Microscopic Picture of Aging in SiO_2: A Computer Simulation

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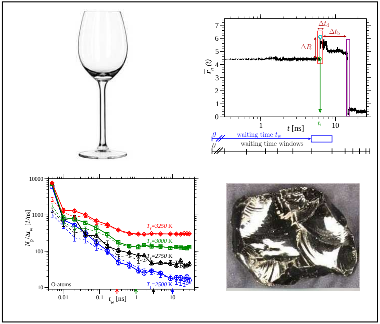
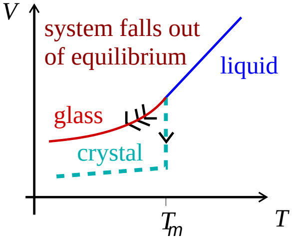
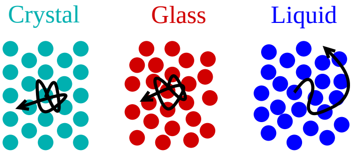


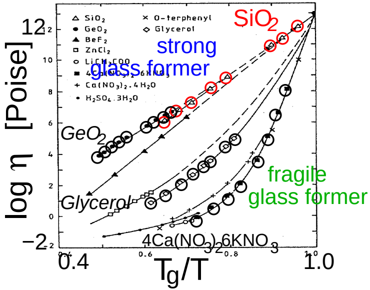
Mainz, June 25, 2013

Acknowledgments: J. Horbach & A. Zippelius

Introduction: Glass







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

Dynamics:

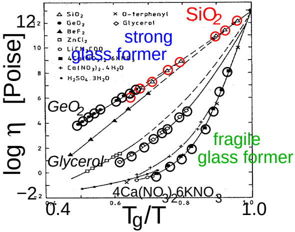
Viscocity η as function of inverse temperature T

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

System: SiO_2

Properties:

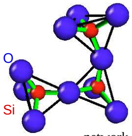
- rich phase diagram (like H_2O)
- density maximum
- network former
- strong glass former



Model: BKS Potential

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

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



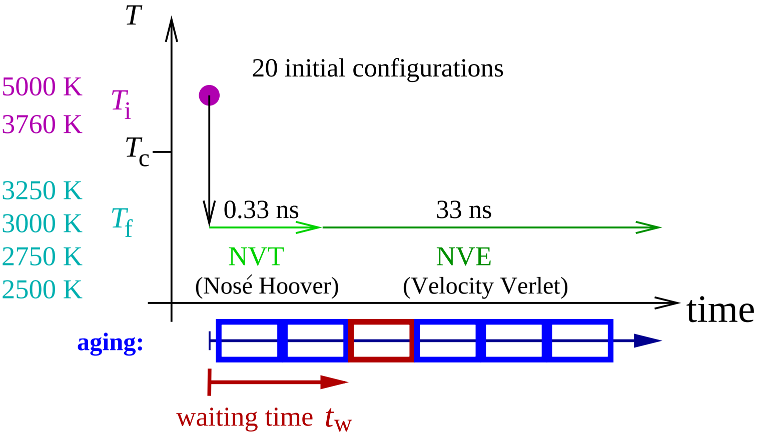
network
(potential only "spheres")

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

$T_c = 3330$ K

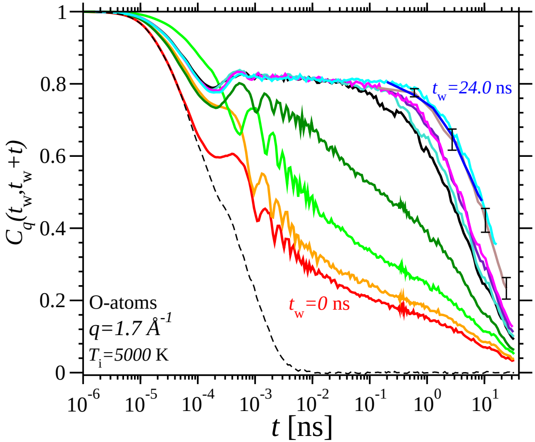
Simulation Runs

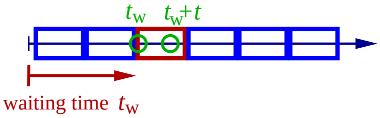
Molecular Dynamics Simulations



Generalized Intermediate Incoherent Scattering Function

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

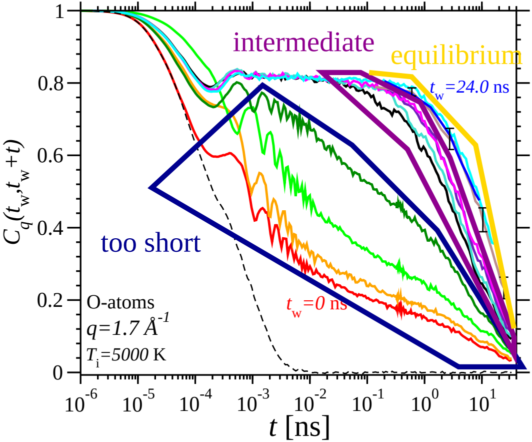


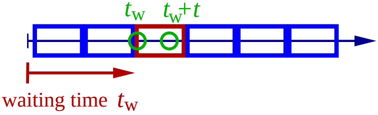


- $C_q(t_w, t_w + t)$ depends on waiting time t_w (colors)

Generalized Intermediate Incoherent Scattering Function

$$C_q(t_{\mathrm{w}}, t_{\mathrm{w}} + t) = \left\langle \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} \mathrm{e}^{i\vec{q}\cdot(\vec{r}_j(t_{\mathrm{w}}+t) - \vec{r}_j(t_{\mathrm{w}}))} \right\rangle$$



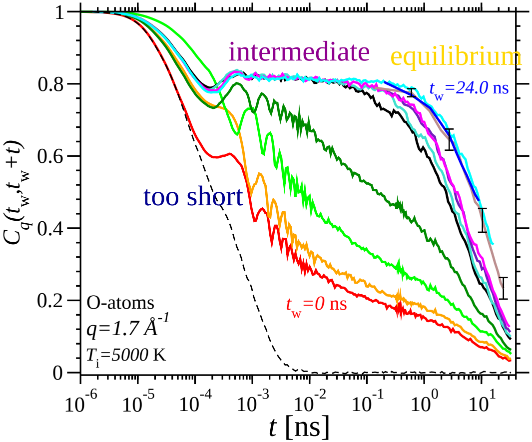


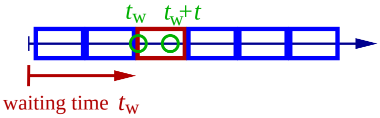
- three time windows:
  - too short
  - intermediate (scaling)
  - equilibrium (t_{eq}^C)

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

Generalized Intermediate Incoherent Scattering Function

$$C_q(t_\mathrm{w}, t_\mathrm{w}+t) = \left\langle \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} \mathrm{e}^{i\vec{q}\cdot(\vec{r}_j(t_\mathrm{w}+t)-\vec{r}_j(t_\mathrm{w}))} \right\rangle$$



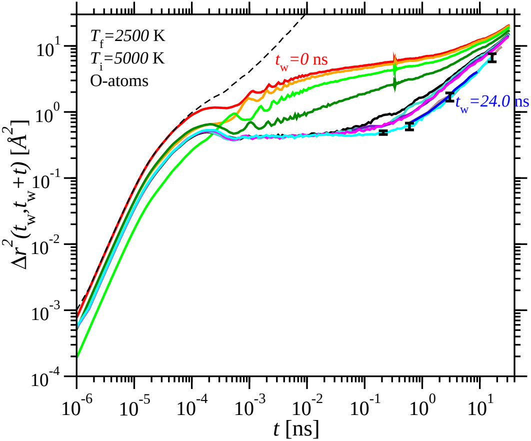


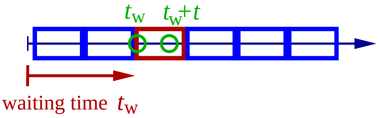
- three time windows:
  - too short
  - intermediate (scaling)
  - equilibrium (t_{eq}^{C})
- equilibrium curve included in scaling

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

Mean Square Displacement

$$\Delta r^2(t_\mathrm{w}, t_\mathrm{w}+t) = \left\langle \frac{1}{N} \sum_{j=1}^{N} \left(\mathbf{r}_j(t_\mathrm{w}+t) - \mathbf{r}_j(t_\mathrm{w})\right)^2 \right\rangle$$



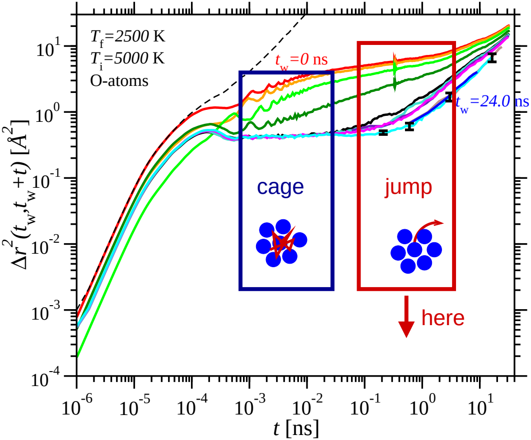


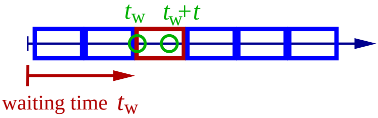
- three time windows:

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

Mean Square Displacement

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





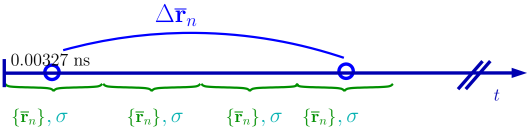
- three time windows:

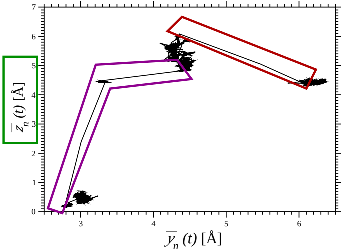
Goal:

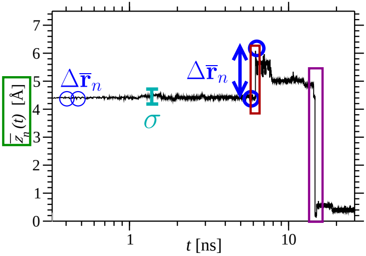
Single Particle Picture

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

Jump Definition



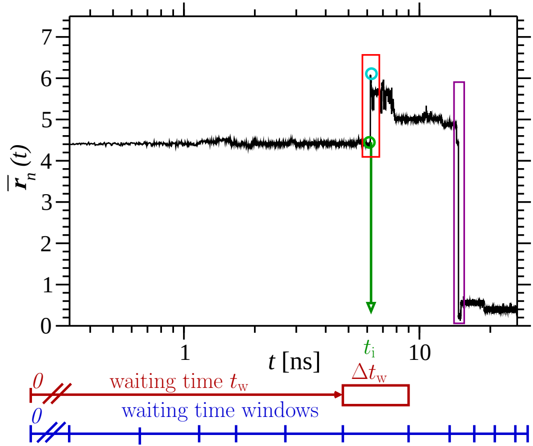




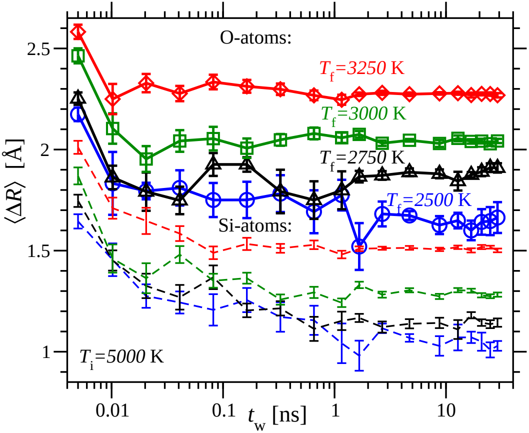
$$\Delta\bar{\mathbf{r}}_n > 3\ \sigma$$

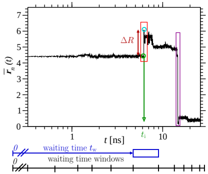
[KVL, R. Bjorkquist, L.M. Chambers,PRL 110, 017801 (2013)]

Jump Definition: Aging Dependence



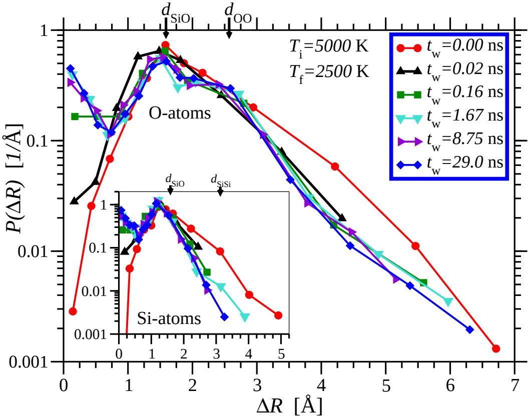
Average Jump Length

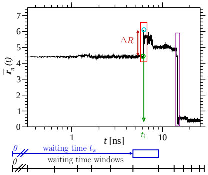




- O-atoms jump farther than Si-atoms
- compare: $d_{\mathrm{SiO}} = 1.59$ Å, $d_{\mathrm{OO}} = 2.57$ Å, $d_{\mathrm{SiSi}} = 3.13$ Å
- ΔR mostly independent of t_{w}

Jump Length Distribution

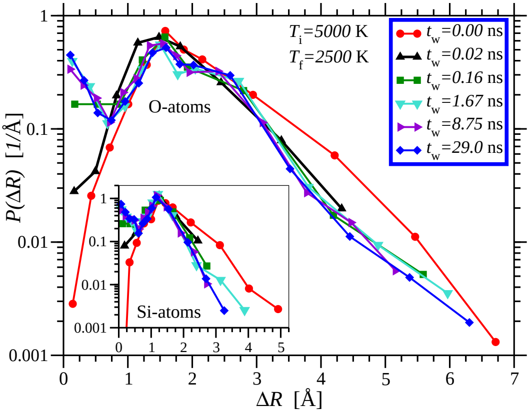




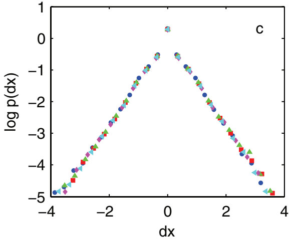
- peak at $\Delta R_{\mathrm{j}} = 0$: reversible jumps
- peaks at d_{SiO} and d_{OO}
- exponential decay
- $P(\Delta R)$ independent of t_{w}

Jump Length Distribution

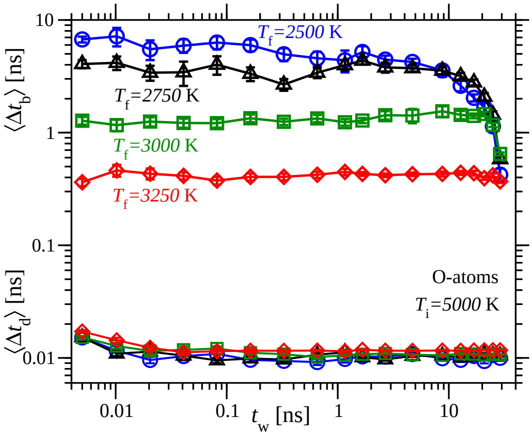
strong glass former SiO_2:

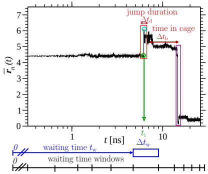


- $P(\Delta R)$ independent of t_w
- exponential decay
- compare fragile glassformer binary LJ (& polymer) [Warren & Rottler,EPL(2009)]



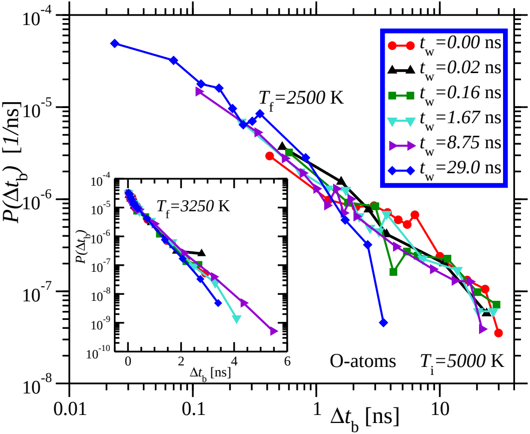
Time Averages: Jump Duration Δt_d & Time in Cage Δt_b

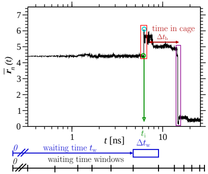




- $\Delta t_b \gg \Delta t_d$
- Δt_b not influenced by Δt_w
- $t_w \gtrsim 10$ artifact due to finite simulation run
- Δt_b independent of t_w!

Distribution of Time in Cage $P(\Delta t_\mathrm{b})$

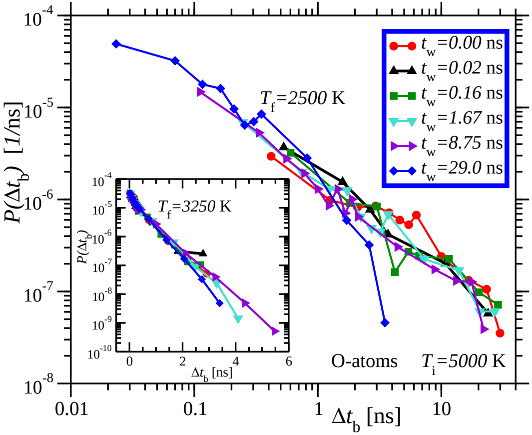




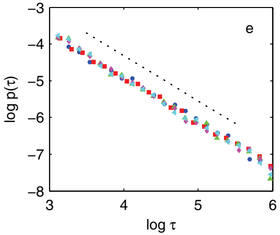
- $P(\Delta t_\mathrm{b})$ independent of t_w!
- 2500 K: powerlaw
- 3250 K: exponential

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

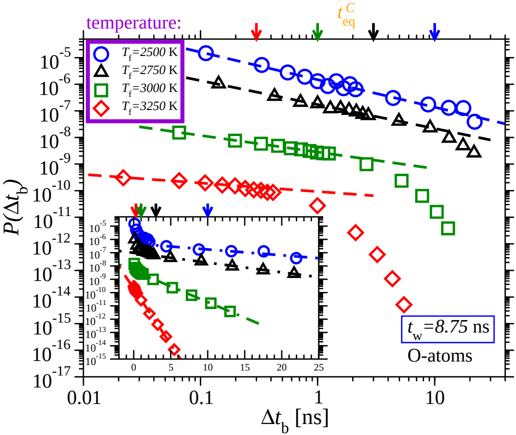
strong glass former SiO_2:

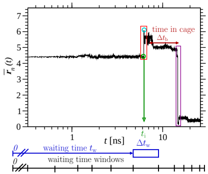


- $P(\Delta t_b)$ independent of t_w!
- compare fragile glassformer (binary LJ &) polymer [Warren & Rottler,EPL(2009)]



Distribution of Time in Cage $P(\Delta t_\mathrm{b})$: T_f varied



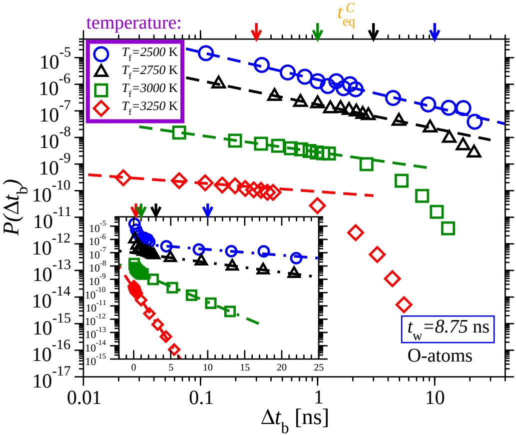


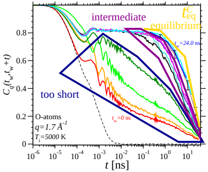
$t_\mathrm{w} = 8.75$ ns fixed

temperature T_f varied

- crossover
  - power law to exponential

Distribution of Time in Cage $P(\Delta t_\mathrm{b})$: T_f varied





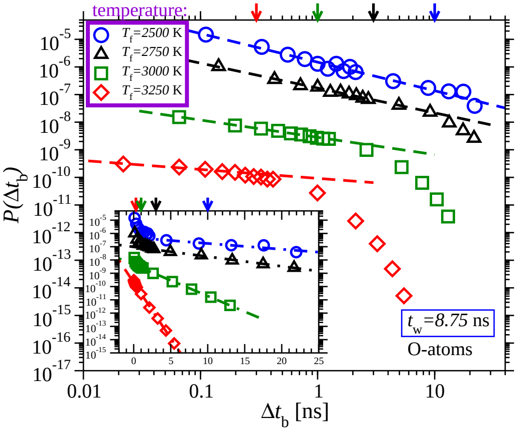
$t_\mathrm{w} = 8.75$ ns fixed

temperature T_f varied

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

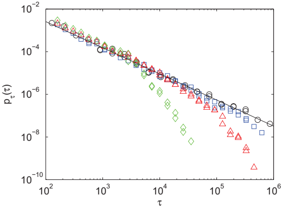
Distribution of Time in Cage $P(\Delta t_{\mathrm{b}})$: T_{f} varied

strong glass former SiO_2:

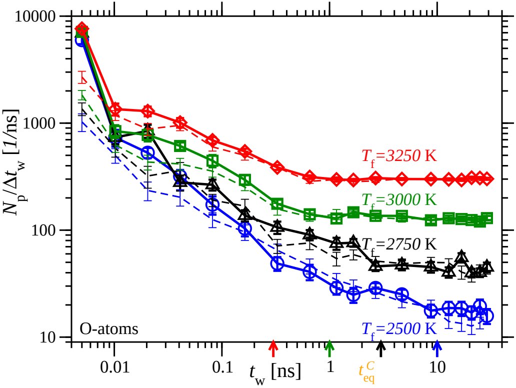


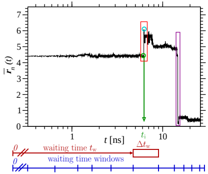
[KVL, R. Bjorkquist, L.M. Chambers, PRL (2013)]

- crossover
  - power law to exponential
  - slope power law: -1.0 to -0.3
    ($T_{\mathrm{f}} = 2500$ K to $T_{\mathrm{f}} = 3250$ K)
  - at $t_{\mathrm{cross}} \approx t_{\mathrm{eq}}^{C}$
- compare fragile glassformer
  binary LJ
  [Warren & Rottler, PRL (2013)]
  - slope power law: -1.23 to -1.34
    ($T_{\mathrm{f}} = 0.28$ to $T_{\mathrm{f}} = 0.37$)



Number of Jumping Particles per Time

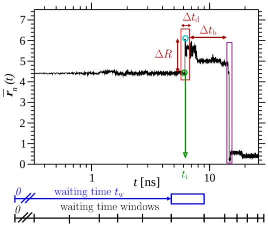


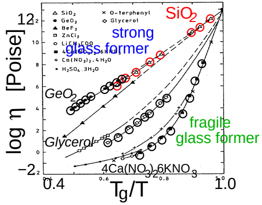


- $N_p/\Delta t_w$ depends strongly on waiting time t_w
  - $N_p/\Delta t_{tw}$ decreasing with increasing t_w
  - compare: soft colloids [Yunker et al.,PRL (2009)]
- equilibration at t_{eq}^j

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

Summary: Microscopic Picture of Aging





Aging of 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 $t_{cross} \approx t_{eq}^j \approx t_{eq}^C$

[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 $\longrightarrow$ self-organized criticality

  [KVL & Baker,EPL(2006)]
- granular fluid: simulation and hydrodynamic theory

  [KVL,T.Aspelmeier,A.Zippelius,PRE 2010]

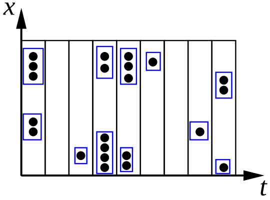
PRESENT:

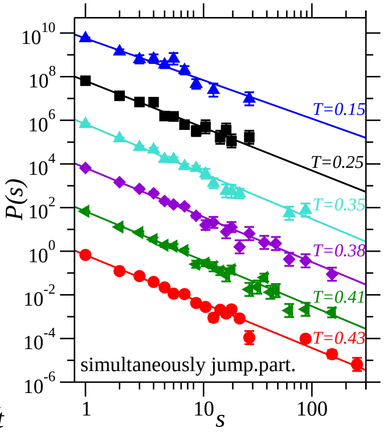
Strong & Fragile Glass Former Similar?

- SiO_2: scaling (χ_4,$P(C_q)$)
  together with H. Castillo
- SiO_2: defects & jumps
  together with A. Zippelius

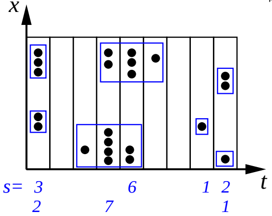
Acknowledgments: Supported by SFB 602, NSF REU grants PHY-0552790 & REU-0997424. Thanks to J. Horbach, A. Zippelius & University Göttingen.

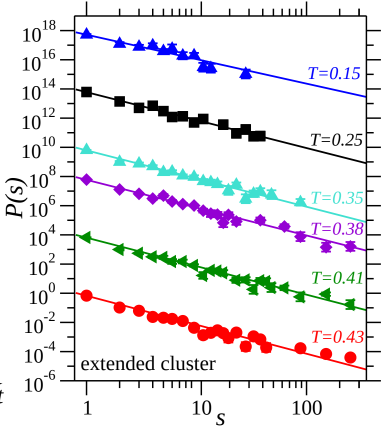
Binary Lennard-Jones: Clusteranalysis (Simultaneous)





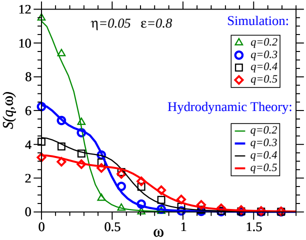
Binary Lennard-Jones: Clusteranalysis (Space-Time Cluster)





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)]

Theory: Fluctuating Hydrodynamics

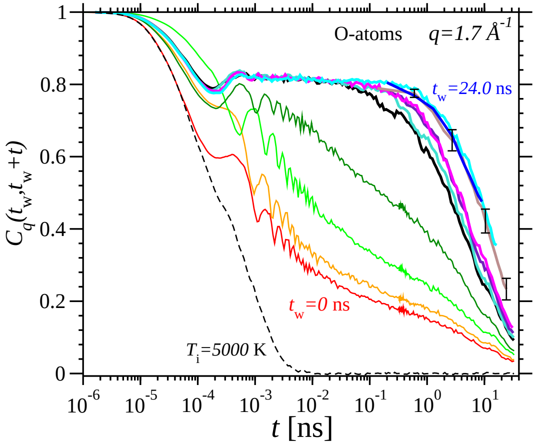
$$\begin{aligned}
\partial_t \delta n &= -iqn_0 u \\
\partial_t u &= -\frac{iq}{\rho_0}\left(\frac{\partial p}{\partial n}\delta n + \frac{\partial p}{\partial T}\delta T\right) - \nu_l\, q^2 u + \xi_l \\
\partial_t \delta T &= -D_T q^2 \delta T - \frac{3\Gamma_0}{2T_0}\delta T - iq\frac{2p_0}{dn_0}u - \Gamma_0\left(\frac{1}{n_0} + \frac{1}{\chi}\frac{\mathrm{d}\chi}{\mathrm{d}n}\right)\delta n + \theta
\end{aligned}$$

fluctuating number density $\delta n(\vec{q}, t) = n - n_0$
longitudinal flow velocity $u(\vec{q}, t) = \vec{u} \cdot \frac{\vec{q}}{q}$
fluctuating temperature $\delta T = T - T_0$

[Noije et al., PRE **59**, 4326 (1999)]

Generalized Intermediate Incoherent Scattering Function

$$C_q(t_\mathrm{w}, t_\mathrm{w}+t) = \left\langle \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} \mathrm{e}^{i\vec{q}\cdot(\vec{r}_j(t_\mathrm{w}+t)-\vec{r}_j(t_\mathrm{w}))} \right\rangle$$

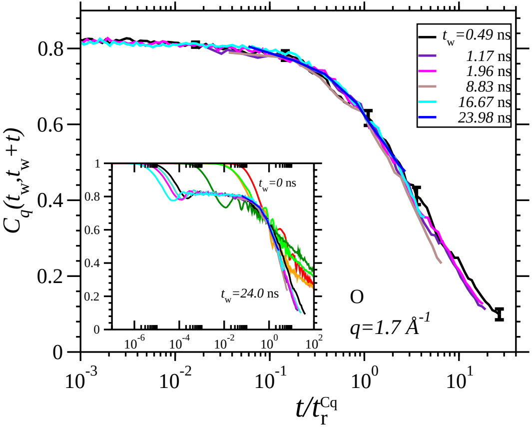


- t_w **small:**
  - $t_\mathrm{w} = 0 \,\&\, t \lesssim 5\cdot 10^{-5}$ ns: T_i good approx.
  - no plateau
  - decay t_w-dependent
- t_w **intermediate:**
  - plateau t_w-indep.
  - decay t_w-dependent
  - time superposition ?
- t_w **large:** t_w-indep. $\longrightarrow$ equilibrium

Generalized Intermediate Incoherent Scattering Function

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

Superposition: $C_q(t_\mathrm{w}, t_\mathrm{w}+t) = C_q^{\mathrm{ST}}(t) + C_q^{\mathrm{AG}}\left(\frac{t}{t_\mathrm{r}^{\mathrm{Cq}}(t_\mathrm{w})}\right)$



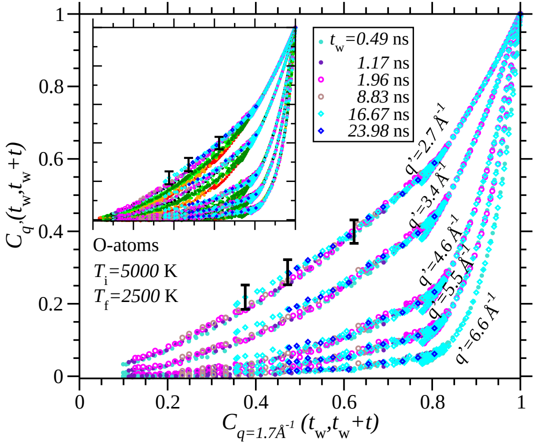
- t_w **small:** no time superposition
- t_w **intermediate:** time superposition
- t_w **large:** superposition includes equilibrium curve

LJ: [Kob & Barrat, PRL 78, 24 (1997)]

Generalized Intermediate Incoherent Scattering Function

$$C_q(t_\mathrm{w}, t_\mathrm{w}+t) = C_q^{\mathrm{ST}}(t) + C_q^{\mathrm{AG}}\left(\frac{h(t_\mathrm{w}+t)}{h(t_\mathrm{w})}\right)$$

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

LJ: [Kob & Barrat, EPJ B 13, 319 (2000)]

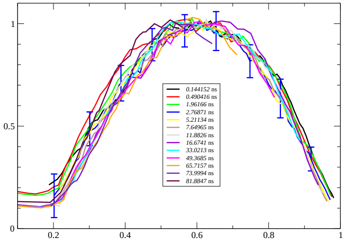
Dynamic Susceptibility

$$\chi_4(t_w, t_w+t) = N_\alpha \left[\left\langle (f_s(t_w, t_w+t))^2 \right\rangle - \langle f_s(t_w, t_w+t) \rangle^2 \right]$$

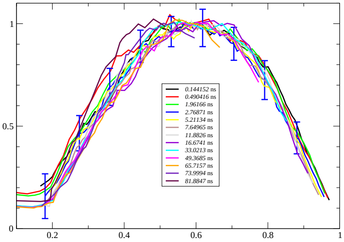
$$f_s(t_w, t_w+t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} e^{i\vec{q}\cdot(\vec{r}_j(t_w+t) - \vec{r}_j(t_w))}$$

$$C_q(t_w, t_w+t) = \langle f_s \rangle$$

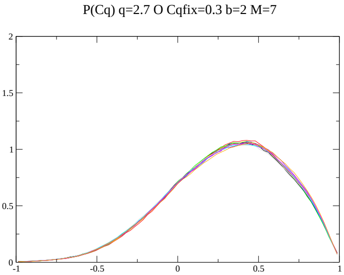
$\chi_4^{Fs}/\chi_4^{max}(1\text{-}Fs)$ q=1.7 O



$\chi_4^{Fs}/\chi_4^{max}(1\text{-}Fs)$ q=1.7 SiO



Local Incoherent Intermediate Scattering Function



Incoherent Intermediate Scattering Function