Aging of a Glass: A Computer Simulation

Katharina Vollmayr-Lee, Jake Roman, Jürgen Horbach
Bucknell University

\[ C_q(t_w + t) \]

\[ t_w = 24.0 \text{ ns} \]

\[ t_w = 0 \text{ ns} \]

\[ T_i = 5000 \text{ K} \]

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Introduction: Glass

Glass:
- System falls out of equilibrium

Structure: discordered
Introduction: Glass

Glass:
- System falls out of equilibrium

Structure: disordered
Dynamics: frozen in
Introduction: Dynamics


- slowing down of many decades
- strong and fragile glass formers
- $\text{SiO}_2$ strong glass former
System: SiO$_2$

- rich phase diagram
- similar to water (H$_2$O)

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

\[ T_c = 3330 \text{ K} \]
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**

**Initialize:**

\[
\vec{x}_i(t_0), \quad \vec{v}_i(t_0), \quad \vec{a}_i(t_0)
\]

particles \( i=1, \ldots, N \)

three dimensions

**Iteration Step:** (Velocity Verlet)

\[
\begin{align*}
\vec{x}_i(t + \Delta t) &= \vec{x}_i(t) + \vec{v}_i(t) \Delta t + \vec{a}_i(t) (\Delta t)^2 / 2 \\
\vec{v}_i(t + \Delta t) &= \vec{v}_i(t) + (\vec{a}_i(t) + \vec{a}_i(t + \Delta t)) \Delta t / 2 \\
\vec{a}_i(t) &= \vec{F}_i(t) / m_i = -\nabla_i U(t) / m_i
\end{align*}
\]
Dynamics: Aging to Equilibrium

20 initial configurations

T

Simulation Runs

5000 K $T_i$
3760 K

3250 K $T_f$
3000 K

2750 K
2500 K

NVT (Nose Hoover)
NVE (Velocity Verlet)

0.33 ns 33 ns

waiting time

$T$

$t_w$

Simulation Runs

NVT (Nose Hoover)
NVE (Velocity Verlet)

waiting time $t_w$

Simulation Runs

NVT (Nose Hoover)
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Simulation Runs

NVT (Nose Hoover)
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waiting time $t_w$
Partial Structure Factors

\[ S_{\alpha\beta}(q, t_w) = \frac{1}{N} \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} e^{i \mathbf{q} \cdot (\mathbf{r}_i(t_w) - \mathbf{r}_j(t_w))} \]

- \( t_w \) dependence weak
- in following:
  - \( C_q(t_w, t_w + t) \)
    (mostly \( q \) of FSDP)
  - \( \Delta r^2(t_w, t_w + t) \)
Generalized Intermediate Incoherent Scattering Function

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

\[ T_i = 5000 \text{ K} \quad T_f = 2500 \text{ K} \]

- **\( t_w \) small:**
  - \( t_w = 0 \) & \( t \lesssim 5 \cdot 10^{-5} \) ns:
    - \( T_i \) good approx.
    - no plateau
    - decay \( t_w \)-dependent

- **\( t_w \) intermediate:**
  - plateau \( t_w \)-indep.
  - decay \( t_w \)-dependent

- **\( t_w \) large:** \( t_w \)-indep.
  - \( \longrightarrow \) equilibrium
Generalized Intermediate Incoherent Scattering Function

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

- \( T_i = 3760 \) K \( T_f = 3000 \) K
- \( t_w \) small:
  - \( t_w = 0 \) & \( t \lesssim 5 \cdot 10^{-5} \) ns:
    - \( T_i \) good approx.
    - no plateau
    - decay \( t_w \)-dependent
- \( t_w \) intermediate:
  - plateau \( t_w \)-indep.
  - decay \( t_w \)-dependent
- \( t_w \) large: \( t_w \)-indep.
  \( \longrightarrow \) equilibrium
Generalized Intermediate Incoherent Scattering Function

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

\[ t_w \text{ small:} \]
- \( t_w = 0 \& t \lesssim 5 \cdot 10^{-5} \text{ ns} \): 
  - \( T_i \) good approx.
  - no plateau
  - decay \( t_w \)-dependent

\[ t_w \text{ intermediate:} \]
- plateau \( t_w \)-indep.
- decay \( t_w \)-dependent

\[ t_w \text{ large:} \]
- \( t_w \)-indep.
- equilibrium

\( t_w = 24.0 \text{ ns} \)

\( q = 1.7 \text{ Å}^{-1} \)

\( T_i = 5000 \text{ K} \)

\( T_f = 2500 \text{ K} \)
Plateau Height

\[ F(q) \]

- \( T_f = 2500 \text{ K} \)
- \( T_f = 2750 \text{ K} \)
- \( T_f = 3000 \text{ K} \)
- \( T_f = 3250 \text{ K} \)
- \( T_i = 3760 \text{ K} \)
- \( T_i = 5000 \text{ K} \)

**Definition:**

- Intermediate and large \( t_w \): 
  - \( F(t_w) \) indep. of \( t_w \)
  - \( F(q) \) independent of \( T_i \)
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:**
  - \( t_w = 0 \) & \( t \lesssim 5 \cdot 10^{-5} \) ns:
    - \( T_i \) good approx.
    - no plateau
    - decay \( t_w \)-dependent

- **\( t_w \) intermediate:**
  - plateau \( t_w \)-indep.
  - decay \( t_w \)-dependent

- **\( t_w \) large:** \( t_w \)-indep.
  - \( \rightarrow \) equilibrium
Three $t_w$ Ranges:

- **$t_w$ small:**
  - $t_r^{Cq}$ incr. with incr. $t_w$
  - slope $T_i$ & $T_f$ dep.

- **$t_w$ intermediate:**
  - $t_r^{Cq}$ incr. with incr. $t_w$

- **$t_w$ large:**
  - $t_r^{Cq}$ indep. of $t_w$ & $T_i$
  - $\Rightarrow$ equilibrium reached

$t_w$ Ranges dependent on $T_i$
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:**
  - \( t_w = 0 \) & \( t \lesssim 5 \cdot 10^{-5} \) ns:
    - \( T_1 \) 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.
  - \( \rightarrow \) equilibrium
Generalized Intermediate Incoherent Scattering Function

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

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

- $t_w$ 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

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

Is \( h \) dependent on \( C_q \)?

\[ \begin{array}{c|c}
\text{\( t_w \) small:} & \text{no superposition} \\
\text{\( t_w \) intermediate:} & \text{superposition of } C_q'(C_q) \\
& \Rightarrow h \text{ indep. of } C_q \\
\text{\( t_w \) large:} & \text{superposition includes equilibrium curve} \\
\end{array} \]

O-atoms
\( T_i = 5000 \text{ K} \)
\( T_f = 2500 \text{ K} \)

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

\[
\Delta r^2(t_w, t_w + t) = \frac{1}{N} \sum_{i=1}^{N} (r_i(t_w + t) - r_i(t_w))^2
\]

Three \( t_w \) Ranges:

- **\( t_w \) small:**
  - \( t_w = 0 \) & \( t \lesssim 5 \cdot 10^{-5} \) ns:
    - \( T_i \) good approx.
    - no plateau
    - increase \( t_w \)-dependent

- **\( t_w \) intermediate:**
  - plateau \( t_w \)-indep.
  - increase \( t_w \)-dependent

- **\( t_w \) large:** \( t_w \)-indep.
  \( \longrightarrow \) equilibrium
Mean Square Displacement

\[ \Delta r^2(t_w, t_w + t) = (\Delta r^2)^{ST}(t) + (\Delta r^2)^{AG}\left(\frac{t}{t_r^{msd}(t_w)}\right) \]

- **\(t_w\) small:** no time superposition
- **\(t_w\) intermediate:** no time superposition
- **\(t_w\) large:** no time superposition
Summary

\(C_q(t_w, t_w + t)\) and \(\Delta r^2(t_w, t_w + t)\):

Three \(t_w\) Ranges:

- **\(t_w\) small:**
  - \(t_w = 0\) and \(t\) small: \(T_i\) good approx.
  - dependent on \(t_w\), \(T_i\), \(T_f\)

- **\(t_w\) intermediate:**
  - plateau indep. of \(t_w\) and \(T_i\)
  - \(C_q\) time superposition (not \(\Delta r^2\))
  - \(C_q^{\text{AG}}\left(\frac{h(t_w+t)}{h(t_w)}\right): h\) is \(C_q\) indep.

- **\(t_w\) large:**
  - indep. of \(t_w\) and \(T_i\) \(\rightarrow\) equilibrium
  - for \(C_q\) equilibrium included in superposition
Past & Future:

Binary Lennard Jones:

- jumps [KVL, JCP 121, 4781 (2004)]
- self-organized criticality (correlated jumps) [KVL, E.A. Baker, EPL 76, 1130 (2006)]

SiO$_2$:

- aging to equilibrium [to be submitted to PRE]
- local $C'_q$ [A. Parsaeian, H.E. Castillo, KVL, to be published]
- jumps (R. Bjorkquist, L. Chambers)

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