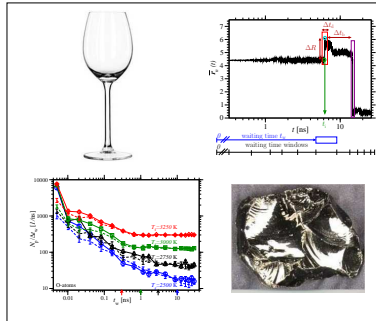


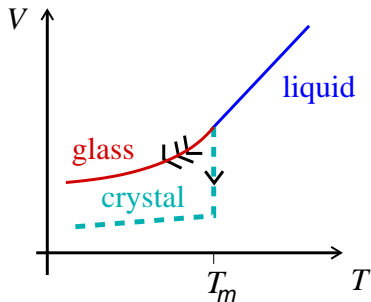
# Microscopic Picture of Aging in SiO<sub>2</sub>: A Computer Simulation

Katharina Vollmayr-Lee, Robin Bjorkquist, Landon M. Chambers  
Bucknell University & Göttingen



Acknowledgments: J. Horbach & A. Zippelius

# Introduction: Glass



Glass:

→ system falls  
out of equilibrium

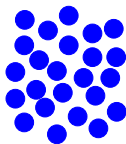
Crystal



Glass

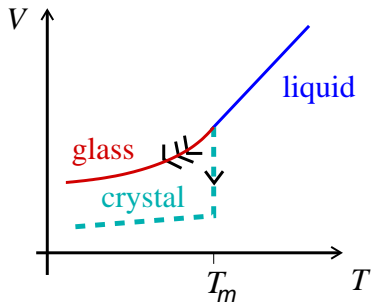


Liquid



Structure: disordered  
Dynamics: frozen in

# Introduction: Glass



Glass:

→ system falls  
out of equilibrium

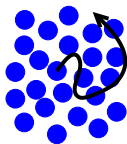
Crystal



Glass

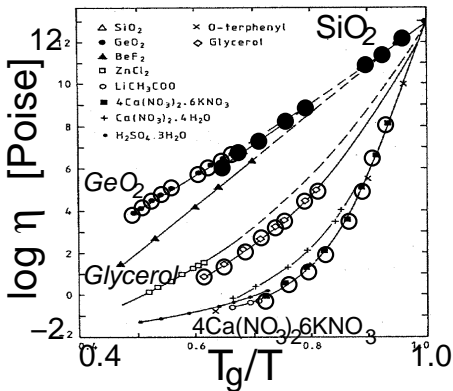


Liquid



Structure: disordered  
Dynamics: frozen in

# Introduction: Glass

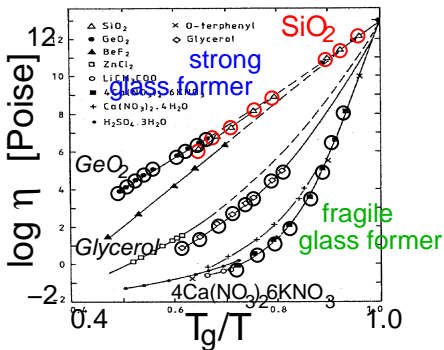


## Dynamics:

Viscosity  $\eta$  as function of inverse temperature  $T$

- ▶ slowing down of many decades  
→ very interesting dynamics

# Introduction: Glass



## Dynamics:

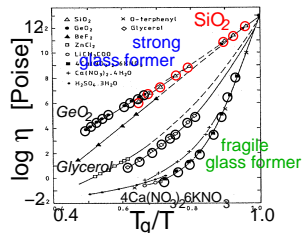
Viscosity  $\eta$  as function of inverse temperature  $T$

- ▶ slowing down of many decades  
→ very interesting dynamics
- ▶ strong and fragile glass formers  
Here: SiO<sub>2</sub> (strong glass former)  
Below: comparison with fragile glass former

# System: SiO<sub>2</sub>

## Properties:

- ▶ rich phase diagram (like H<sub>2</sub>O)
- ▶ density maximum
- ▶ network former
- ▶ **strong glass former**



## Model: BKS Potential

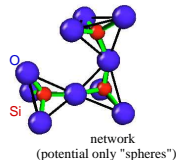
[B.W.H. van Beest *et al.*, PRL 64, 1955 (1990)]

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

112 Si & 224 O

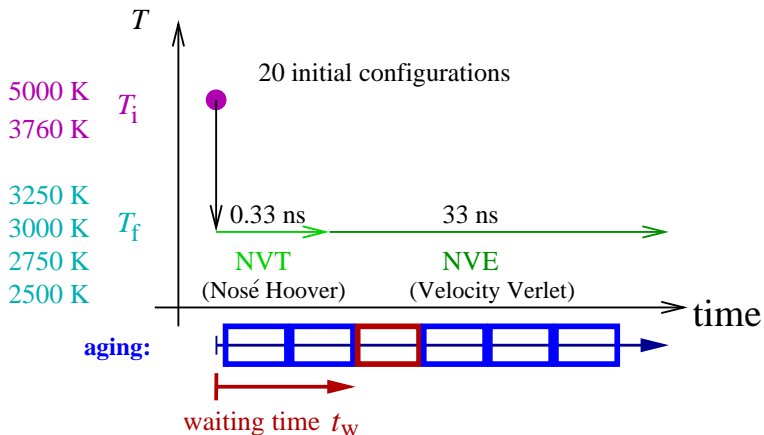
$\rho = 2.32 \text{ g/cm}^3$

$T_c = 3330 \text{ K}$



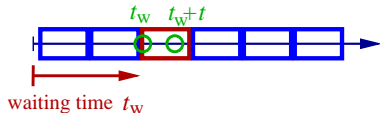
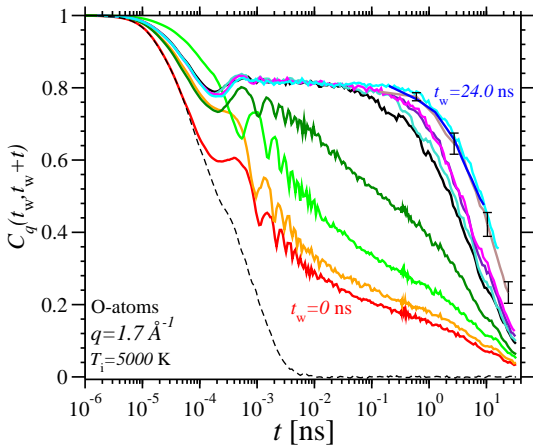
# Simulation Runs

## Molecular Dynamics Simulations



# Generalized Intermediate Incoherent Scattering Function

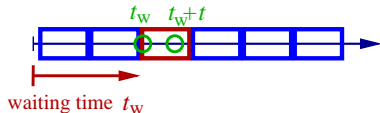
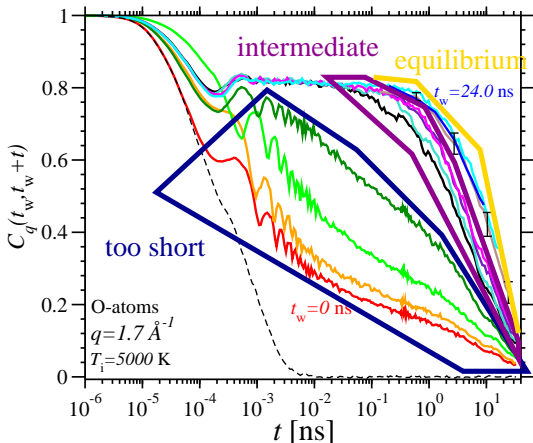
$$C_q(t_w, t_w + t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} e^{i\vec{q} \cdot (\vec{r}_j(t_w+t) - \vec{r}_j(t_w))}$$



- ▶  $C_q(t_w, t_w + t)$  depends on waiting time  $t_w$  (colors)

# Generalized Intermediate Incoherent Scattering Function

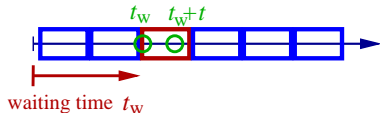
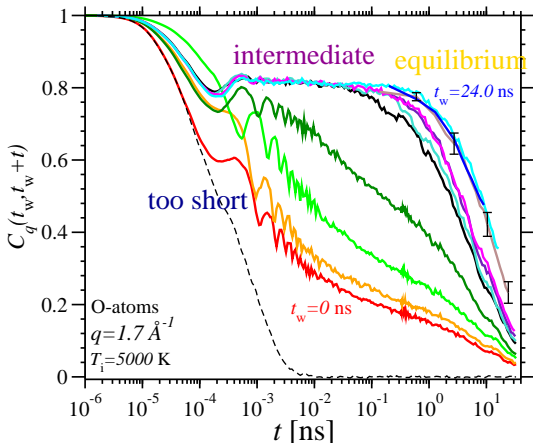
$$C_q(t_w, t_w + t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} e^{i\vec{q} \cdot (\vec{r}_j(t_w+t) - \vec{r}_j(t_w))}$$



- ▶ three time windows:
  - ▶ too short
  - ▶ intermediate (scaling)
  - ▶ equilibrium ( $t_{eq}^C$ )

# Generalized Intermediate Incoherent Scattering Function

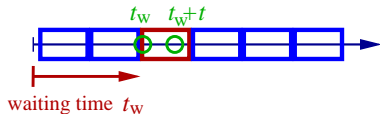
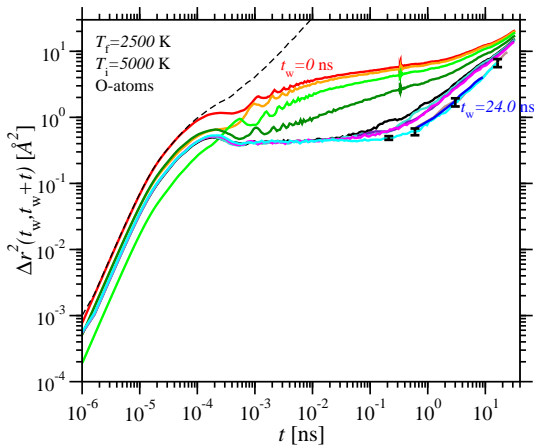
$$C_q(t_w, t_w + t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} e^{i\vec{q} \cdot (\vec{r}_j(t_w+t) - \vec{r}_j(t_w))}$$



- ▶ three time windows:
  - ▶ too short
  - ▶ intermediate (scaling)
  - ▶ equilibrium ( $t_{eq}^C$ )
- ▶ equilibrium curve included in scaling

# Mean Square Displacement

$$\Delta r^2(t_w, t_w + t) = \frac{1}{N} \sum_{j=1}^N (\mathbf{r}_j(t_w + t) - \mathbf{r}_j(t_w))^2$$

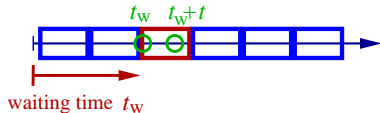
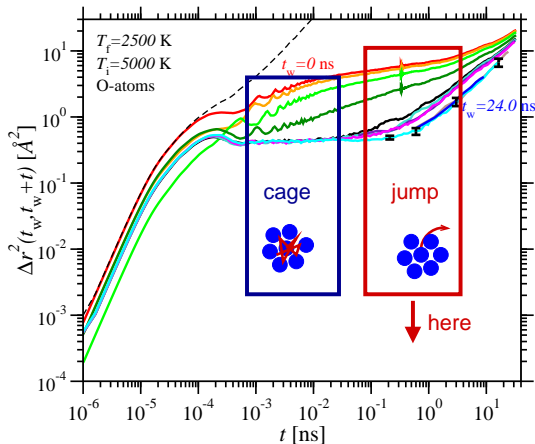


► three time windows:

[KVL, J. Roman, J.Horbach, PRE 81, 061203 (2010)]

# Mean Square Displacement

$$\Delta r^2(t_w, t_w + t) = \frac{1}{N} \sum_{j=1}^N (\mathbf{r}_j(t_w + t) - \mathbf{r}_j(t_w))^2$$



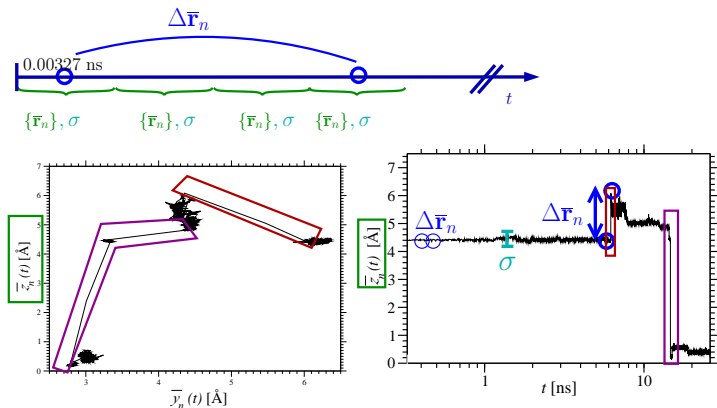
▶ three time windows:

**Goal:**

**Single Particle Picture**

(not  $\frac{1}{N} \sum_{j=1}^N$ )

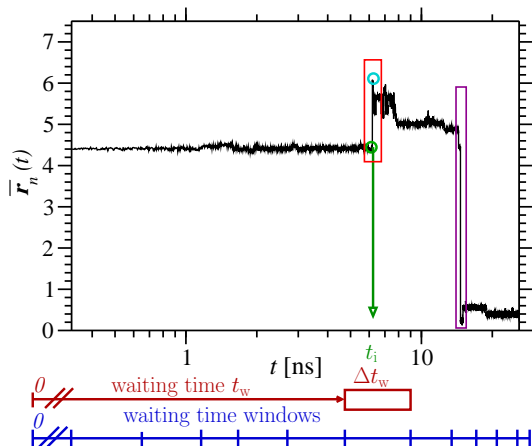
# Jump Definition



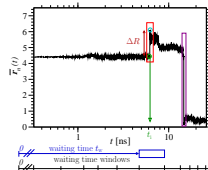
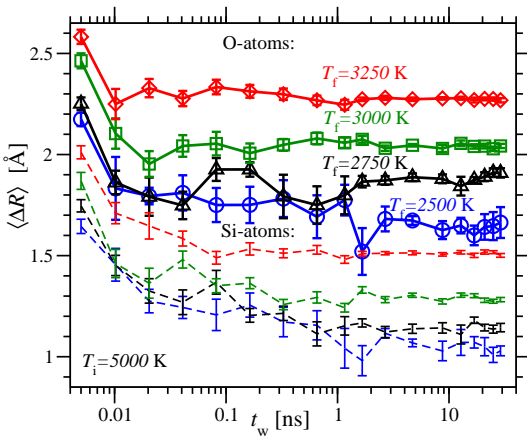
$$\Delta \bar{\Gamma}_n > 3 \sigma$$

[KVL, R. Bjorkquist, L.M. Chambers, PRL 110, 017801 (2013)]

# Jump Definition: Aging Dependence

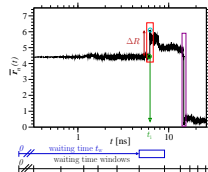
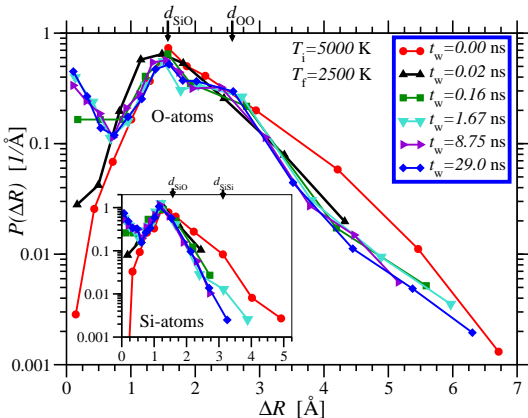


# Average Jump Length



- ▶ O-atoms jump farther than Si-atoms
- ▶ compare:  
 $d_{\text{SiO}} = 1.58 \text{ \AA}$ ,  $d_{\text{OO}} = 2.58 \text{ \AA}$ ,  
 $d_{\text{SiSi}} = 3.13 \text{ \AA}$
- ▶  $\Delta R$  mostly independent of  $t_w$

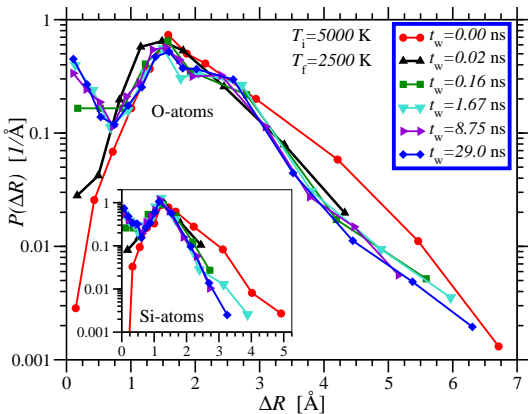
# Jump Length Distribution



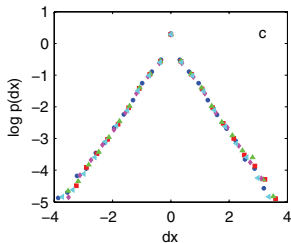
- ▶ peak at  $\Delta R_j = 0$ : reversible jumps
- ▶ peaks at  $d_{\text{SiO}}$  and  $d_{\text{OO}}$
- ▶ exponential decay
- ▶  $P(\Delta R)$  independent of  $t_w$

# Jump Length Distribution

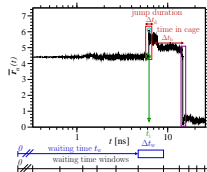
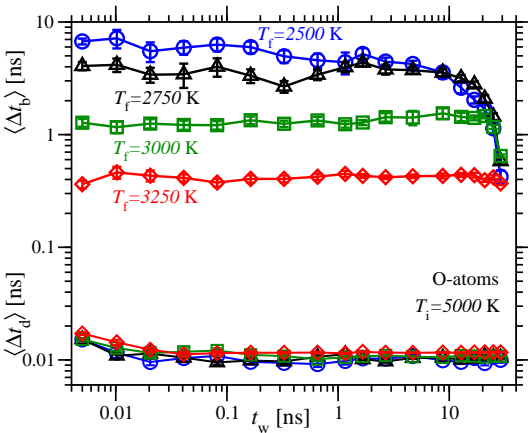
strong glass former  $\text{SiO}_2$ :



- ▶  $P(\Delta R)$  independent of  $t_w$
- ▶ exponential decay
- ▶ compare fragile glassformer binary LJ (& polymer) [Warren & Rottler, EPL(2009)]

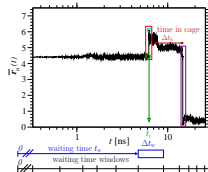
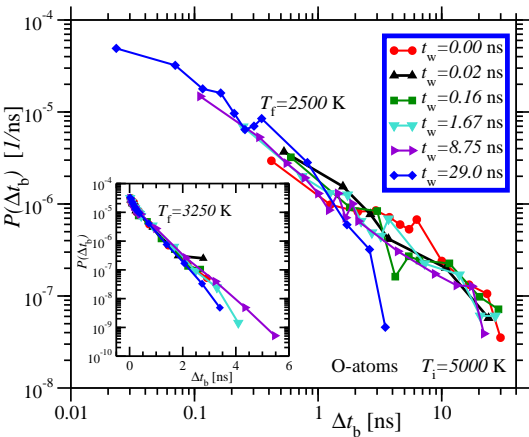


# Time Averages: Jump Duration $\Delta t_d$ & Time in Cage $\Delta t_b$



- ▶  $\Delta t_b \gg \Delta t_d$
- ▶  $\Delta t_b$  not influenced by  $\Delta t_w$
- ▶  $t_w \gtrsim 10$  artifact due to finite simulation run
- ▶  $\Delta t_b$  independent of  $t_w$ !

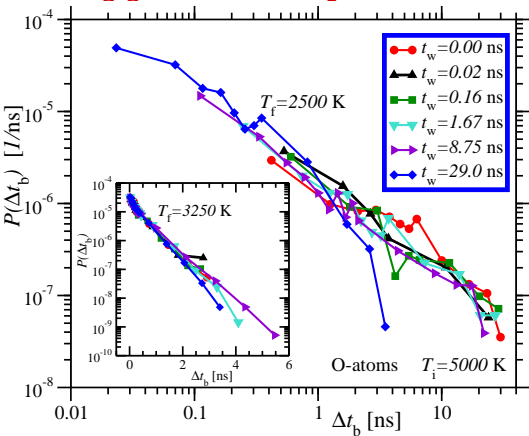
# Distribution of Time in Cage $P(\Delta t_b)$



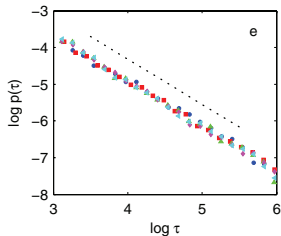
- ▶  $P(\Delta t_b)$  independent of  $t_w$ !
- ▶ 2500 K: powerlaw
- ▶ 3250 K: exponential

# Distribution of Time in Cage $P(\Delta t_b)$

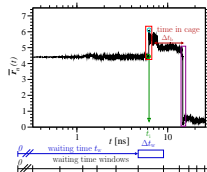
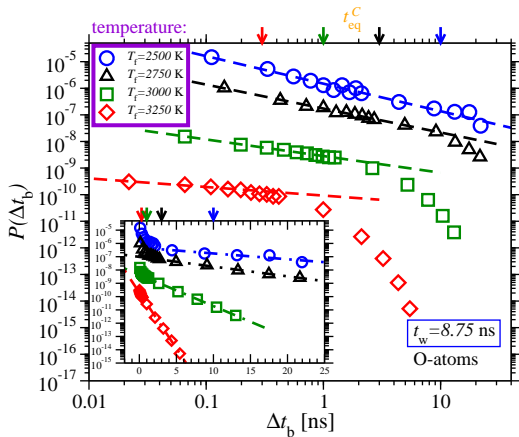
strong glass former  $\text{SiO}_2$ :



- ▶  $P(\Delta t_b)$  independent of  $t_w$ !
- ▶ compare fragile glassformer (binary LJ &) polymer [Warren & Rottler, EPL(2009)]



# Distribution of Time in Cage $P(\Delta t_b)$ : $T_f$ varied



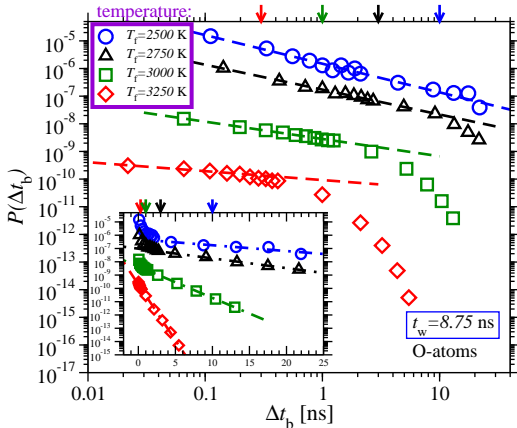
$t_w = 8.75$  ns fixed  
temperature  $T_f$  varied

► crossover

- power law to exponential
- at  $t_{cross} \approx t_{eq}^C$  (arrows)

# Distribution of Time in Cage $P(\Delta t_b)$ : $T_f$ varied

strong glass former  $\text{SiO}_2$ :



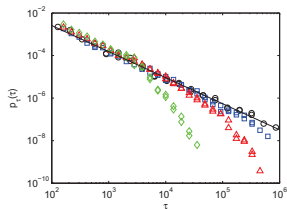
► crossover

- power law to exponential
- slope power law: -1.0 to -0.3 ( $T_f = 2500$  K to  $T_f = 3250$  K)
- at  $t_{\text{cross}} \approx t_{\text{eq}}^C$

► compare fragile glassformer binary LJ

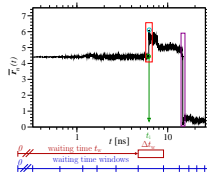
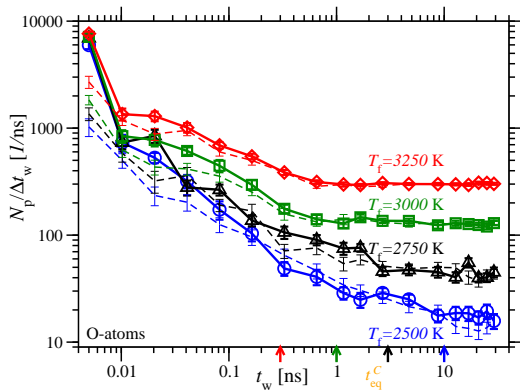
[Warren & Rottler, PRL (2013)]

- slope power law: -1.23 to -1.34 ( $T_f = 0.28$  to  $T_f = 0.37$ )



[KVL, R. Bjorkquist, L.M. Chambers, PRL (2013)]

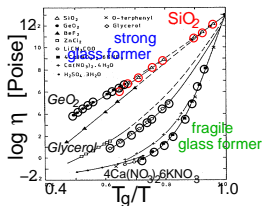
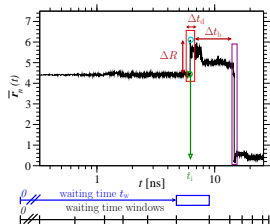
# Number of Jumping Particles per Time



- ▶  $N_p / \Delta t_w$  depends strongly on waiting time  $t_w$ 
  - $N_p / \Delta t_w$  decreasing with increasing  $t_w$
  - compare: soft colloids [Yunker et al., PRL (2009)]
- ▶ equilibration at  $t_{eq}^j$ 

$$t_{eq}^j \approx t_{eq}^C \text{ (arrows)}$$

# Summary: Microscopic Picture of Aging



## Aging of $\text{SiO}_2$ :

- ▶ Only  $t_w$ -dependence:  $N_p/\Delta t_w$  (not  $P(\Delta R)$  and  $P(\Delta t_b)$ )
- ▶  $P(\Delta t_b)$  crossover power law to exponential
  - at  $t_{\text{cross}} \approx t_{\text{eq}}^j \approx t_{\text{eq}}^C$

[KVL, R. Bjorkquist, L.M. Chambers, PRL 110, 017801 (2013)]

## Compare with Fragile Glassformer:

- ▶ Surprising similar jump dynamics of strong and fragile glass formers
  - $P(\Delta R)$  and  $P(\Delta t_b)$   $t_w$ -independent
  - $P(\Delta t_b)$  crossover

## PAST:

- ▶ Fragile Glass Former (Binary LJ): clusters of jumping particles  
→ self-organized criticality  
[KVL & Baker, EPL(2006)]
- ▶ granular fluid: simulation and hydrodynamic theory  
[KVL, T. Aspelmeier, A. Zippelius, PRE 2010]

## PRESENT & FUTURE:

Strong & Fragile Glass Former Similar?

- ▶ SiO<sub>2</sub>: scaling ( $\chi_4, P(C_q)$ )  
together with H. Castillo
- ▶ SiO<sub>2</sub>: defects & jumps  
together with A. Zippelius

**Acknowledgments:** Supported by SFB 602, NSF REU grants PHY-0552790 & REU-0997424. Thanks to J. Horbach, A. Zippelius & University Göttingen.

# Molecular Dynamics Simulation

Newton's Equations:

$$\frac{d^2 \vec{r}_i(t)}{dt^2} = \vec{a}_i(t) = \vec{F}_i(t)/m_i = -\vec{\nabla}_i U(t)/m_i = -\vec{\nabla}_i \sum_{j,k} \phi(r_{jk})/m_i$$

Initialize:

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

particles  $i=1, \dots, N$   
three dimensions

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

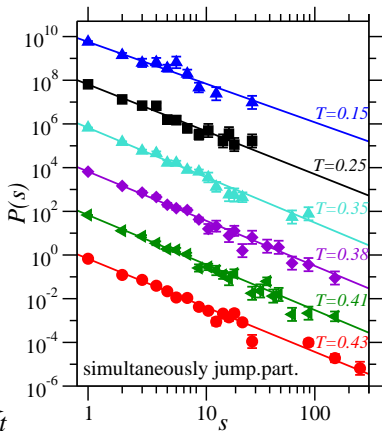
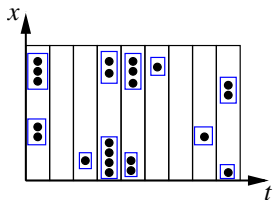
$$\vec{r}_i(t_0 + 2\Delta t), \vec{v}_i(t_0 + 2\Delta t), \vec{a}_i(t_0 + 2\Delta t)$$

etc.

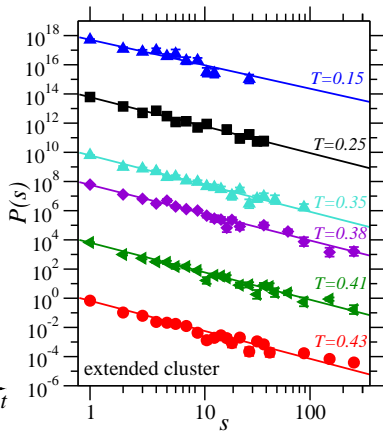
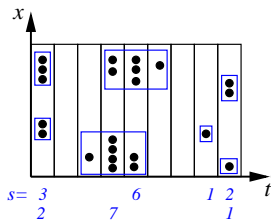
↓ = Iteration Step: (Velocity Verlet)

$$\begin{aligned} \vec{r}_i(t + \Delta t) &= \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \vec{a}_i(t)(\Delta t)^2/2 \\ \vec{v}_i(t + \Delta t) &= \vec{v}_i(t) + (\vec{a}_i(t) + \vec{a}_i(t + \Delta t))\Delta t/2 \\ \vec{a}_i(t) &= \vec{F}_i(t)/m_i = -\vec{\nabla}_i U(t)/m_i \end{aligned}$$

# Binary Lennard-Jones: Clusteranalysis (Simultaneous)

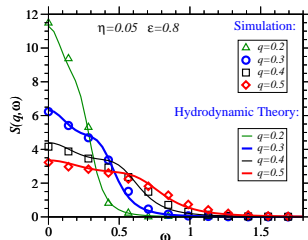


# Binary Lennard-Jones: Clusteranalysis (Space-Time Cluster)



# Summary of Granular Fluid Work

- ▶ Damped Sound Waves
- ▶ Fluctuating Hydrodynamic Theory:
  - ▶  $D_T q^2 \approx \frac{3\Gamma_0}{2T_0}$  (full solution)
  - ▶  $S(q, \omega)$  well approximated
  - ▶ transport coefficients agree with kinetic theory



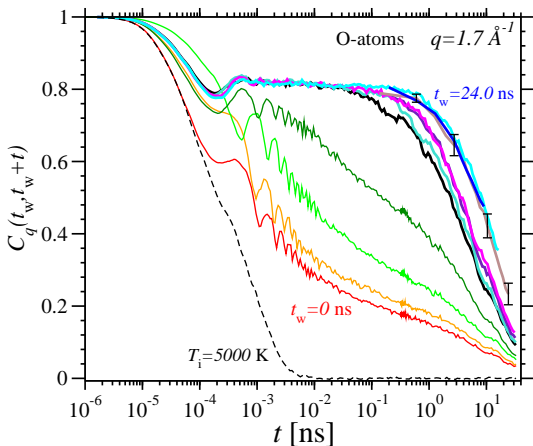
[KVL, T. Aspelmeier, A. Zippelius, PRE **83**, 011301 (2011)]

Acknowledgments:

Support from Institute of Theoretical Physics, University Göttingen

# Generalized Intermediate Incoherent Scattering Function

$$C_q(t_w, t_w + t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} e^{i\vec{q} \cdot (\vec{r}_j(t_w+t) - \vec{r}_j(t_w))}$$

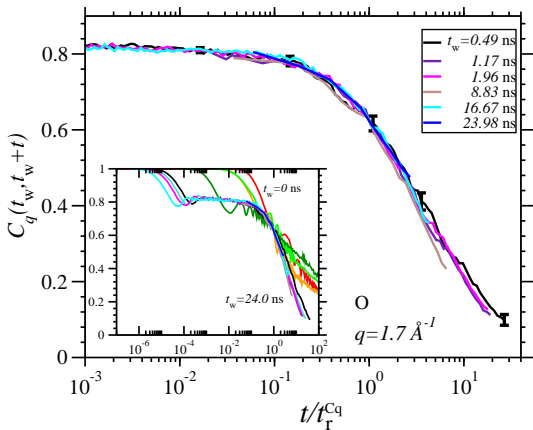


- ▶  $t_w$  **small:**
  - $t_w = 0$  &  $t \lesssim 5 \cdot 10^{-5} \text{ ns}$ :  
 $T_i$  good approx.
  - no plateau
  - decay  $t_w$ -dependent
- ▶  $t_w$  **intermediate:**
  - plateau  $t_w$ -indep.
  - decay  $t_w$ -dependent
  - **time superposition ?**
- ▶  $t_w$  **large:**  $t_w$ -indep.  
→ **equilibrium**

# Generalized Intermediate Incoherent Scattering Function

$$\text{MF: } C_q(t_w, t_w + t) = C_q^{\text{ST}}(t) + C_q^{\text{AG}}\left(\frac{h(t_w+t)}{h(t_w)}\right)$$

$$\text{Superposition: } C_q(t_w, t_w + t) = C_q^{\text{ST}}(t) + C_q^{\text{AG}}\left(\frac{t}{t_r^{\text{Cq}}(t_w)}\right)$$

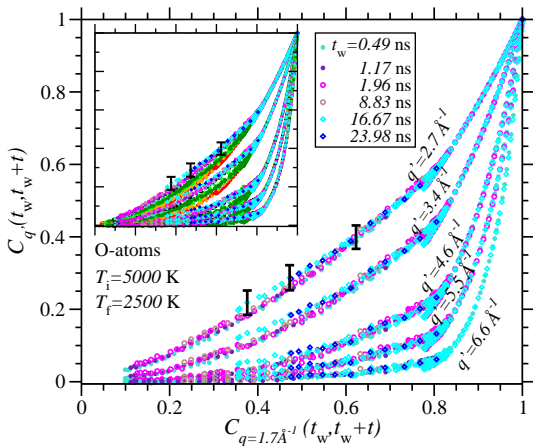


- ▶  $t_w$  **small**:  
no time  
superposition
- ▶  $t_w$  **intermediate**:  
time superposition
- ▶  $t_w$  **large**:  
superposition  
includes equilibrium  
curve

# Generalized Intermediate Incoherent Scattering Function

$$C_q(t_w, t_w + t) = C_q^{\text{ST}}(t) + C_q^{\text{AG}}\left(\frac{h(t_w+t)}{h(t_w)}\right)$$

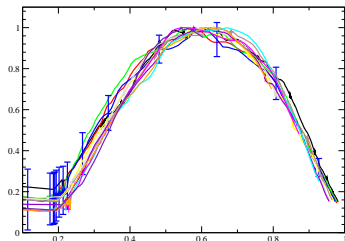
Is  $h$  dependent on  $C_q$ ?



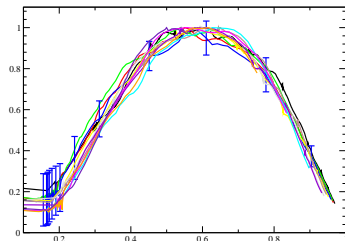
- ▶  $t_w$  **small**:  
no superposition
- ▶  $t_w$  **intermediate**:  
superposition of  $C_{q'}(C_q)$   
 $\Rightarrow h$  indep. of  $C_q$
- ▶  $t_w$  **large**:  
superposition  
includes equilibrium  
curve

# Dynamic Susceptibility

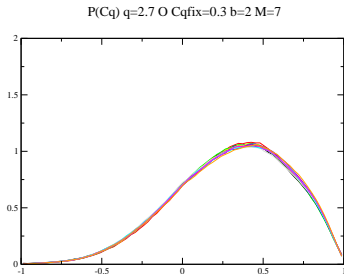
$$\chi_d^{Fs} / \chi_d^{\max}(1-Fs) q=1.7 O$$



$$\chi_d^{Fs} / \chi_d^{\max}(1-Fs) q=1.7 SiO$$



## Local Incoherent Intermediate Scattering Function



## Incoherent Intermediate Scattering Function

