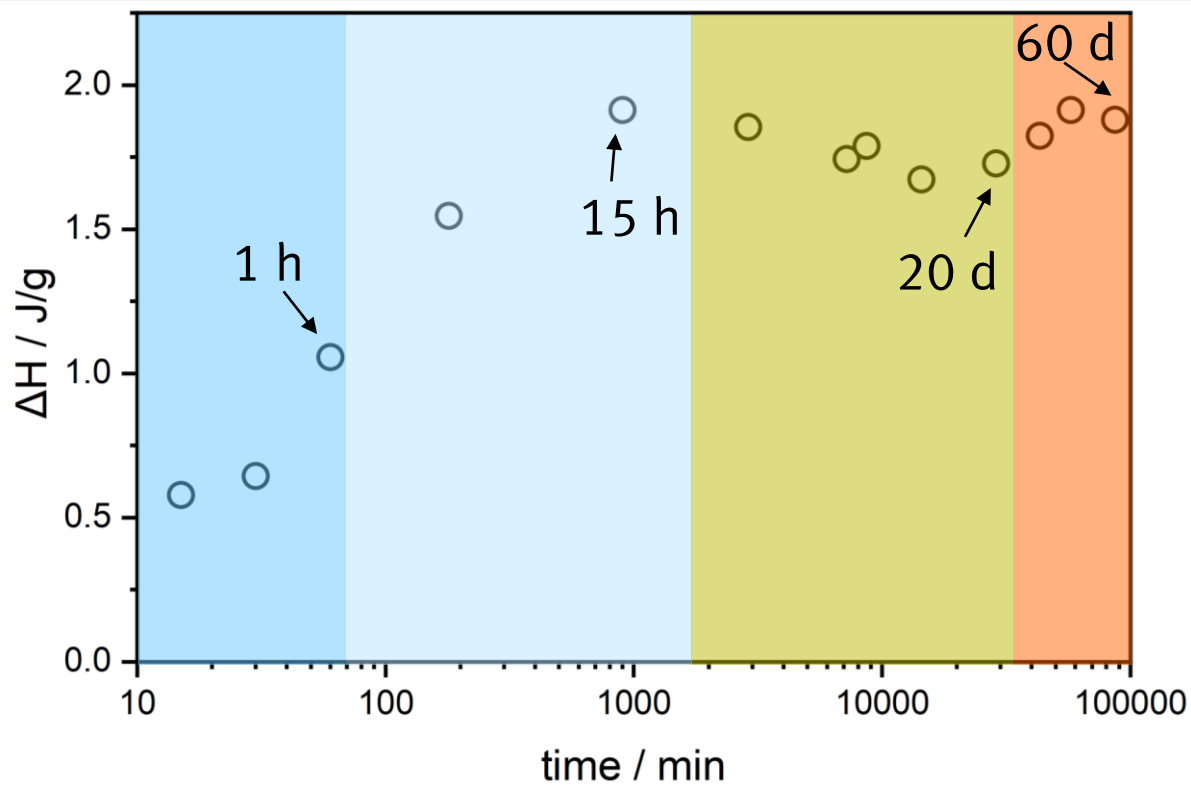
DSC, XRD
Raman
NMR
MD simulations



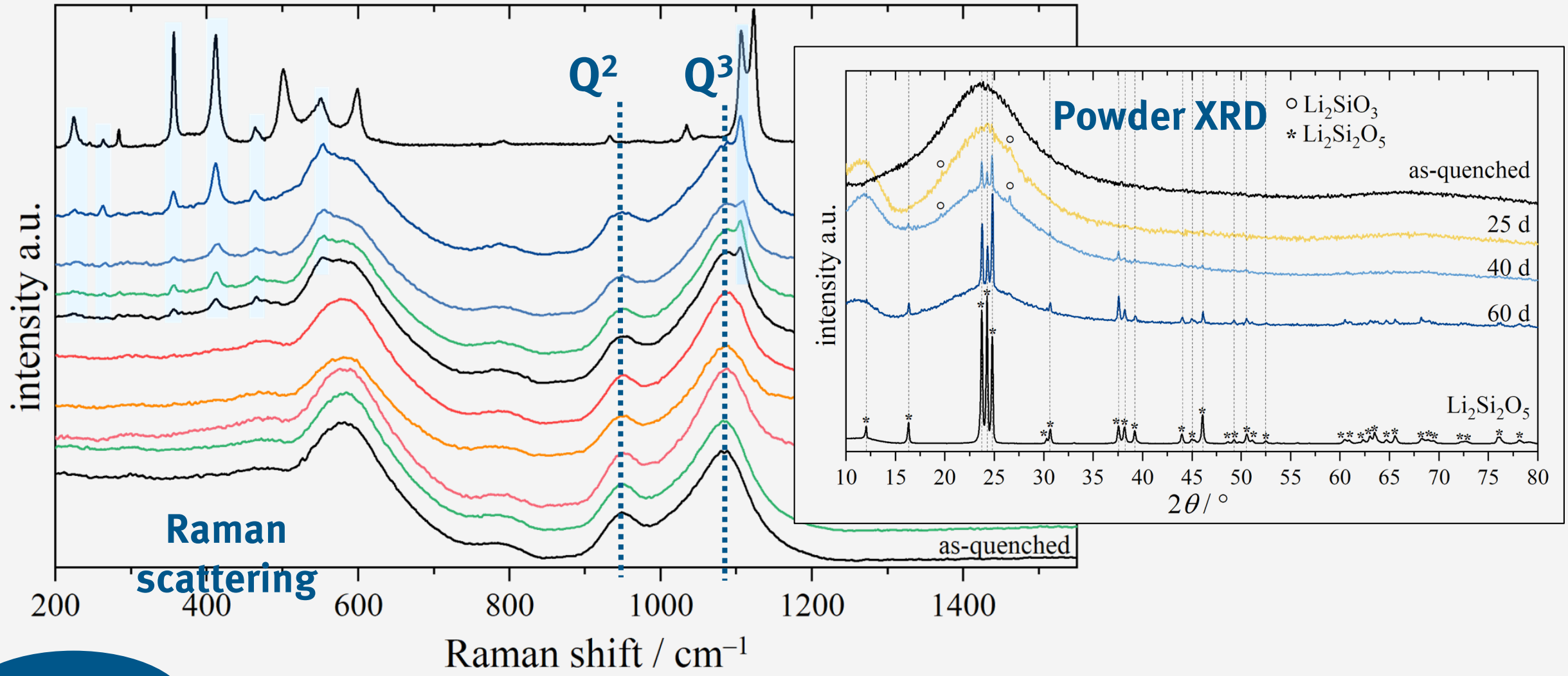
The „reversing“ of relaxation is quantifiable via DSC







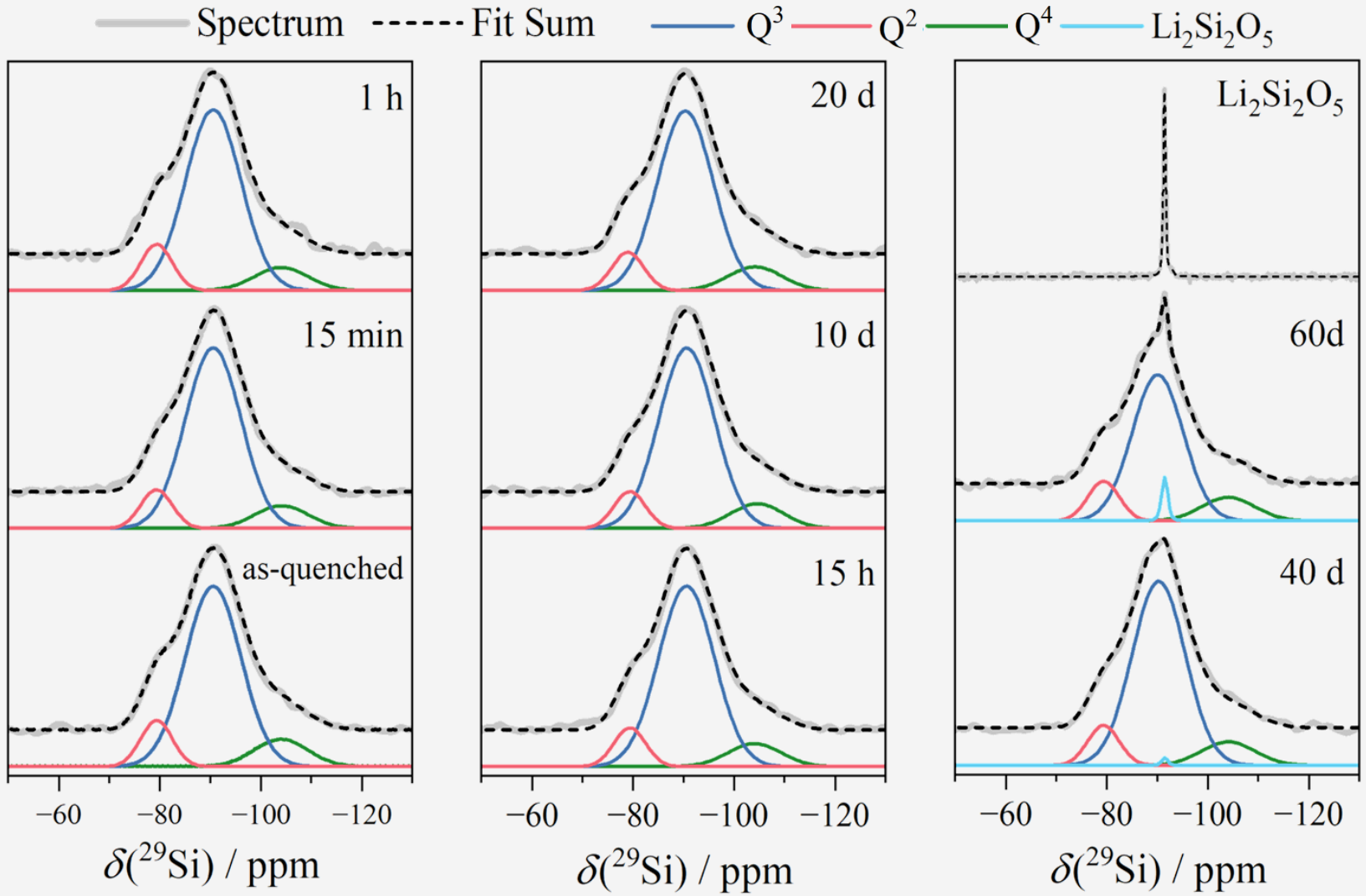
No detectable change in Q^n speciation upon annealing



Network former

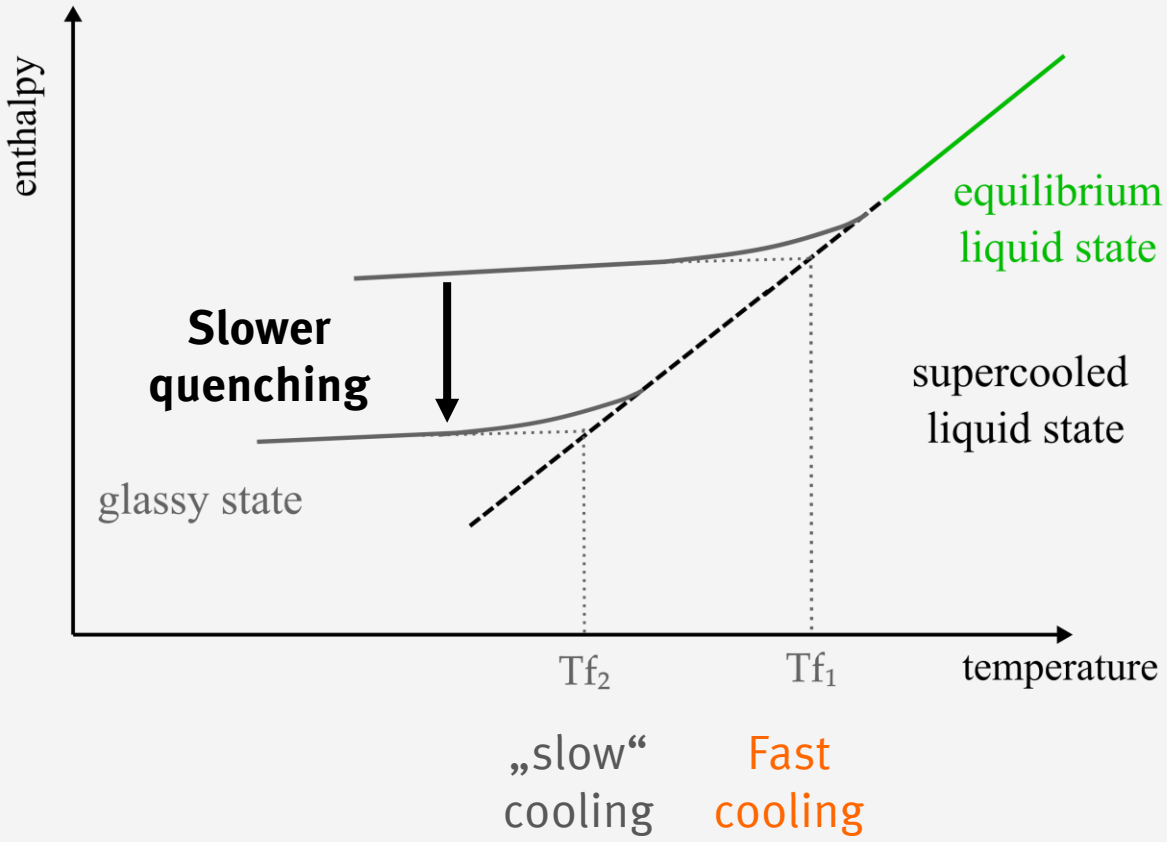
No detectable change in Q^n speciation upon annealing

^{29}Si MAS NMR

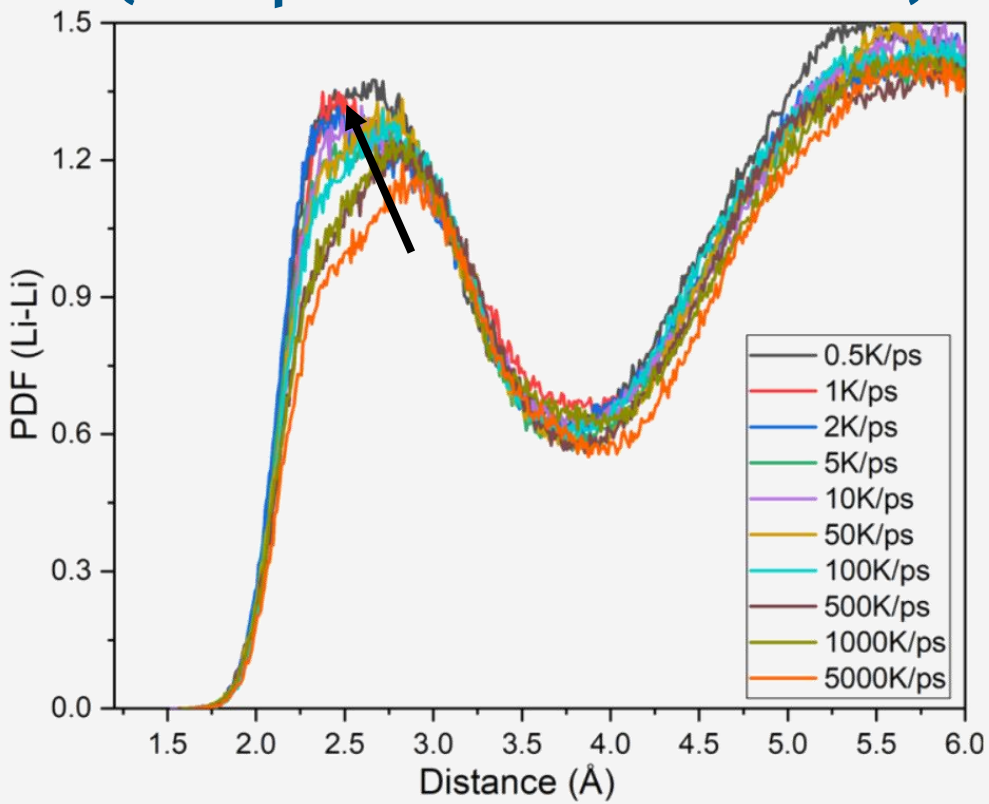


Network former

MD simulations indicate changes in network modifier distribution



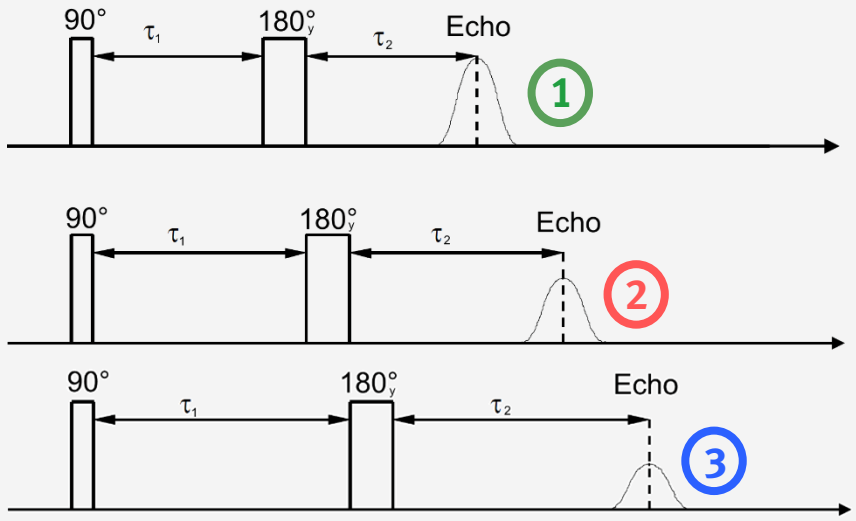
MD simulations (Li–Li pair distribution function)

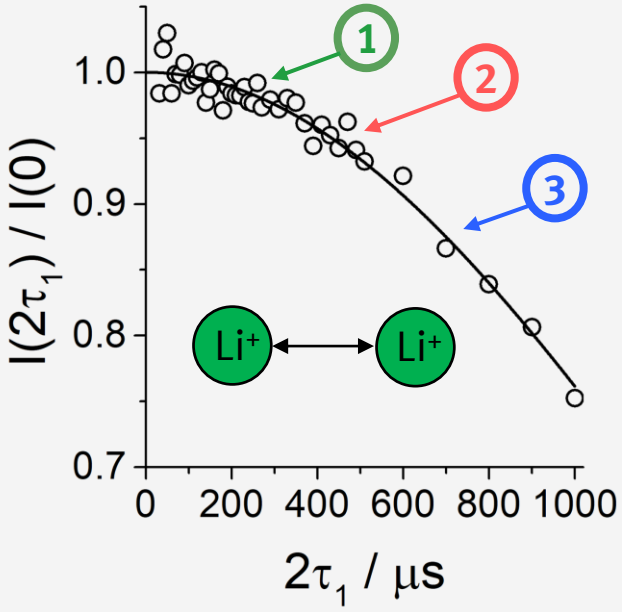


Network modifier

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

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





Experimental

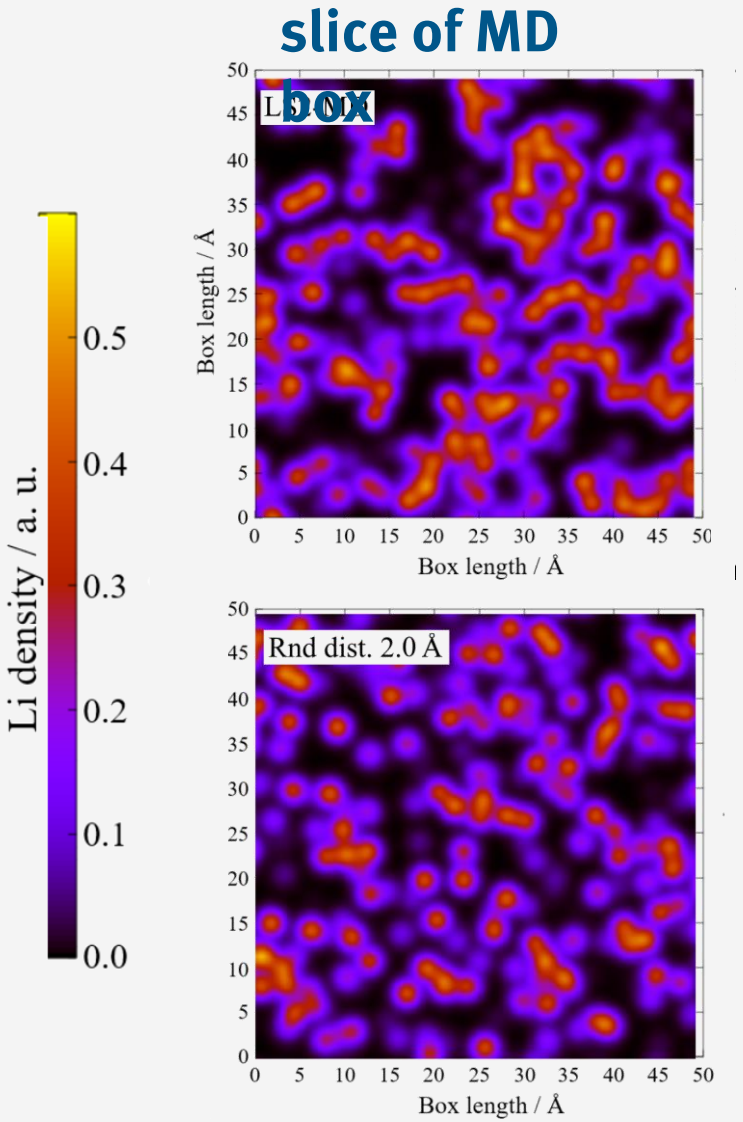
$$\frac{I(2\tau)}{I(0)} = \exp\left[-\frac{\boldsymbol{M_{2E}}}{2}(2\tau_1)^2\right]$$

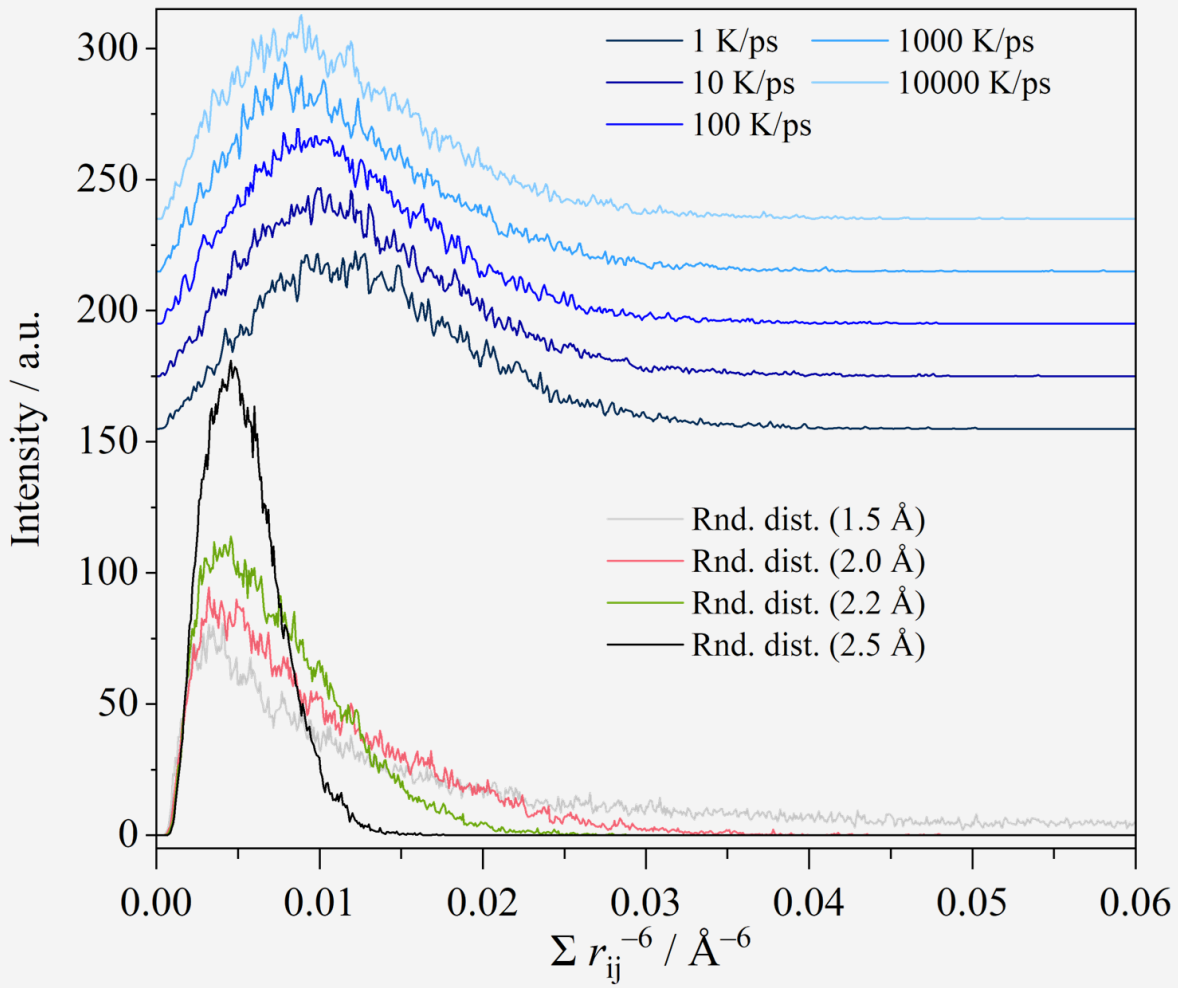
Theoretical

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

Network modifier

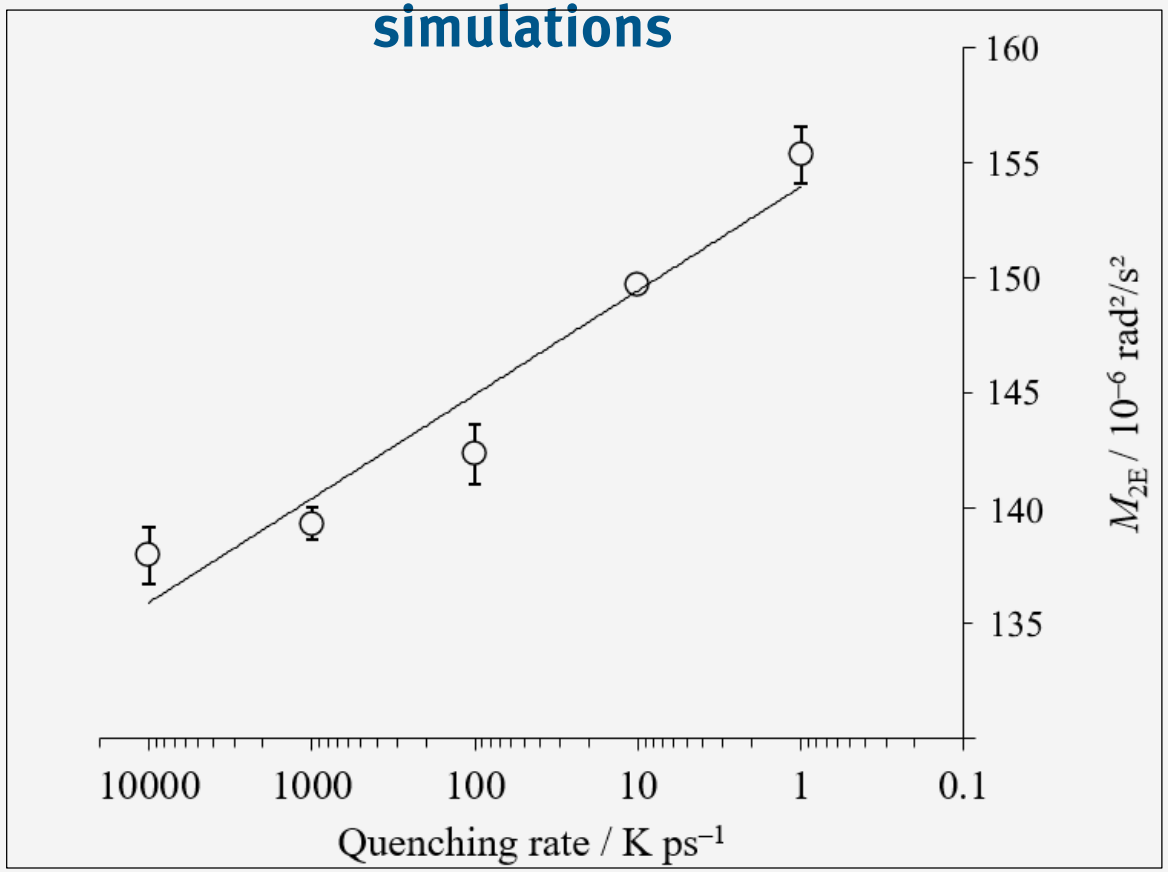
MD simulations show some Li^+ clustering for decreasing T_f



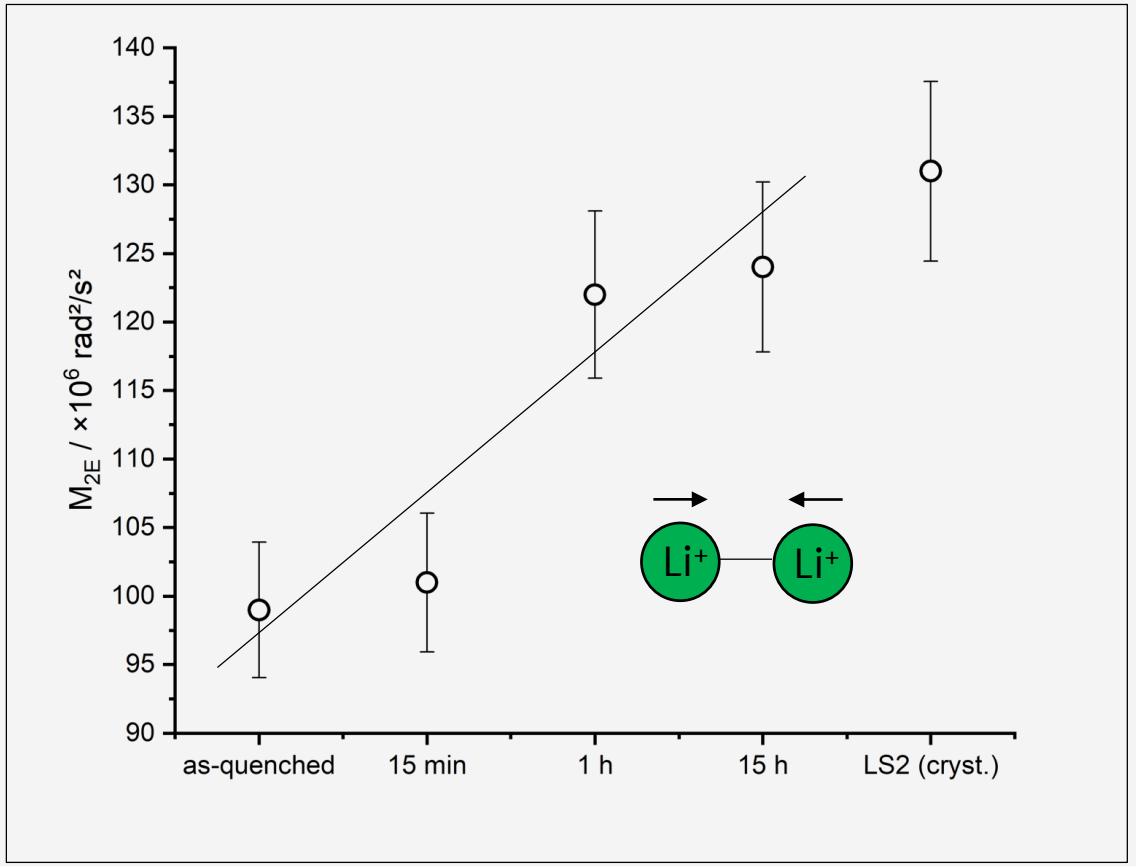


^{7}Li dipolar NMR confirms clustering with relaxation

MD simulations



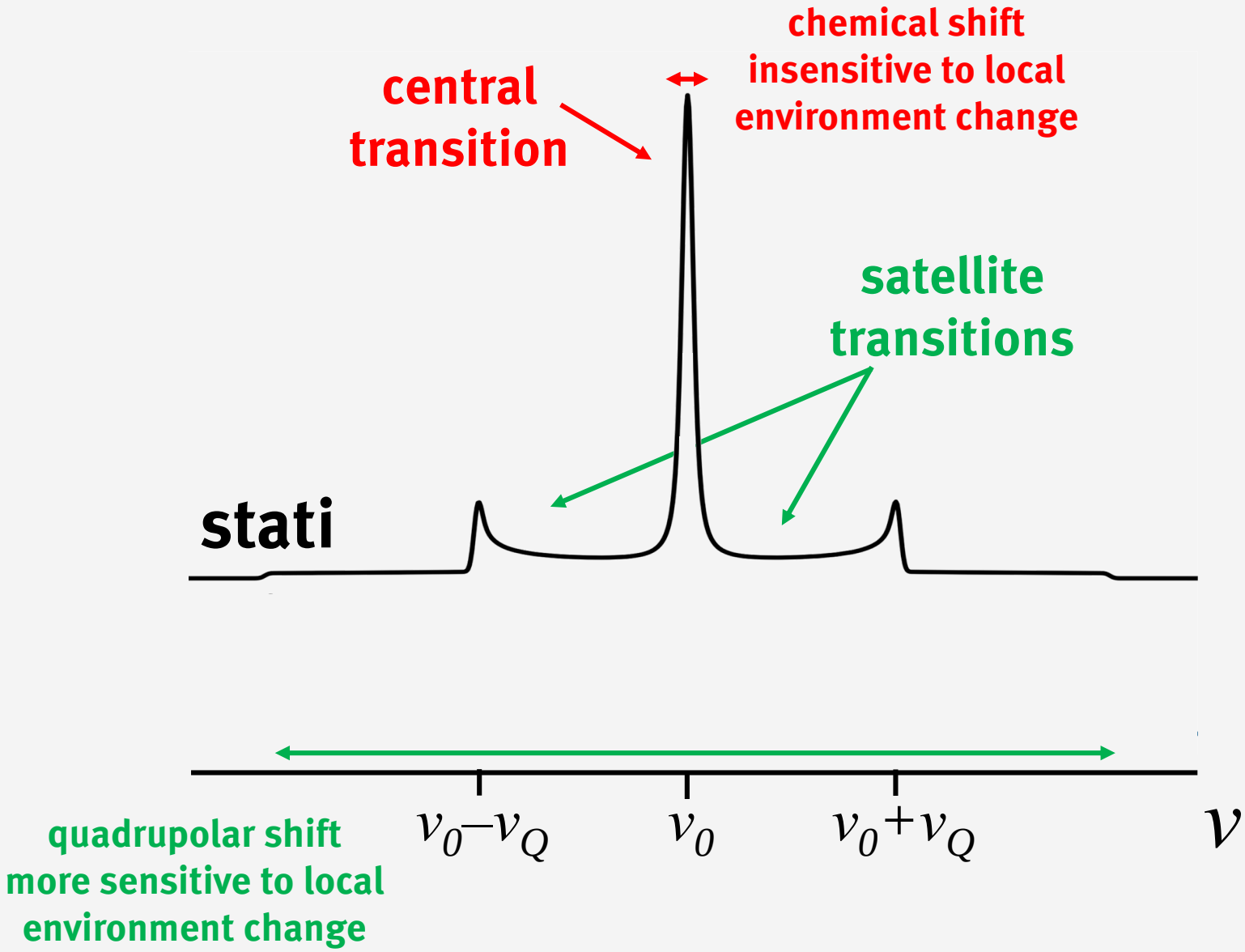
^{7}Li spin echo decay NMR



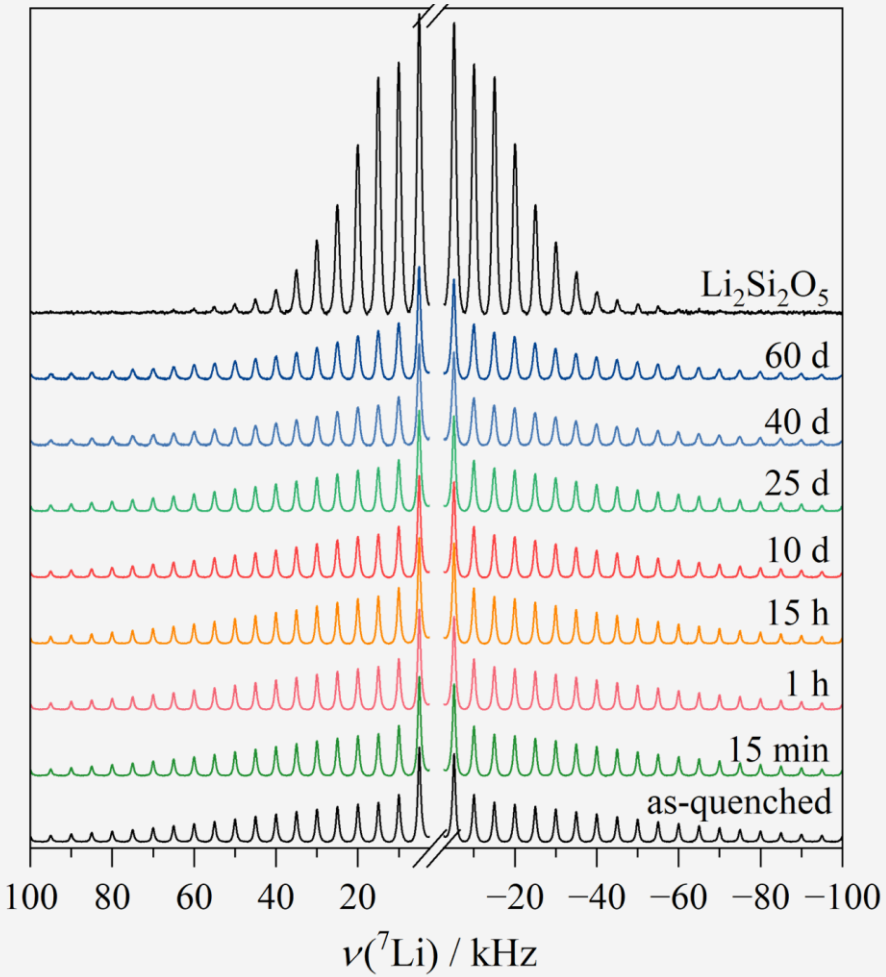
← fictive temperature

glass relaxation →

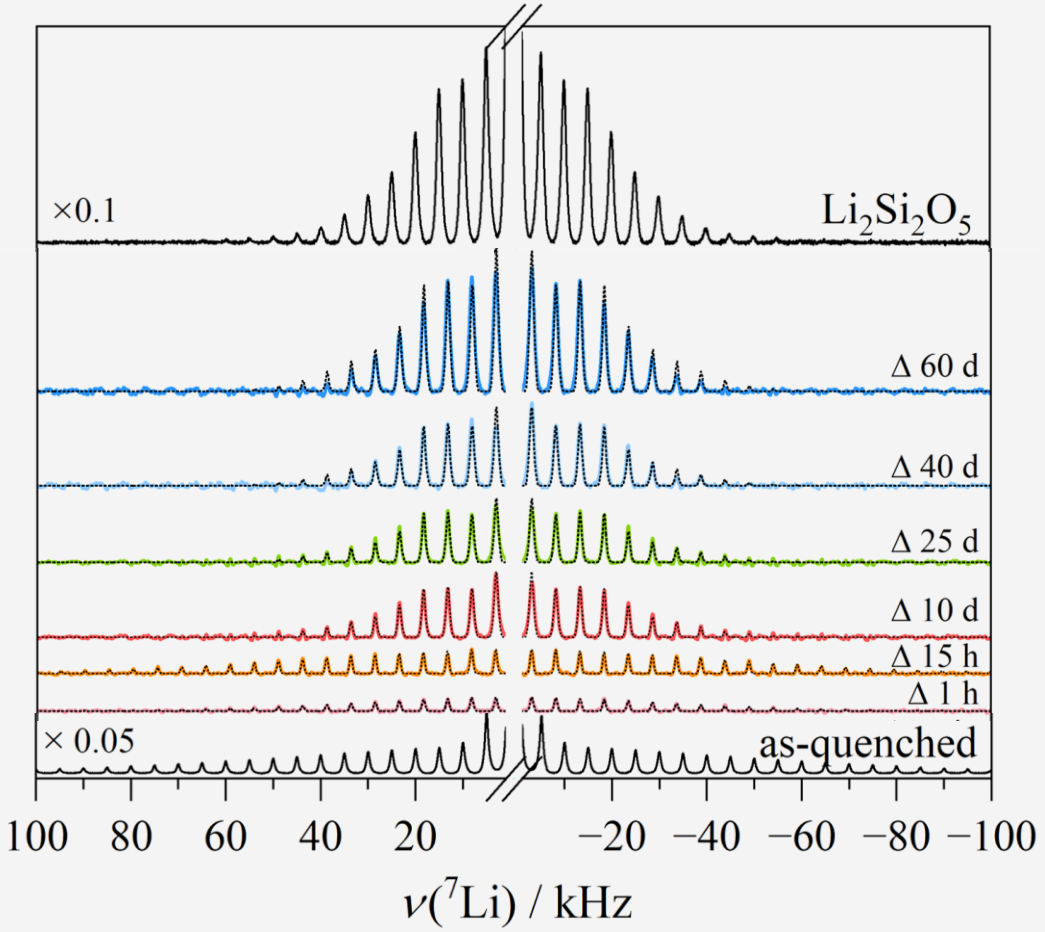
^{7}Li spin is also sensitive to changes in its local environment



^{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

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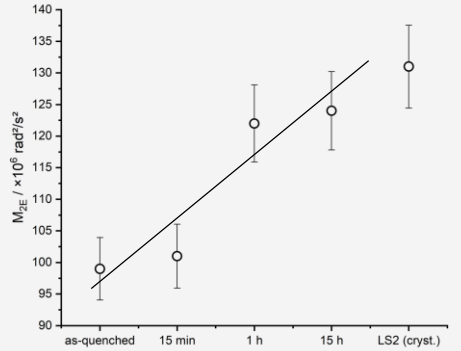
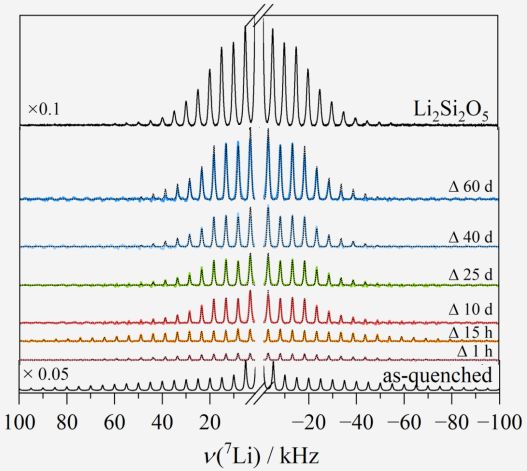


Nucleation: profound change in electric field gradient distribution

^{7}Li SATRAS difference spectroscopy



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

Acknowledgements

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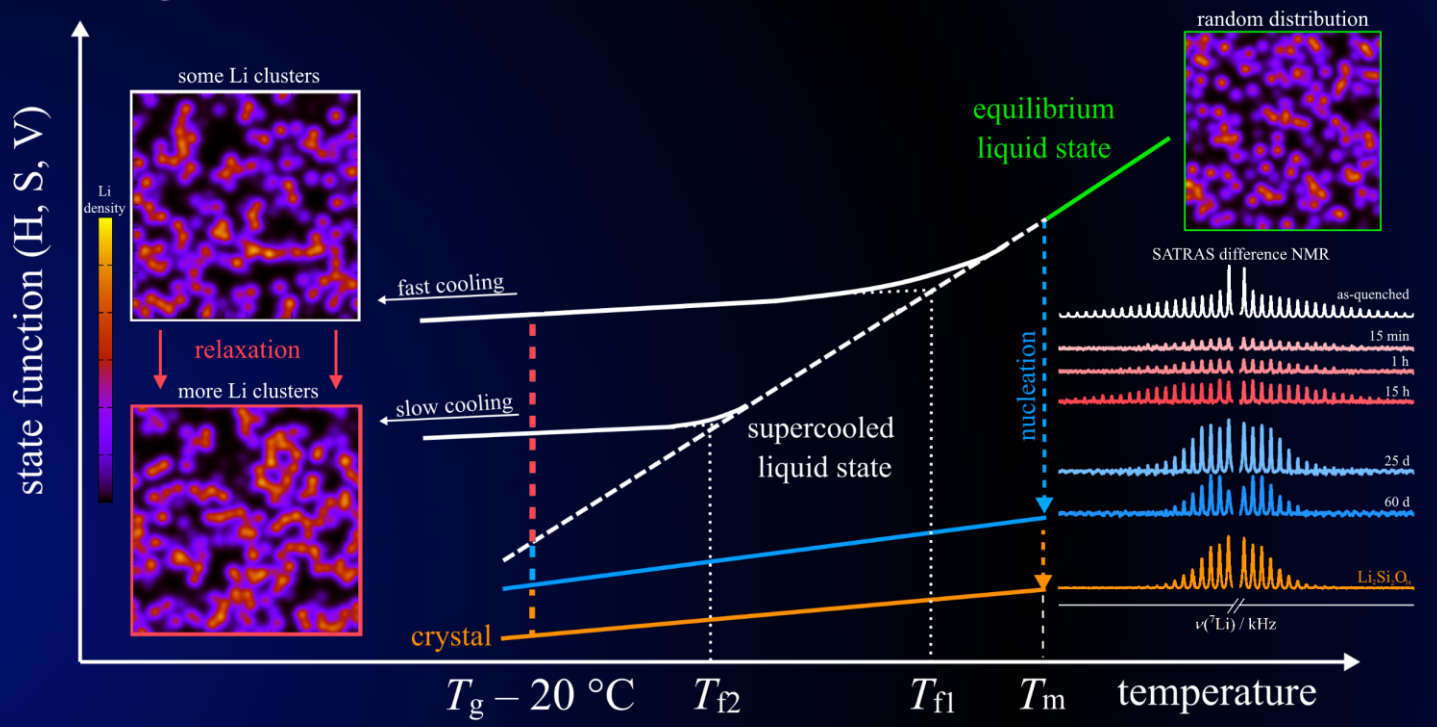
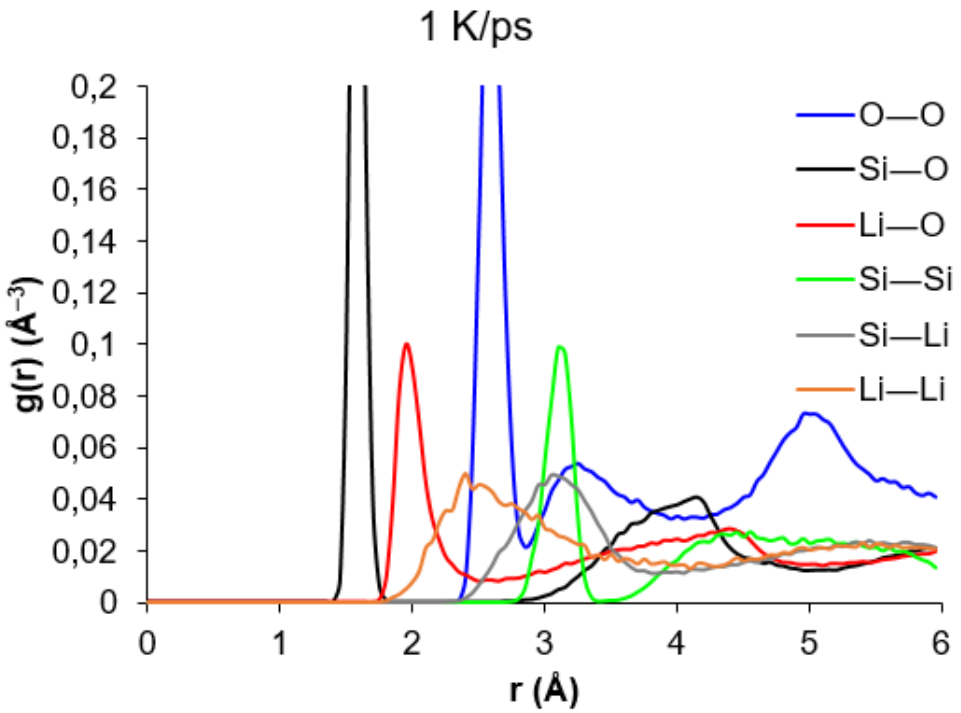


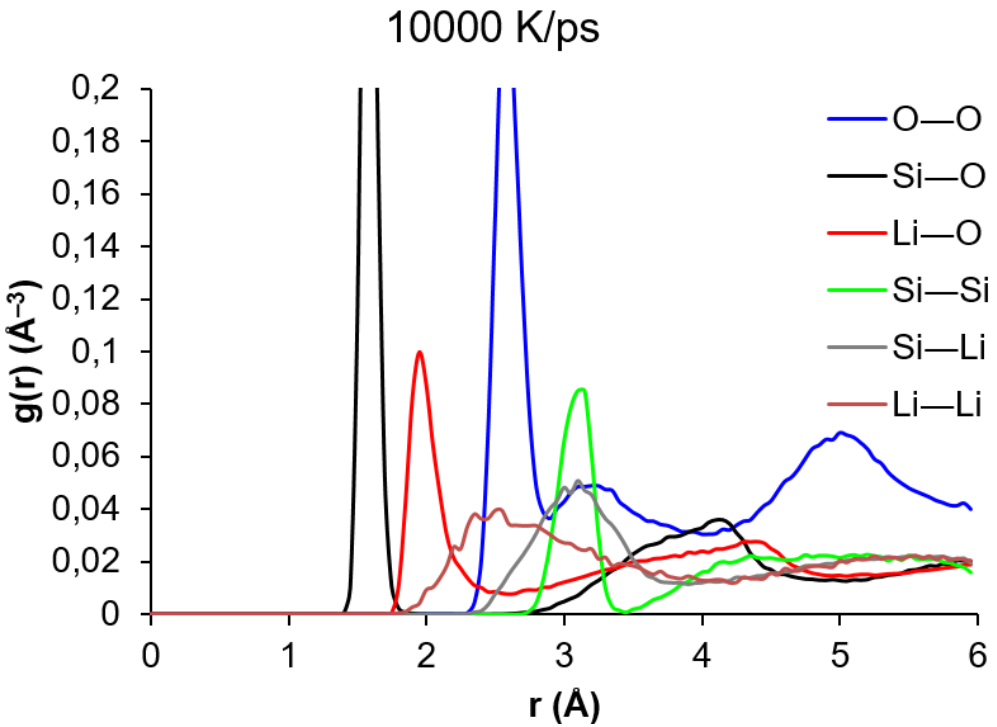
H.B. https://hbrmn.github.io
mail@bradtmueller.net

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