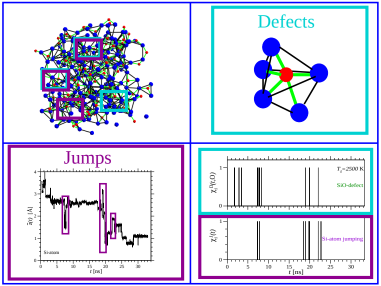
Defects in Silica Glass: A Computer Simulation

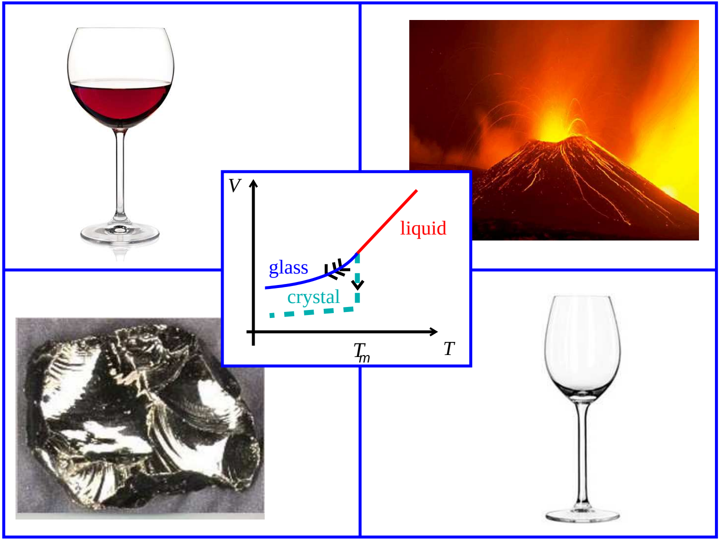
Katharina Vollmayr-Lee



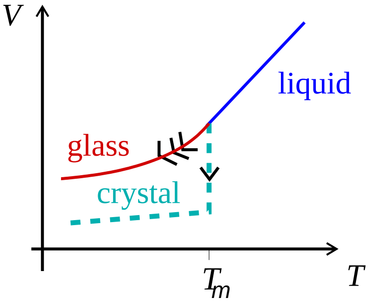
Bucknell University, April 14, 2014

Acknowledgments: A. Zippelius (Göttingen, Germany)
Supported by DFG via SFB 602 & FOR1394

Introduction: Glass

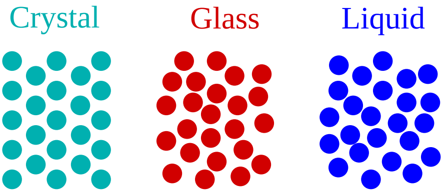


Introduction: Glass



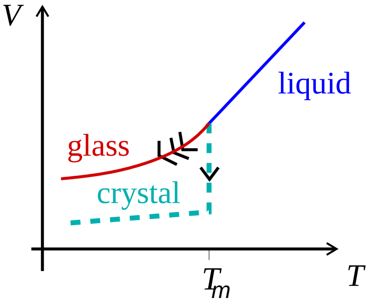
Glass:

$\longrightarrow$ system falls out of equilibrium



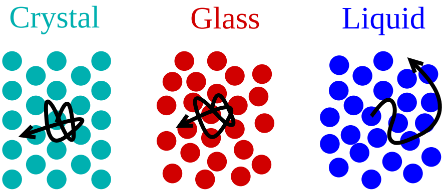
Structure: disordered

Introduction: Glass



Glass:

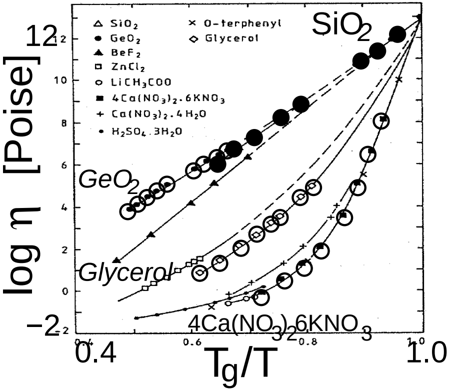
⟶ system falls out of equilibrium



Structure: disordered

Dynamics: frozen in

Introduction: Glass



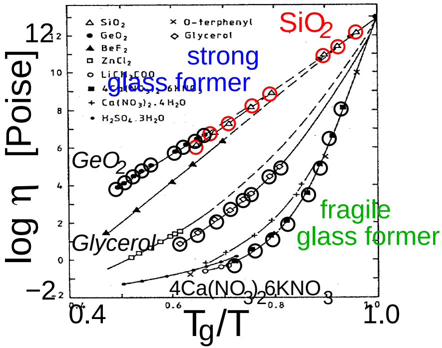
Dynamics:

Viscocity η as function of inverse temperature T

- slowing down of many decades
  $\longrightarrow$ very interesting dynamics

[C.A. Angell and W. Sichina, Ann. NY Acad. Sci. 279, 53 (1976)]

Introduction: Glass



Dynamics:

Viscocity η as function of inverse temperature T

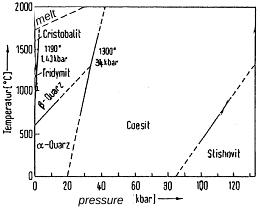
- slowing down of many decades $\longrightarrow$ very interesting dynamics
- strong and fragile glass formers
  Here: SiO_2 (strong glass former)

[C.A. Angell and W. Sichina, Ann. NY Acad. Sci. 279, 53 (1976)]

System: SiO_2

Special Properties:

- sand, rock, window glass, stove top
- similar to water (H_2O):
  - rich phase diagram
  - density maximum

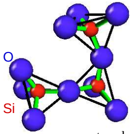


[S. Stoeffler and J. Arndt, Naturwissenschaften 56, 100 (1969)]

Model: BKS Potential

[B.W.H. van Beest *et al.*, PRL 64, 1955 (1990)]

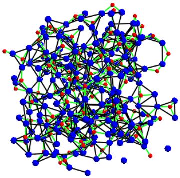
$$\phi(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} e^{-B_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^6}$$



network
(potential only "spheres")

112 Si & 224 O $\quad \rho = 2.32$ g/cm^3

$T_c = 3330$ K



Numerical Solution: Euler Step

Initialize:

$x(t_0),\ v(t_0),\ a(t_0)$

↓

$x(t_0+\Delta t),\ v(t_0+\Delta t),\ a(t_0+\Delta t)$

↓

$x(t_0+2\Delta t),\ v(t_0+2\Delta t),\ a(t_0+2\Delta t)$

↓ etc.

↓ = Iteration Step:

$$x(t+\Delta t)=x(t)+v(t)\Delta t$$
$$v(t+\Delta t)=v(t)+a(t)\Delta t$$
$$a(t)=F(t)/m=-(dU/dx)(t)$$

Molecular Dynamics Simulation

particles $i = 1, \ldots, N$

three dimensions

Initialize:

$\vec{x}_i(t_0), \ \vec{v}_i(t_0), \ \vec{a}_i(t_0)$

↓

$\vec{x}_i(t_0 + \Delta t), \ \vec{v}_i(t_0 + \Delta t), \ \vec{a}_i(t_0 + \Delta t)$

↓

$\vec{x}_i(t_0 + 2\Delta t), \ \vec{v}_i(t_0 + 2\Delta t), \ \vec{a}_i(t_0 + 2\Delta t)$

↓ etc.

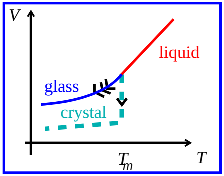
↓ = Iteration Step: (Velocity Verlet)

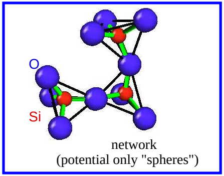
$$\vec{x}_i(t+\Delta t) = \vec{x}_i(t) + \vec{v}_i(t)\Delta t + \vec{a}_i(t)(\Delta t)^2/2$$

$$\vec{v}_i(t+\Delta t) = \vec{v}_i(t) + (\vec{a}_i(t) + \vec{a}_i(t+\Delta t))\,\Delta t/2$$

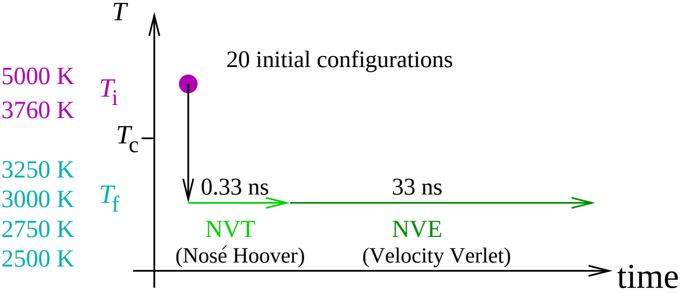
$$\vec{a}_i(t) = \vec{F}_i(t)/m_i = -\vec{\nabla}_i U(t)/m_i$$

Molecular Dynamics Simulations

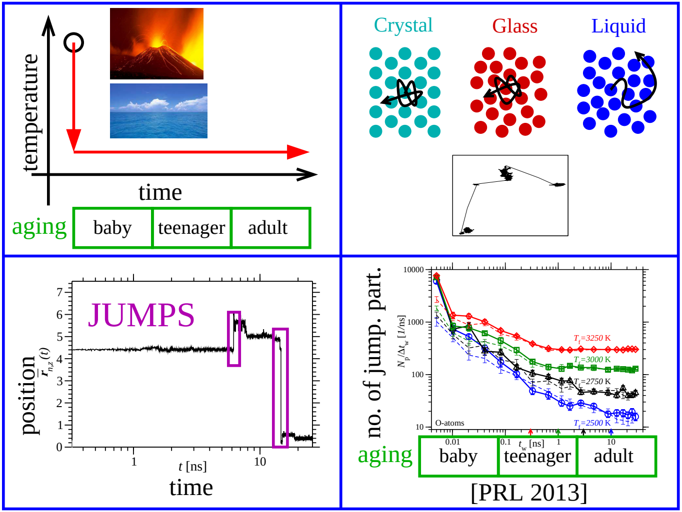




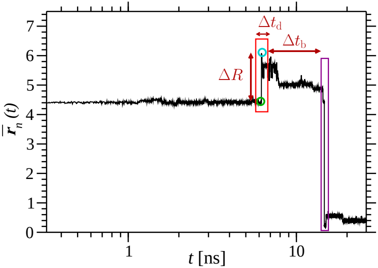
Molecular Dynamics Simulations:



Dynamics of SiO_2: Single Particle Jumps



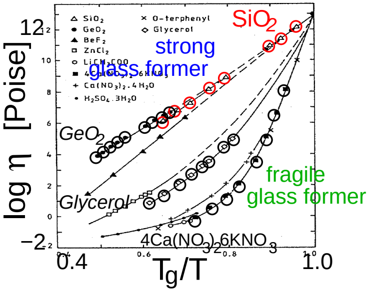
Motivation for Defect-Studies



Single Particle Jump Dynamics:

- Jump-Size and Time in Cage t_w-independent!
- Number of Jumping Particles t_w-dependent

[KVL, R. Bjorkquist, L. Chambers, PRL 2013]



[C.A. Angell and W. Sichina, Ann. NY Acad. Sci. 279, 53

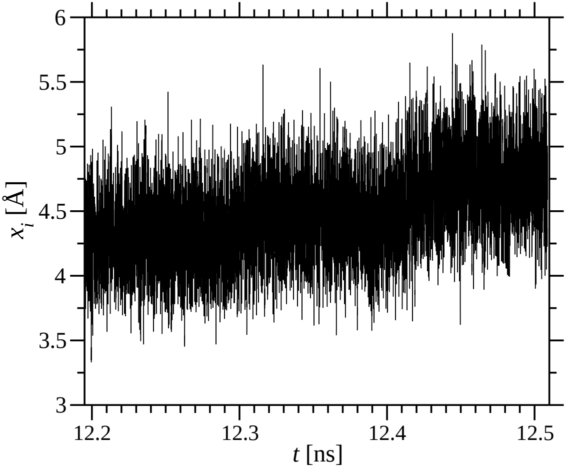
Comparison:

compare with fragile glass former [Warren, Rottler]

Surprising similarity
of strong and fragile glass formers
$\longrightarrow$ study SiO_2 specific microscopic dynamics

Single Particle Trajectory

Goal: study SiO_2 specific microscopic dynamics

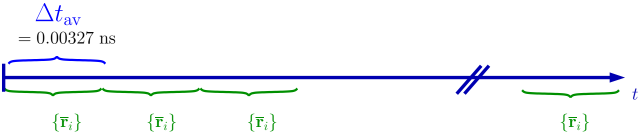


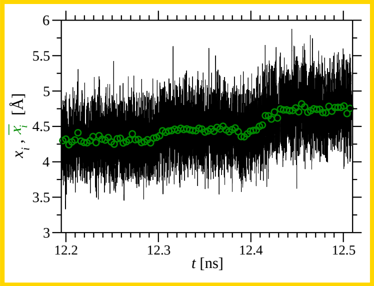
⟶ Extract key features of structural changes.

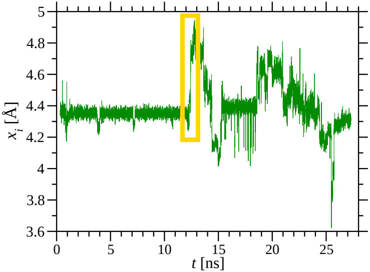
Time Averaged Trajectories

Goal: Extract key features of structural changes.

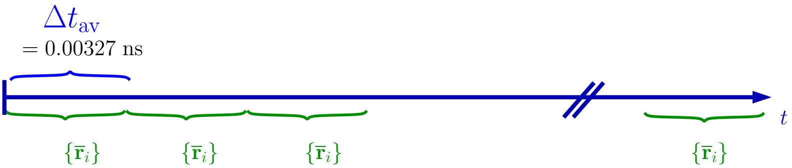
Time Averaged Single Particle Trajectory:

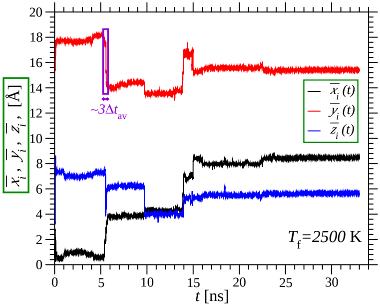


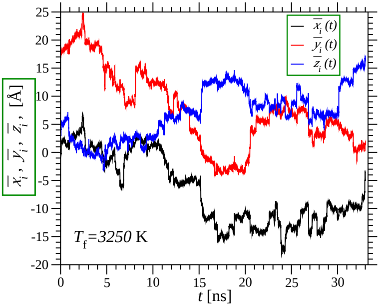




Time Averaged Trajectories



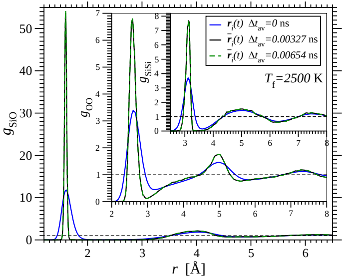


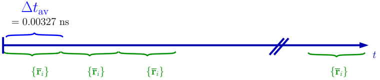


$\longrightarrow$ strong temperature dependence

Structure: Radial Distribution Function

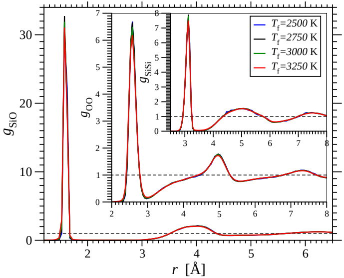
$$g_{\alpha\beta}(r) = \left\langle \frac{V}{N_\alpha N_\beta} \sum_{i=1}^{N_\alpha} \sum_{\substack{j=1 \\ j\neq i}}^{N_\beta} \delta(|\mathbf{r}| - |\bar{\mathbf{r}}_{ij}(t)|) \right\rangle \qquad \alpha, \beta \in \{\text{Si,O}\}$$





Time Average:

- time average sharpens peaks



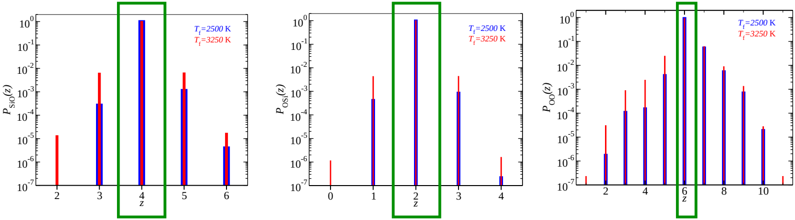
Temperature Dependence:

- highly ordered
- almost no temperature dependence

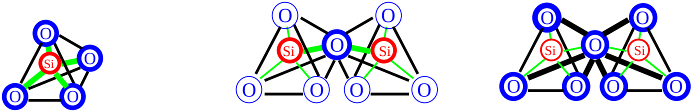
Structure: Coordination Number

$z_i^{\alpha\beta}$ = number of nearest neighbors

via minimum of $g_{\alpha\beta}$ $(\alpha, \beta \in \{\text{Si,O}\})$



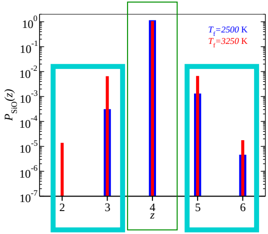
$z^{\mathrm{SiO}}_{\mathrm{perfect}} = 4$ $z^{\mathrm{OSi}}_{\mathrm{perfect}} = 2$ $z^{\mathrm{OO}}_{\mathrm{perfect}} = 6$



$\longrightarrow$ sharply peaked

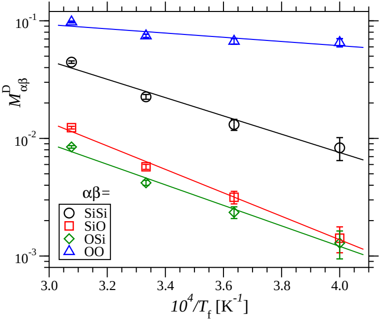
$\longrightarrow$ temperature dependence in defects

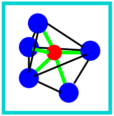
Defects



$$z^{\mathrm{SiO}}_{\mathrm{perfect}} = 4$$

$$z^{\mathrm{SiO}} \neq 4$$



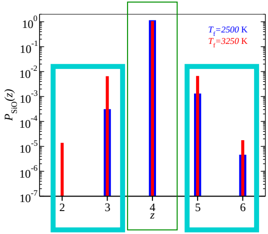


Defect Definition:

$$z_i^{\alpha\beta} \neq z_{\mathrm{perfect}}^{\alpha\beta}$$

Number of Defects:

- mostly OO-defects
- strong temperature dependence (Arrhenius)



$z^{\mathrm{SiO}}_{\mathrm{perfect}} = 4$

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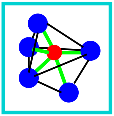

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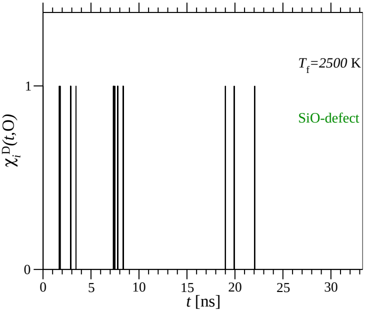


Dynamics of Defects:

$$\chi_i^{\mathrm{D}}(t,\beta) = \begin{cases} 1 & \text{if} \quad z_i^{\alpha\beta}(t) \neq z_{\mathrm{perfect}}^{\alpha\beta} \\ 0 & \text{if} \quad z_i^{\alpha\beta}(t) = z_{\mathrm{perfect}}^{\alpha\beta} \end{cases}$$

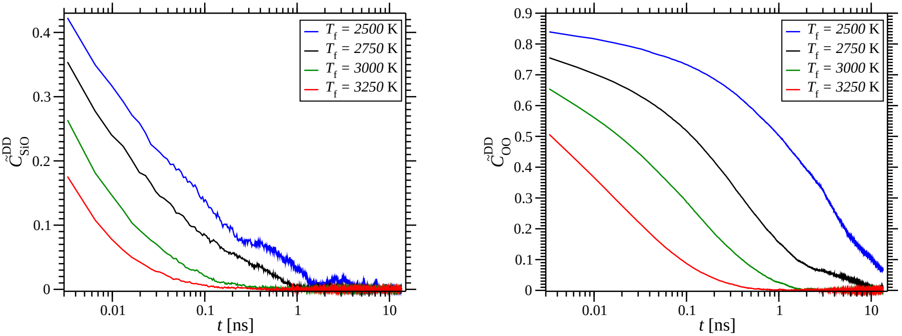
- SiO-defects are sudden rare events

Defect-Defect Correlation

$$\chi_i^{\mathrm{D}}(t,\beta) = \begin{cases} 1 & \text{if at time } t \quad z_i^{\alpha\beta}(t) \neq z_{\mathrm{perfect}}^{\alpha\beta} \\ 0 & \text{if at time } t \quad z_i^{\alpha\beta}(t) = z_{\mathrm{perfect}}^{\alpha\beta} \end{cases}$$

$$C^{\mathrm{DD}}(t,\alpha,\beta) = \left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t_0,\beta)\chi_i^{\mathrm{D}}(t_0+t,\beta) \right\rangle - \left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t_0,\beta) \right\rangle \left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t_0+t,\beta) \right\rangle$$

$$\tilde{C}_{\alpha,\beta}^{\mathrm{DD}}(t) = \frac{C^{\mathrm{DD}}(t,\alpha,\beta)}{C^{\mathrm{DD}}(t=0,\alpha,\beta)}$$

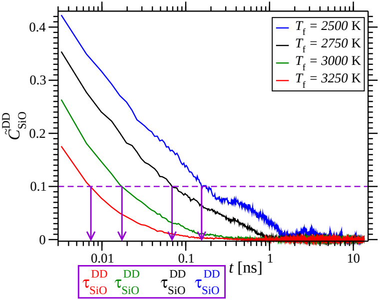


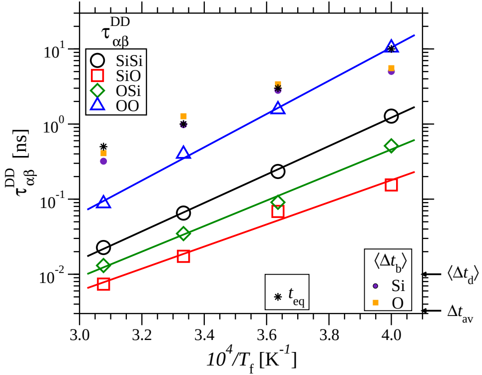
$\longrightarrow$ strong temperature dependence

$\longrightarrow$ life time of defects?

Life Time of Defects

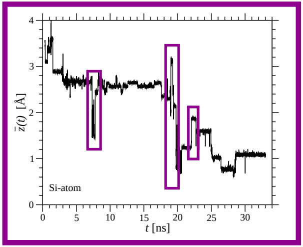
$$C^{\mathrm{DD}}(t,\alpha,\beta) = \left\langle \frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t_0,\beta)\chi_i^{\mathrm{D}}(t_0+t,\beta)\right\rangle - \left\langle \frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t_0,\beta)\right\rangle \left\langle \frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t_0+t,\beta)\right\rangle$$

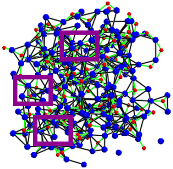


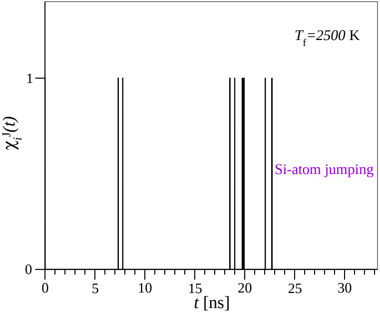


- SiO- & OSi-defects short-lived (flashes)
- OO-defects longer lived
- Arrhenius fits

Jumps





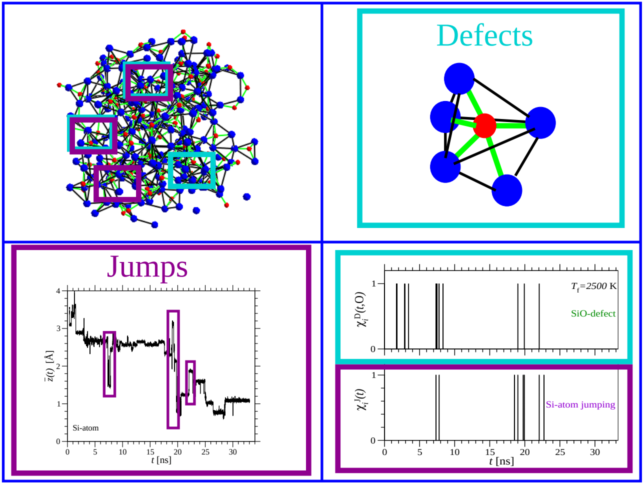


Jump Dynamics:

$$\chi_i^{\mathrm{J}}(t) = \begin{cases} 1 & \text{during jump} \\ 0 & \text{otherwise} \end{cases}$$

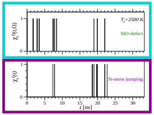
- sudden and rare events

Jumps and Defects

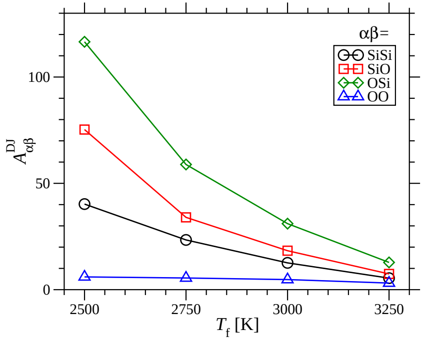


⟶ Are Defects and Jumps Correlated?

Defect-Jump Correlation

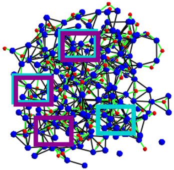


$$A^{\mathrm{DJ}}_{\alpha,\beta} = \frac{\left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t,\beta)\chi_i^{\mathrm{J}}(t) \right\rangle - \left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t,\beta) \right\rangle \left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{J}}(t) \right\rangle}{\left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{D}}(t,\beta) \right\rangle \left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \chi_i^{\mathrm{J}}(t) \right\rangle}$$



- strong correlation between defects and jumps
- correlation is decreasing with increasing temperature

Summary



Simulations of SiO_2-Glass

Extract Information:

- time averaged positions
- $\chi_i^{\mathrm{D}}(t,\beta)$, $\chi_i^{\mathrm{J}}(t) \longrightarrow C_{\alpha,\beta}^{\mathrm{DD}}, A_{\alpha,\beta}^{\mathrm{DJ}}$

Defects:

- well defined ($g_{\alpha\beta}(r)$ & $P_{\alpha\beta}(z)$)
- strong temperature dependence of $\tilde{C}_{\alpha,\beta}^{\mathrm{DD}}(t)$
- $\tau_{\alpha,\beta}^{\mathrm{DD}}$:
  - SiO- & OSi-defects short lived and OO-defects long lived
  - $\tau_{\alpha,\beta}^{\mathrm{DD}}$ decreasing with increasing temperature

Jump-Defect Correlation:

- strongly correlated
- $A_{\alpha,\beta}^{\mathrm{DJ}}$ decreases with increasing temperature

[KVL & A. Zippelius, PRE 88, 052145 (2013)]

Acknowledgments: A. Zippelius and DFG (SFB 602 & FOR1394)