Aging of a Glass: A Computer Simulation

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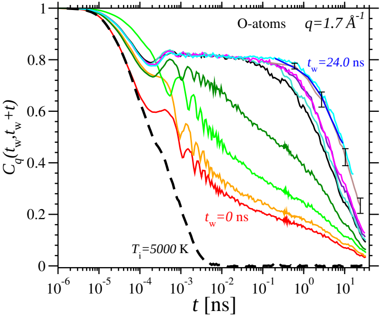
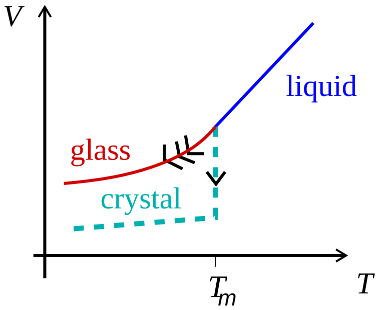


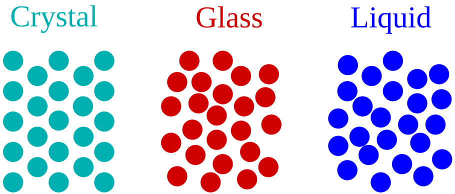
Acknowledgments: A. Zippelius & Institute of Theoretical Physics, University Göttingen, Germany

Introduction: Glass



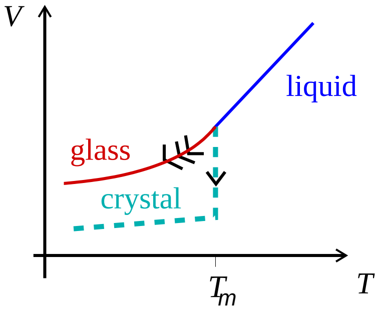
Glass:

⟶ system falls out of equilibrium



Structure: discordered

Introduction: Glass



Glass:

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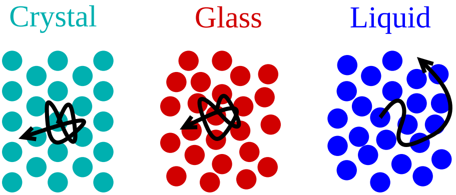
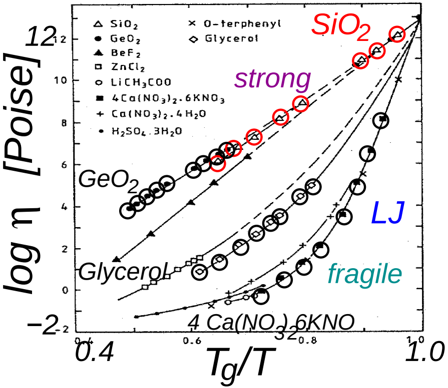


Structure: discordered

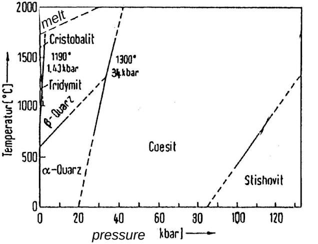
Dynamics: frozen in



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

- slowing down of many decades
- strong and fragile glass formers
- SiO_2 strong glass former

System: SiO_2



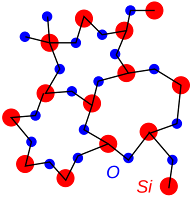
[S. Stoeffler and J. Arndt, Naturwissenschaften 56, 100 (1969)]

- rich phase diagram
- similar to water (H_2O)

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 $\rho = 2.32$ 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

Initialize:

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

particles $i=1,...,N$

three dimensions

↓

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

↓

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

↓ etc.

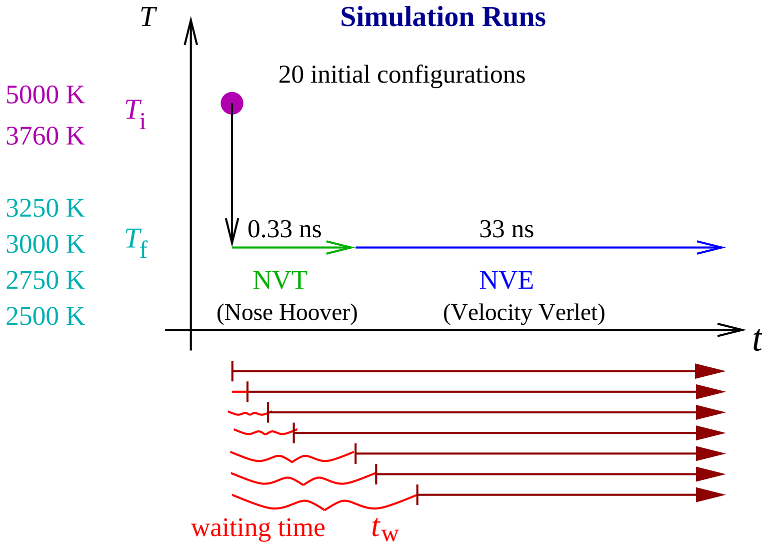
↓ = Iteration Step: (Velocity Verlet)

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

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

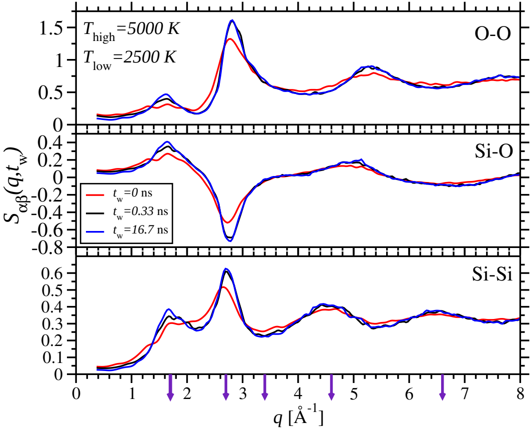
$$\vec{a}_i(t) = \vec{F}_i(t)/m_i = -\vec{\nabla}_i U(t)/m_i$$

Dynamics: Aging to Equilibrium



Partial Structure Factors

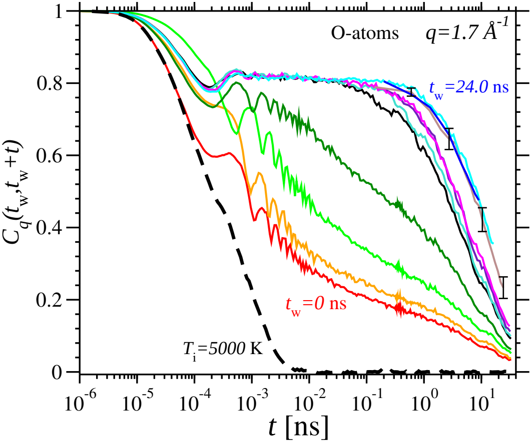
$$S_{\alpha\beta}(q,t_\mathrm{w}) = \frac{1}{N}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta} \mathrm{e}^{i\vec{q}\cdot(\vec{r}_i(t_\mathrm{w})-\vec{r}_j(t_\mathrm{w}))}$$



- t_w dependence weak
- in following:
  - $C_q(t_\mathrm{w}, t_\mathrm{w}+t)$ (mostly q of FSDP)
  - $\Delta r^2(t_\mathrm{w}, t_\mathrm{w}+t)$

Generalized Intermediate Incoherent Scattering Function

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

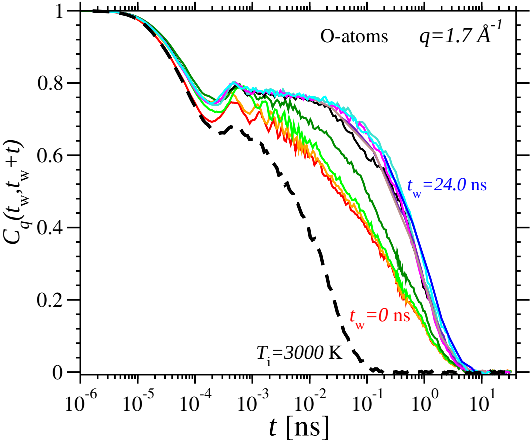


$T_i = 5000$ K $T_f = 2500$ K

- 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

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

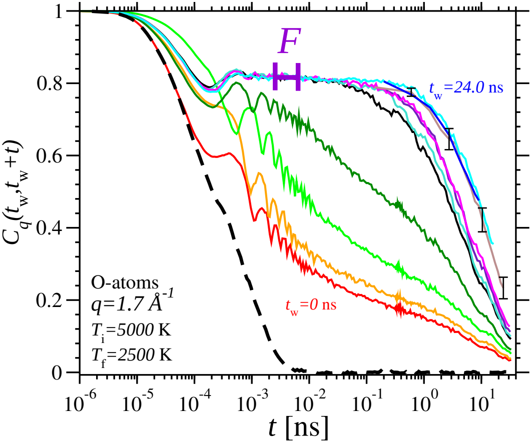


$T_{\rm i} = 3760$ K $T_{\rm f} = 3000$ K

- $t_{\rm w}$ **small:**
  - $t_{\rm w} = 0 \,\&\, t \lesssim 5 \cdot 10^{-5}$ ns: $T_{\rm i}$ good approx.
  - no plateau
  - decay $t_{\rm w}$-dependent
- $t_{\rm w}$ **intermediate:**
  - plateau $t_{\rm w}$-indep.
  - decay $t_{\rm w}$-dependent
- $t_{\rm w}$ **large:** $t_{\rm w}$-indep. $\longrightarrow$ equilibrium

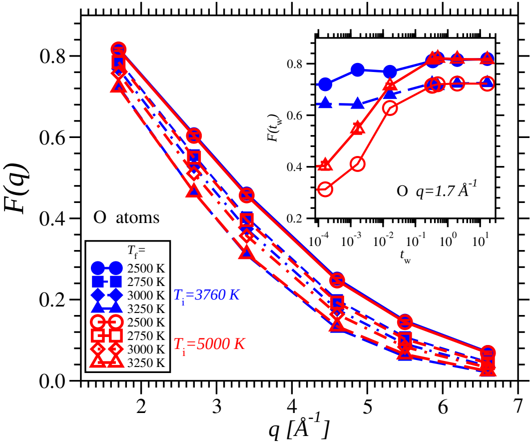
Generalized Intermediate Incoherent Scattering Function

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

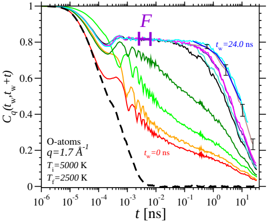


- t_w **small:**
  - $t_\mathrm{w} = 0 \,\&\, t \lesssim 5 \cdot 10^{-5}$ ns: T_i good approx.
  - no plateau
  - decay t_w-dependent
- t_w **intermediate:**
  - plateau t_w-indep.
  - decay t_w-dependent
- t_w **large:** t_w-indep. $\longrightarrow$ equilibrium

Plateau Height



Definition:

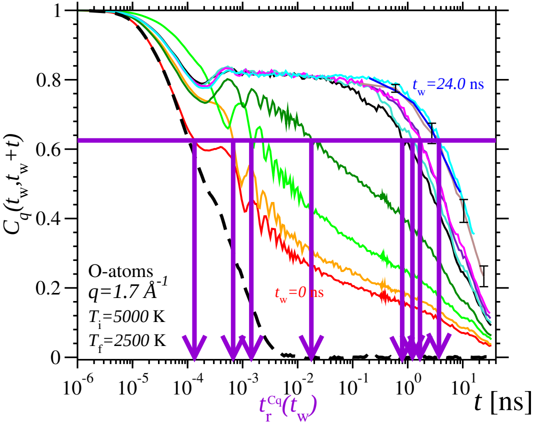


intermediate and large t_w:

- $F(t_\mathrm{w})$ indep. of t_w
- $F(q)$ independent of T_i

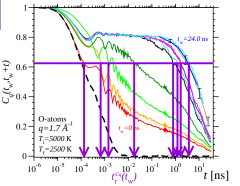
Generalized Intermediate Incoherent Scattering Function

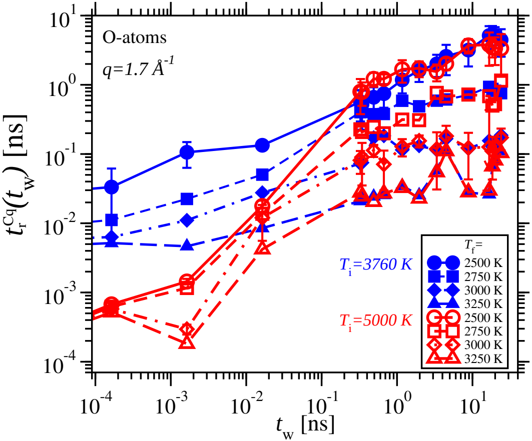
$$C_q(t_\mathrm{w}, t_\mathrm{w}+t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} \mathrm{e}^{i\vec{q}\cdot(\vec{r}_j(t_\mathrm{w}+t)-\vec{r}_j(t_\mathrm{w}))}$$



- 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
- t_w **large:** t_w-indep. $\longrightarrow$ equilibrium

Decay Time





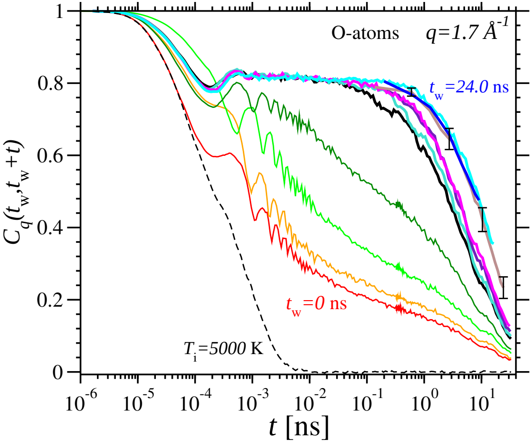
Three t_{w} Ranges:

- t_{w} **small:**
  - $t_{\mathrm{r}}^{\mathrm{Cq}}$ incr. with incr. t_{w}
  - slope T_{i} & T_{f} dep.
- t_{w} **intermediate:**
  $t_{\mathrm{r}}^{\mathrm{Cq}}$ incr. with incr. t_{w}
- t_{w} **large:**
  $t_{\mathrm{r}}^{\mathrm{Cq}}$ indep. of t_{w} & T_{i}
  $\Rightarrow$ equilibrium reached

t_{w} Ranges dependent on T_{i}

Generalized Intermediate Incoherent Scattering Function

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

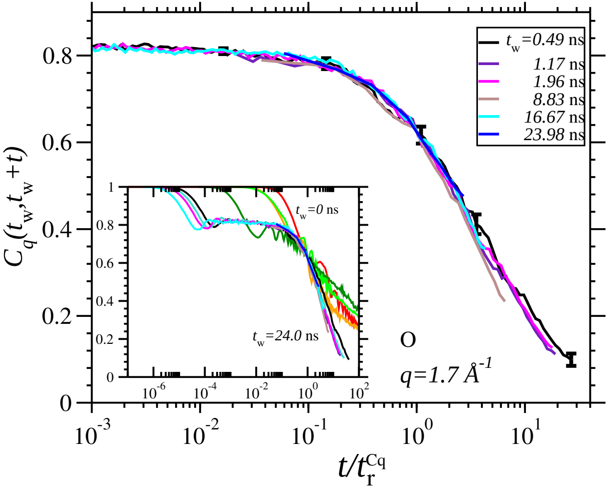


- t_w **small:**
  - $t_w = 0 \,\&\, t \lesssim 5 \cdot 10^{-5}$ ns: T_i good approx.
  - no plateau
  - decay t_w-dependent
- t_w **intermediate:**
  - plateau t_w-indep.
  - decay t_w-dependent
  - time superposition ?
- t_w **large:** t_w-indep. $\longrightarrow$ equilibrium

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



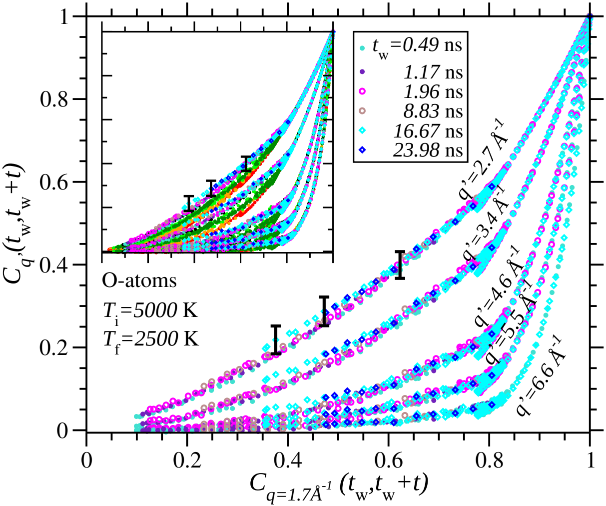
- t_w **small:** no time superposition
- t_w **intermediate:** time superposition
- t_w **large:** superposition includes equilibrium curve

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?

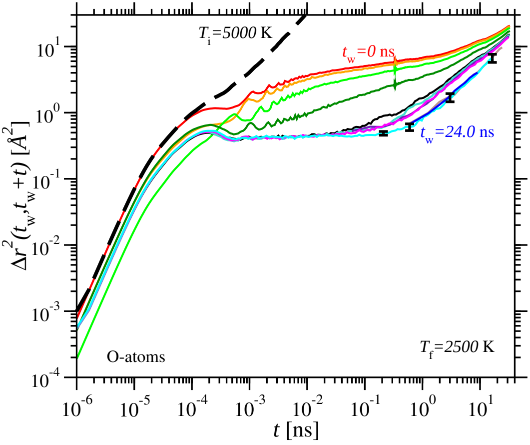


- t_w **small:** no superposition
- t_w **intermediate:** superposition of $C_{q'}(C_q)$ $\Rightarrow h$ indep.of C_q
- t_w **large:** superposition includes equilibrium curve

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

Mean Square Displacement

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

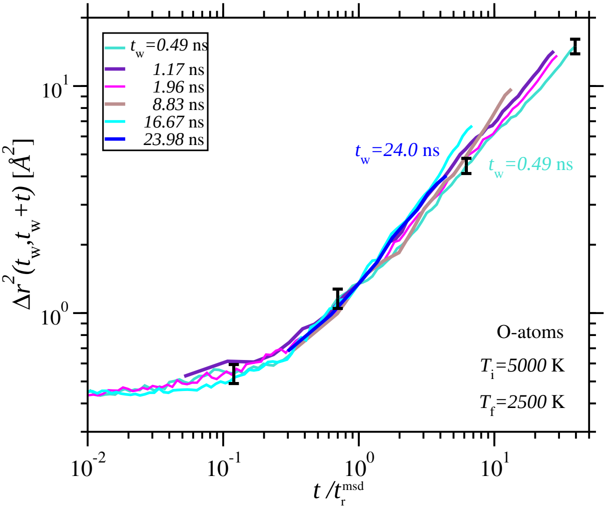


Three t_w Ranges:

- t_w **small:**
  - $t_\mathrm{w} = 0 \,\&\, t \lesssim 5 \cdot 10^{-5}$ 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

$$\Delta r^2(t_{\rm w}, t_{\rm w}+t) = \left(\Delta r^2\right)^{\rm ST}(t) + \left(\Delta r^2\right)^{\rm AG}\left(\frac{t}{t_{\rm r}^{\rm msd}(t_{\rm w})}\right)$$



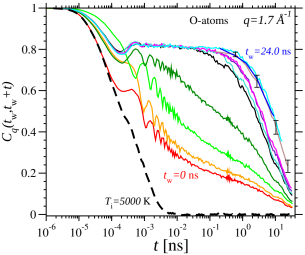
- t_w **small:** no time superposition
- t_w **intermediate:** **no** time superposition
- t_w **large:** **no** time superposition

Summary

$C_q(t_\mathrm{w}, t_\mathrm{w}+t)$ and $\Delta r^2(t_\mathrm{w}, t_\mathrm{w}+t)$:

Three t_w Ranges:

- t_w **small:**
  - $t_\mathrm{w} = 0$ 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 Δr^2)
  - $C_q^{\mathrm{AG}}\left(\frac{h(t_\mathrm{w}+t)}{h(t_\mathrm{w})}\right)$: h is C_q indep.
- t_w **large:**
  - indep. of t_w and $T_i \longrightarrow$ 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)

Acknowledgments:

A. Zippelius & Institute of Theoretical Physics, University Göttingen, Germany