The TN formalism for physical aging

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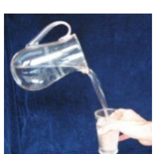
Winter school "Driven Amorphous Materials", Nov. 21, 2022
Weizmann Institute of Science, Rehovot



Supercooled liquid ↔ Glass

Liquid: Metastable equilibrium, given by p and T: No memory
Glass: Out-of-equilibrium state, often formed by cooling

Any glass is continuously relaxing toward the liquid state
[Tammann, Simon, 1920s and 1930s]

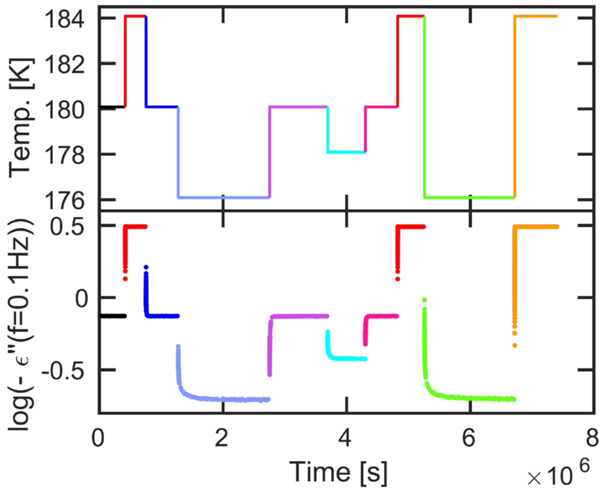
- **"PHYSICAL AGING"**

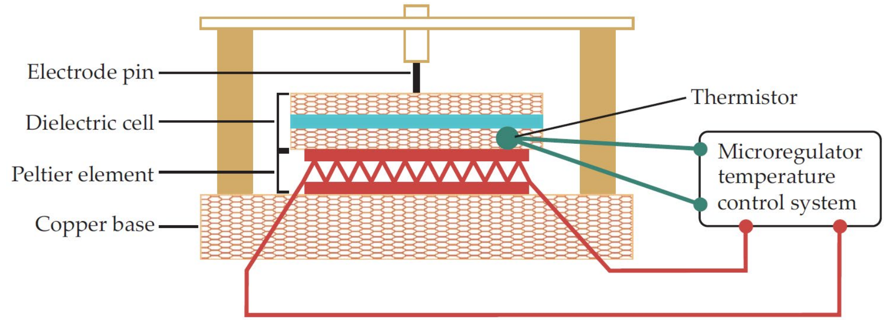
Aging characteristics:

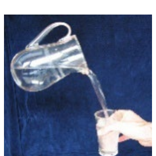
- Relaxation "stretching" after T jump magnitude dependent
- Ritland-Kovacs crossover effect …

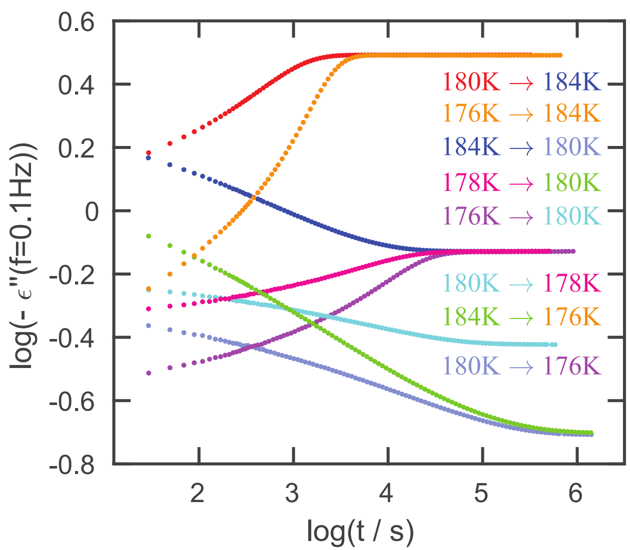
Glycerol data

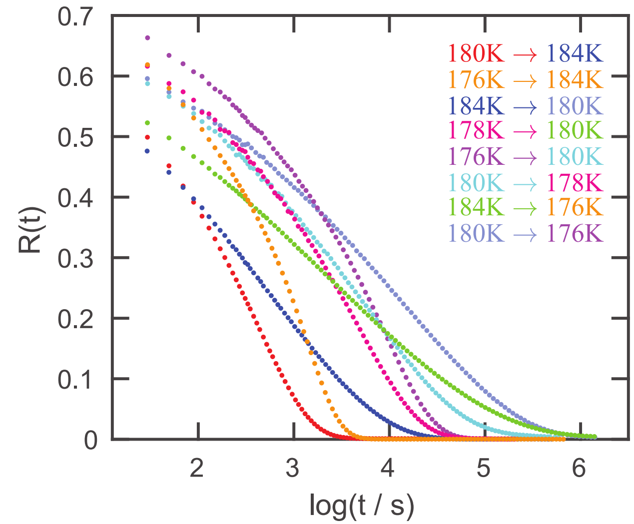
[L. A. Roed *et al.*, J. Chem. Phys. **150**, 044501 (2019)]











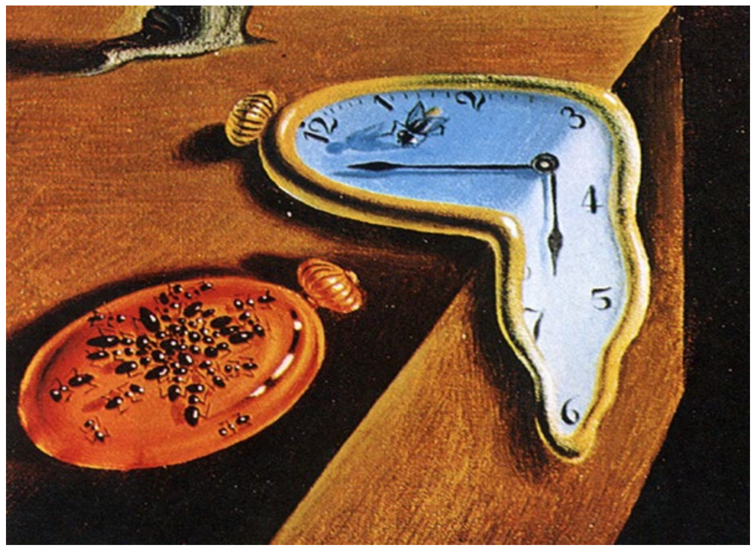
The material time

[O. S. Narayanaswamy, J. Amer. Ceram. Soc. **54**, 491 (1971)]

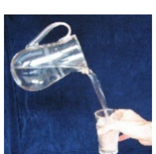
A Model of Structural Relaxation in Glass

O. S. NARAYANASWAMY

Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121

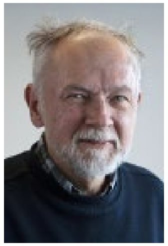


$$R(t) = \phi(\xi)$$ for all temperature jumps



Single-parameter aging

[T. Hecksher *et al.,* J. Chem. Phys. **142**, 241103 (2015); PNAS **116**, 16736 (2019)]



$$R(t) = \phi(\xi) \qquad \dot{R} = \phi'(\xi)\gamma(t) \qquad d\xi = \gamma(t)\,dt$$

$$\dot{R} = -F(R)\,\gamma(t)$$

$$\Delta X \equiv X - X_{\mathrm{eq}} = c_1(Q - Q_{\mathrm{eq}})$$

$$\ln\gamma - \ln\gamma_{\mathrm{eq}} = c_2(Q - Q_{\mathrm{eq}})$$

$$\gamma(t) = \gamma_{\mathrm{eq}}\exp\left(a\frac{\Delta X(0)}{X_{\mathrm{eq}}}R(t)\right)$$

Single-parameter aging II

[T. Hecksher *et al.*, J. Chem. Phys. **142**, 241103 (2015); PNAS **116**, 16736 (2019)]

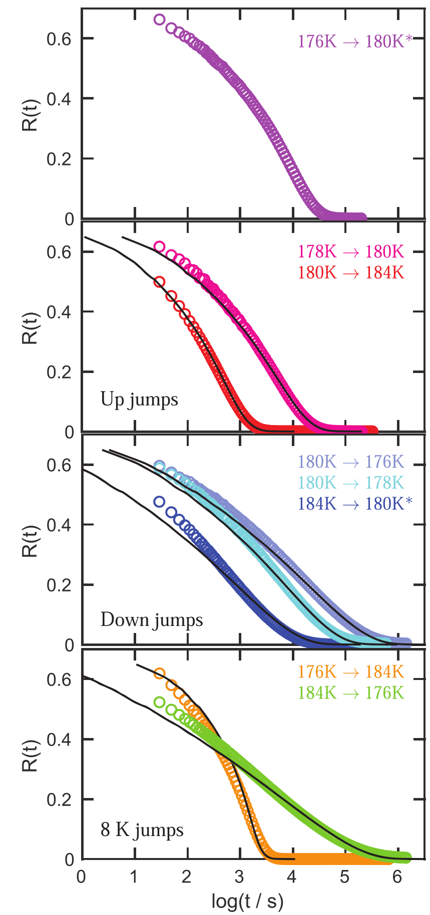
$$\dot{R} = -\gamma_{\mathrm{eq}} F(R) \exp\left(a \frac{\Delta X(0)}{X_{\mathrm{eq}}} R\right)$$

$$R_1 = R_2$$

$$\frac{dR_1}{dt_1} \exp\left(-a \frac{\Delta X_1(0)}{X_{\mathrm{eq}}} R_1\right) = \frac{dR_2}{dt_2} \exp\left(-a \frac{\Delta X_2(0)}{X_{\mathrm{eq}}} R_2\right)$$

$$dR_1 = dR_2 \qquad dt_2 = \exp(\Lambda_{12} R_1) dt_1$$

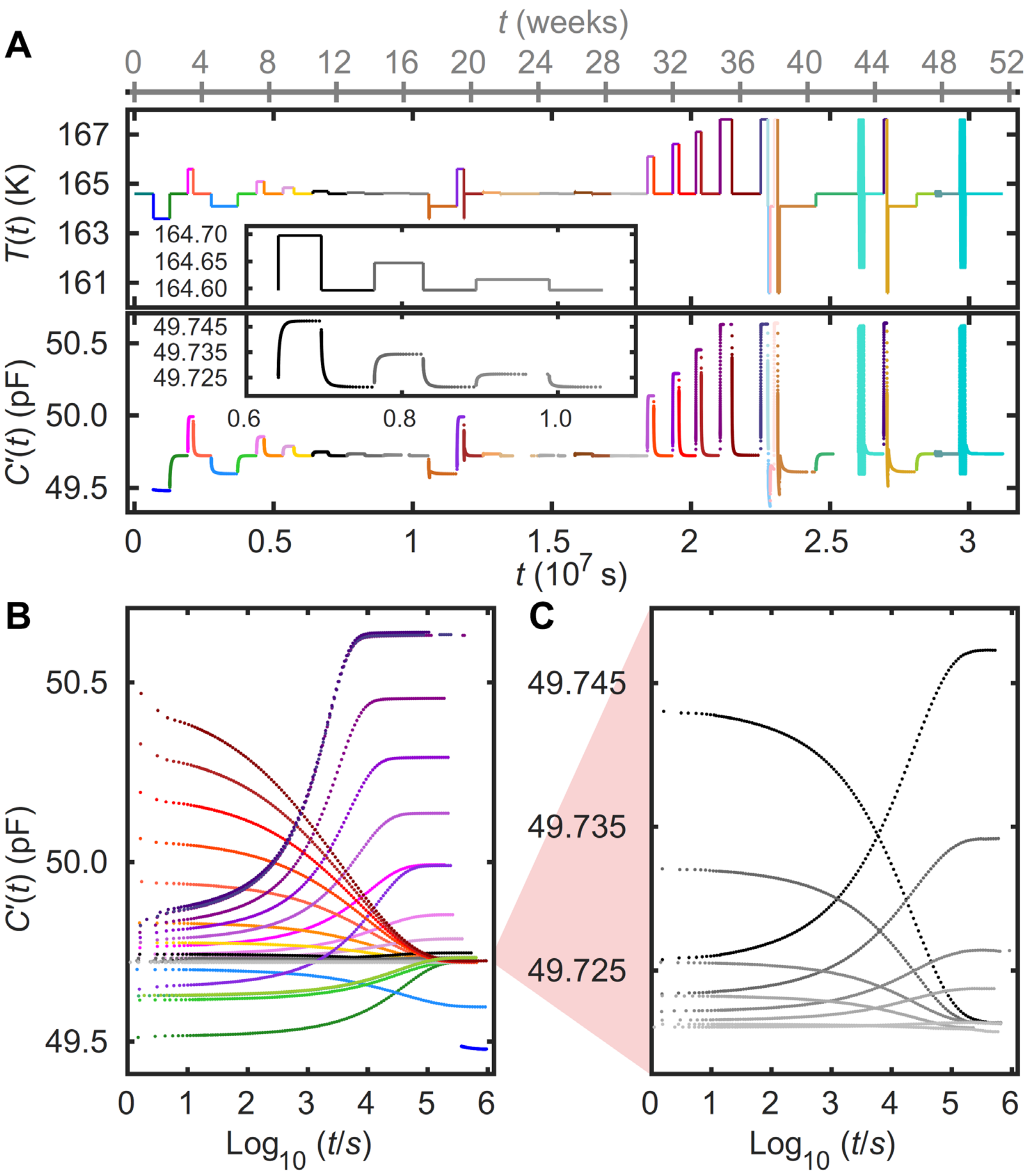
$$t_2(R) = \int_0^{t_2(R)} dt_2 = \int_0^{t_1(R)} e^{\Lambda_{12} R_1(t_1)}\, dt_1$$



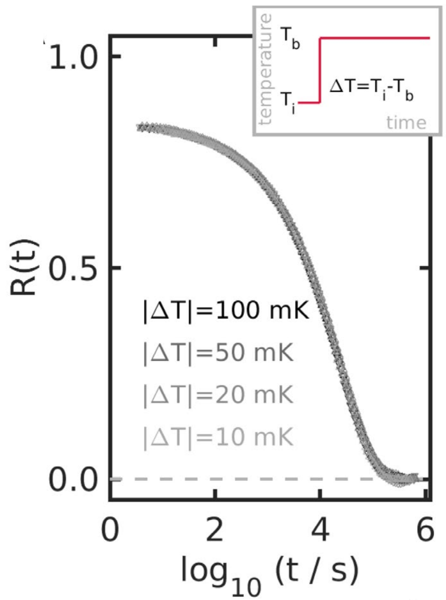
$$\int_0^{\infty} \left(e^{\Lambda_{12} R_1(t_1)} - 1\right) dt_1 + \int_0^{\infty} \left(e^{-\Lambda_{12} R_2(t_2)} - 1\right) dt_2 = 0$$

VEC aging

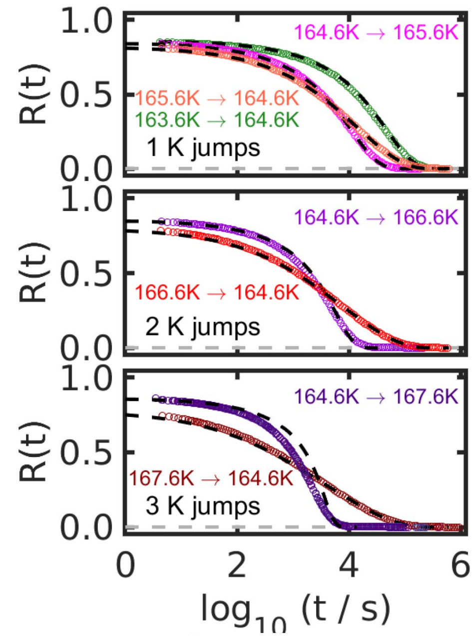
[B. Riechers *et al.*, Sci. Adv. **8**, eabl9809 (2022); 10 kHz capacitance monitored]



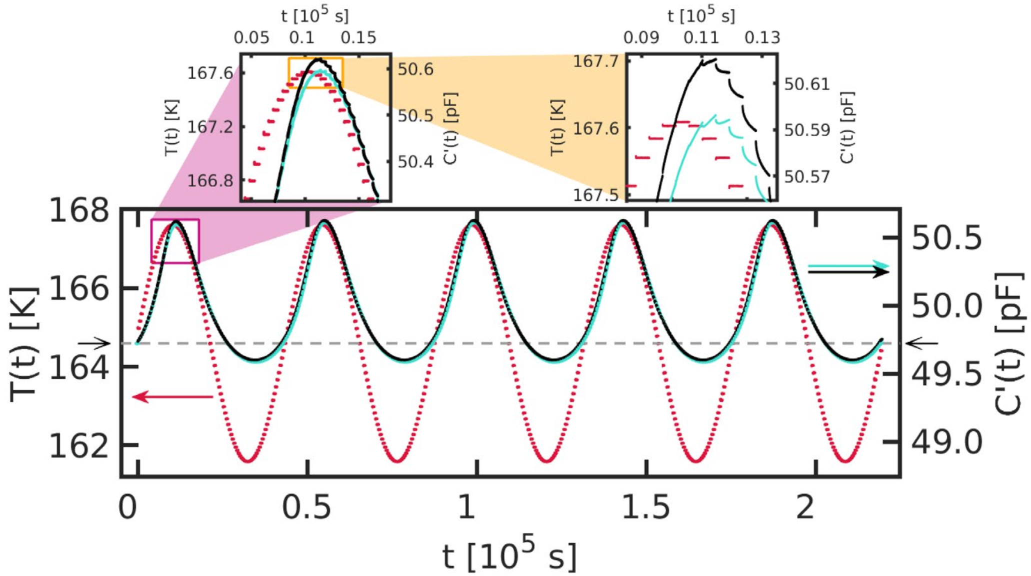
VEC Aging II



temperature
T_b
T_i
$\Delta T = T_i - T_b$
time
R(t)
1.0
0.5
0.0
|ΔT|=100 mK
|ΔT|=50 mK
|ΔT|=20 mK
|ΔT|=10 mK
0 2 4 6
$\log_{10}$ (t / s)



164.6K → 165.6K
165.6K → 164.6K
163.6K → 164.6K
1 K jumps
164.6K → 166.6K
166.6K → 164.6K
2 K jumps
164.6K → 167.6K
167.6K → 164.6K
3 K jumps
R(t)
1.0
0.5
0.0
0 2 4 6
$\log_{10}$ (t / s)



t [10^5 s]
0.05 0.1 0.15
T(t) [K]
167.6
167.2
166.8
C'(t) [pF]
50.6
50.5
50.4
t [10^5 s]
0.09 0.11 0.13
167.7
167.6
167.5
50.61
50.59
50.57
T(t) [K]
168
166
164
162
C'(t) [pF]
50.5
50.0
49.5
49.0
0 0.5 1 1.5 2
t [10^5 s]

What is the material time?

[I. M. Douglass and J. C. Dyre, Phys. Rev. E **106**, 054615 (2022)]

"Distance-as-time" in thermal equilibrium: $\boldsymbol{R} = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$

$\langle \triangle\, \boldsymbol{r}^2(t) \rangle = f(t)$ can be invented into

$$t_2 - t_1 = \mathrm{F}(\mathrm{d}(\boldsymbol{R}_1, \boldsymbol{R}_2))$$

[Related: Haan 1979; JCD cond-mat/9712222]

"Distance-as-time" in physical aging:

$$\xi(t_2) - \xi(t_1) = \mathrm{F}(\mathrm{d}(\boldsymbol{R}_1, \boldsymbol{R}_2))$$

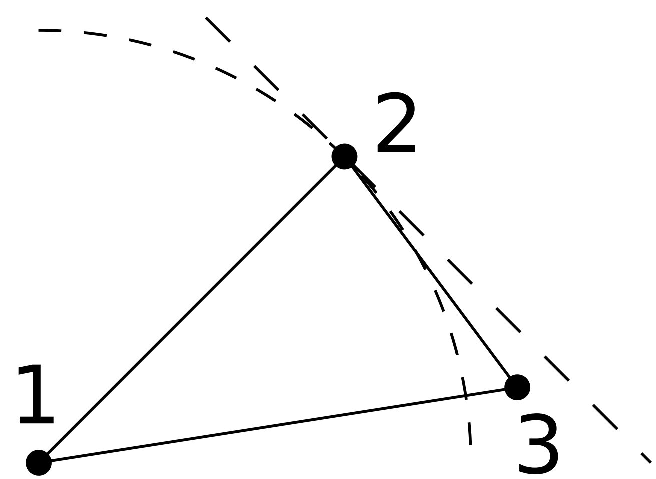
[Related: Schober 2004, 2012, 2021]

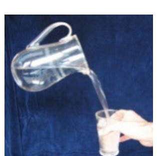
Consequence 1: "Unique-triangle property"

Suppose that $\xi(t_2) - \xi(t_1) = f\big(\mathrm{d}(\boldsymbol{R}_1, \boldsymbol{R}_2)\big)$.

Then likewise for $t_1 < t_2 < t_3$
$\xi(t_3) - \xi(t_2) = f\big(\mathrm{d}(\boldsymbol{R}_2, \boldsymbol{R}_3)\big)$ and $\xi(t_3) - \xi(t_1) = f\big(\mathrm{d}(\boldsymbol{R}_1, \boldsymbol{R}_3)\big)$.

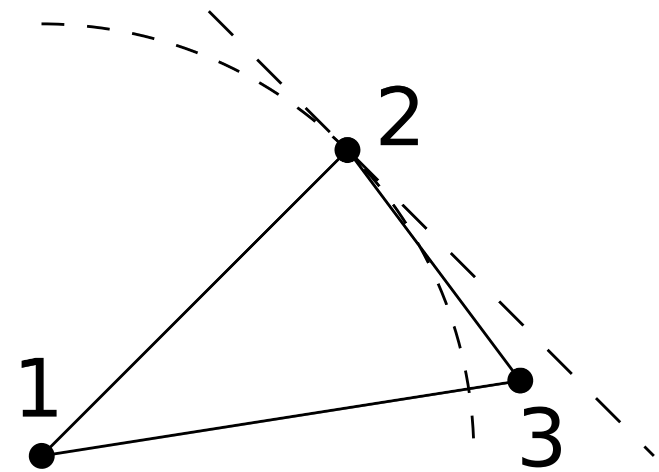
Since $\xi(t_3) - \xi(t_1) = \ (\xi(t_3) - \xi(t_2)) + (\xi(t_2) - \xi(t_1))$, any two side lengths determine the third in the $\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3$ triangle:





Consequence 2: "Geometric reversibility"

$$\xi(t_2) - \xi(t_1) = f\big(\mathrm{d}(\boldsymbol{R}_1, \boldsymbol{R}_2)\big)$$

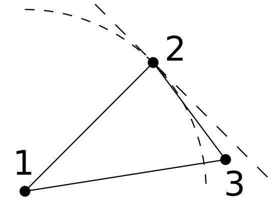


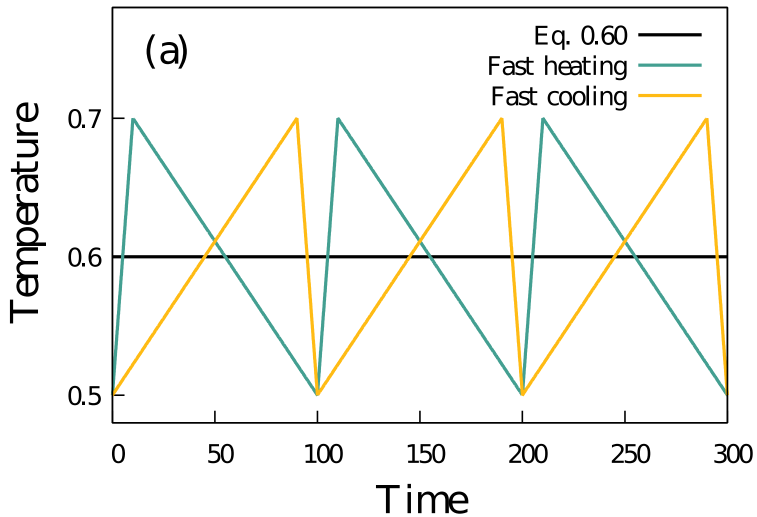
$$\mathrm{d}(\boldsymbol{R}_1, \boldsymbol{R}_3) = \mathrm{F}(\mathrm{d}(\boldsymbol{R}_1, \boldsymbol{R}_2), \mathrm{d}(\boldsymbol{R}_2, \boldsymbol{R}_3)) = \mathrm{F}(\mathrm{d}(\boldsymbol{R}_2, \boldsymbol{R}_3), \mathrm{d}(\boldsymbol{R}_1, \boldsymbol{R}_2))$$

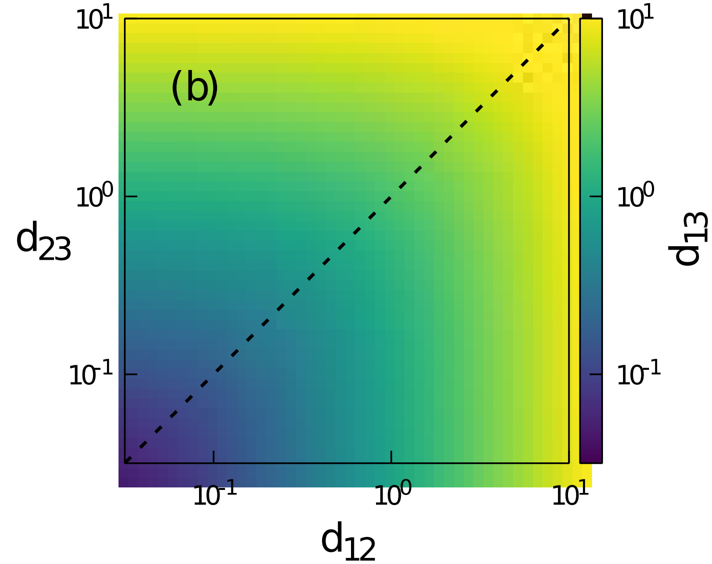
Inherited from equilibrium.

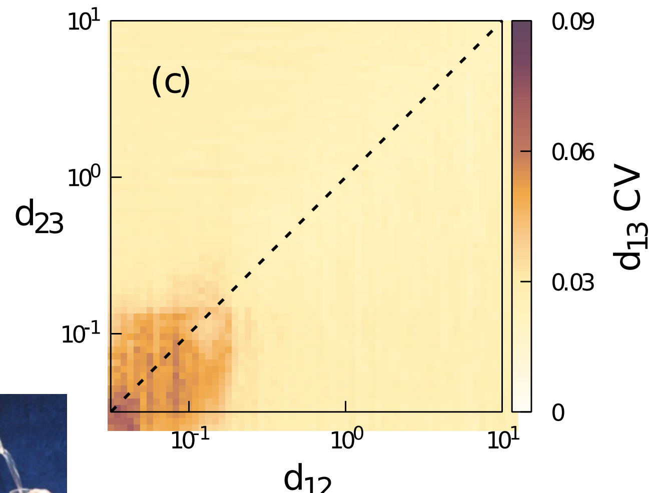
Closely related **triangular relation and commutativity**:
Kurchan & Cugliandolo, 1994 $C_{13} = F(C_{12}, C_{23})$

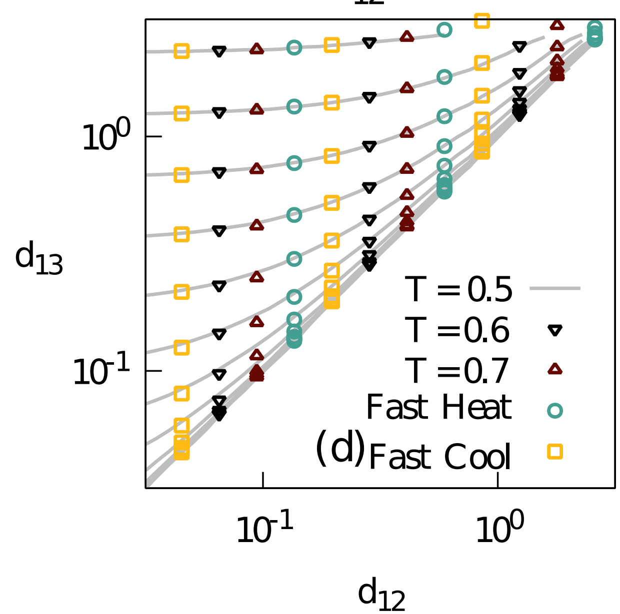
Kob-Andersen model simulations



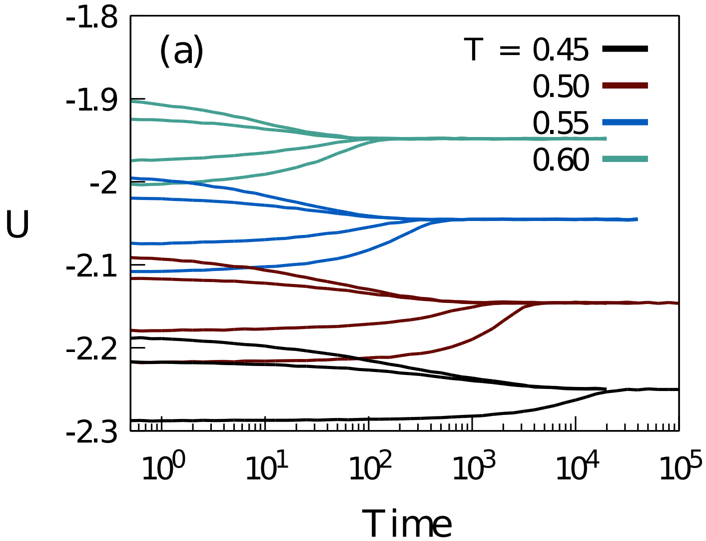


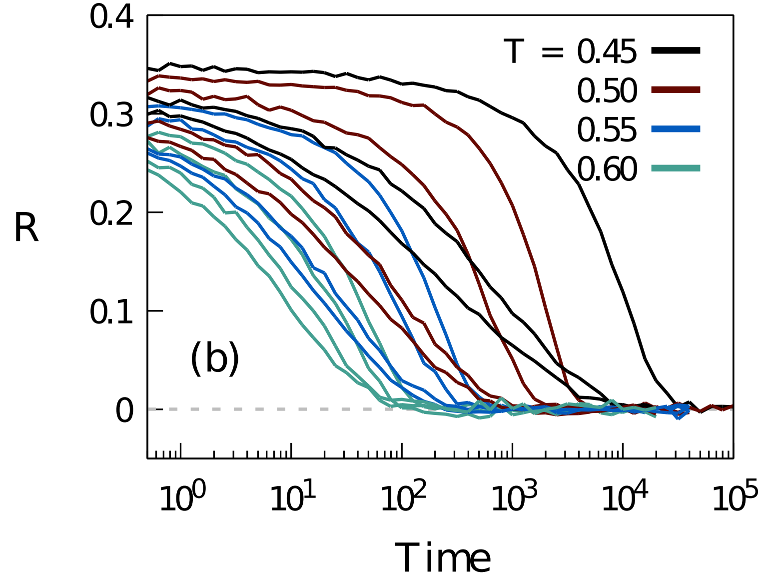


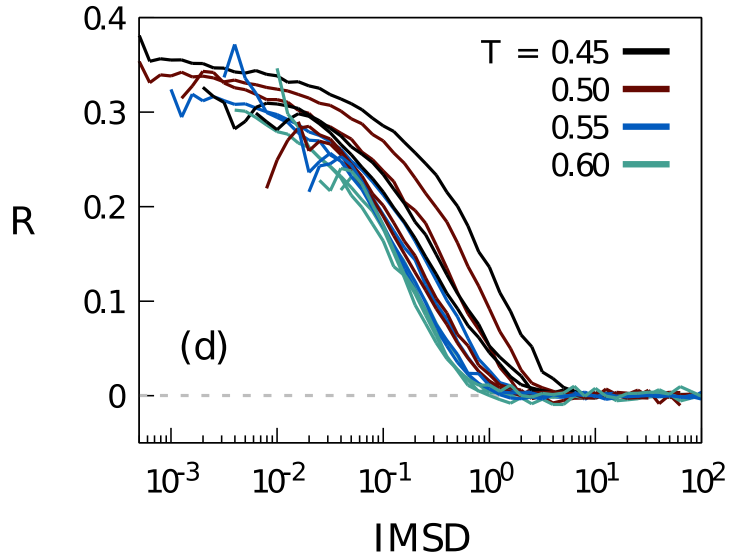




Does $R(t) = \phi(\xi)$ apply?





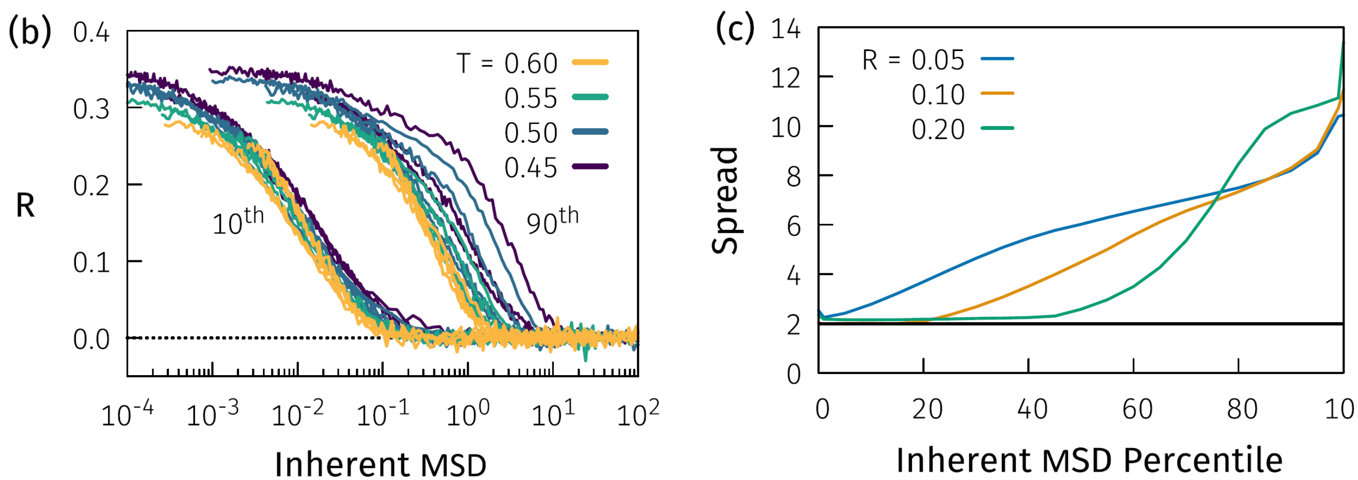


Inherent MSD

Role of dynamic heterogeneity

Fast-moving particles contribute a lot to the MSD but do not really relax the structure (leading to Stokes-Einstein relation violations).

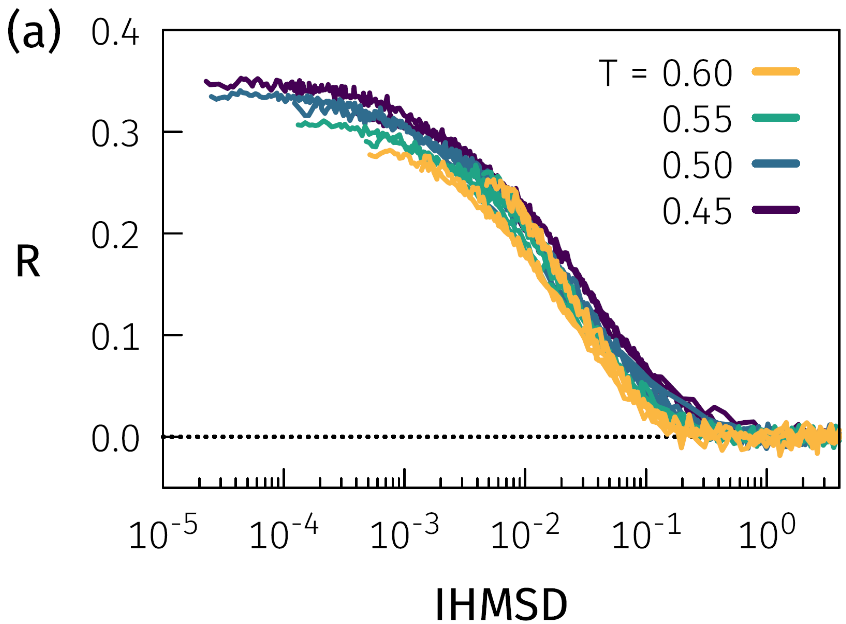
Should one define the material time in terms of the (inherent) MSD of the slowest particles? **Median square displacement** instead of MSD?

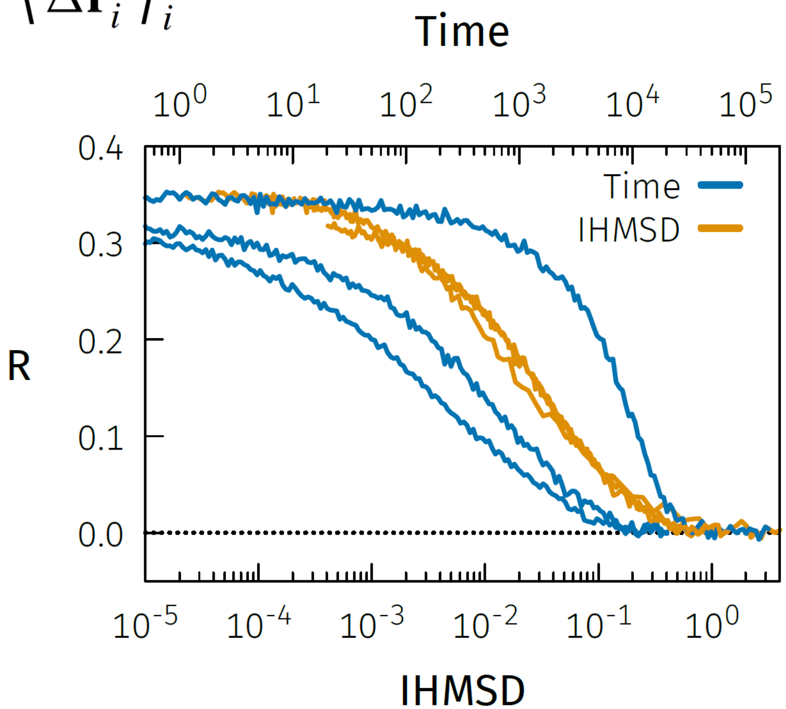


Role of dynamic heterogeneity II

Results for **Inherent harmonic mean square displacement**

$$\frac{1}{\langle \Delta \mathbf{r}^2 \rangle_{\mathrm{IHMSD}}} \equiv \left\langle \frac{1}{\Delta \mathbf{r}_i^2} \right\rangle_i$$



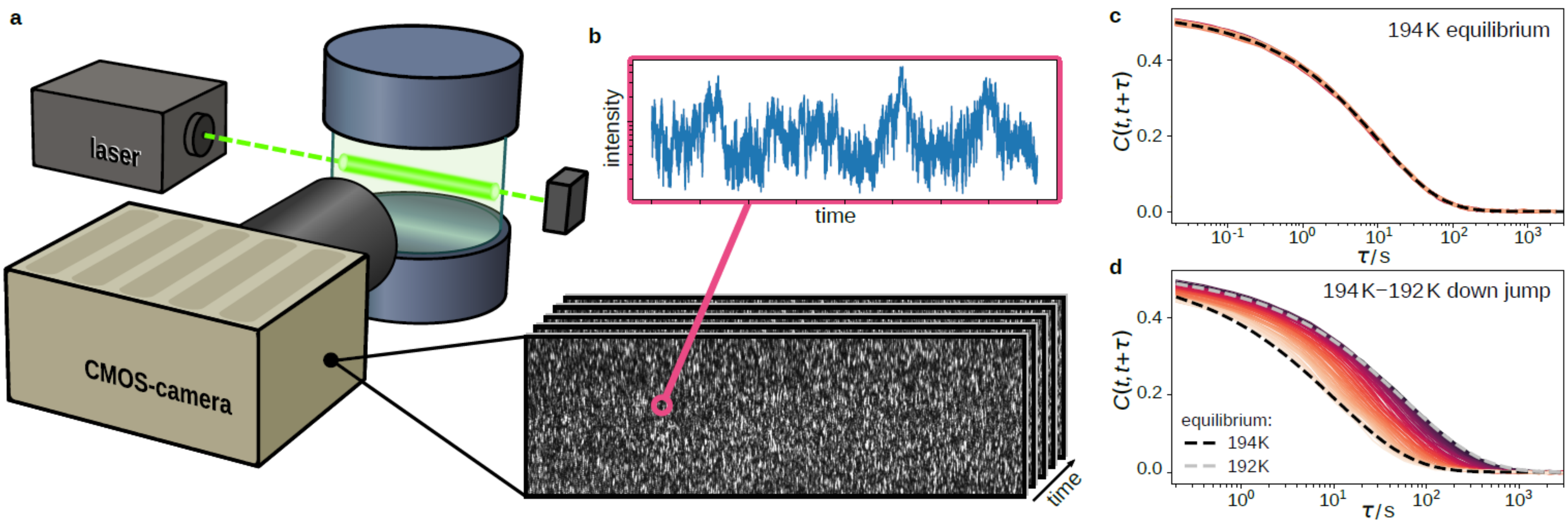


Jumps to T=0.45

Dynamic light scattering

[Ongoing work with Thomas Blochowicz and Till Böhmer, (Darmstadt), Jan Gabriel and Tina Hecksher, (Roskilde)]

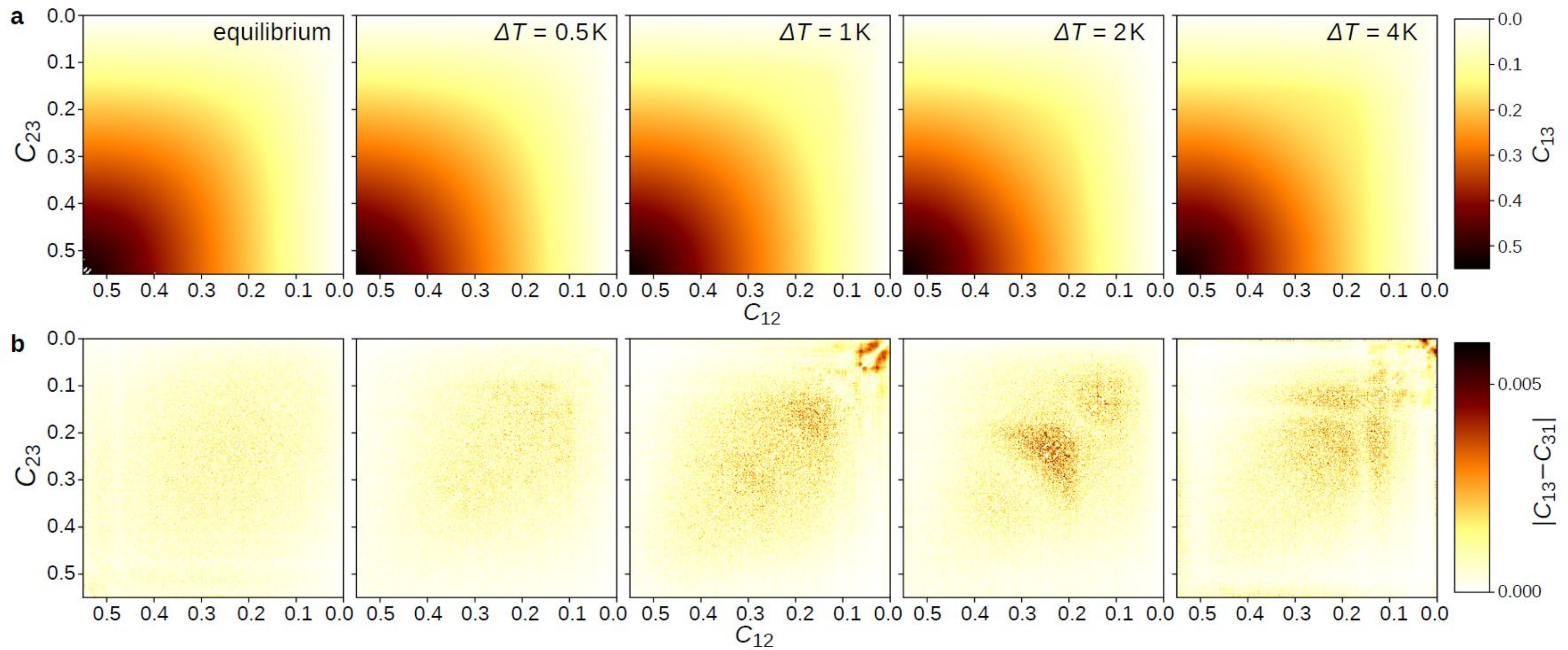
Determine the intensity time-autocorrelation function



Dynamic light scattering II

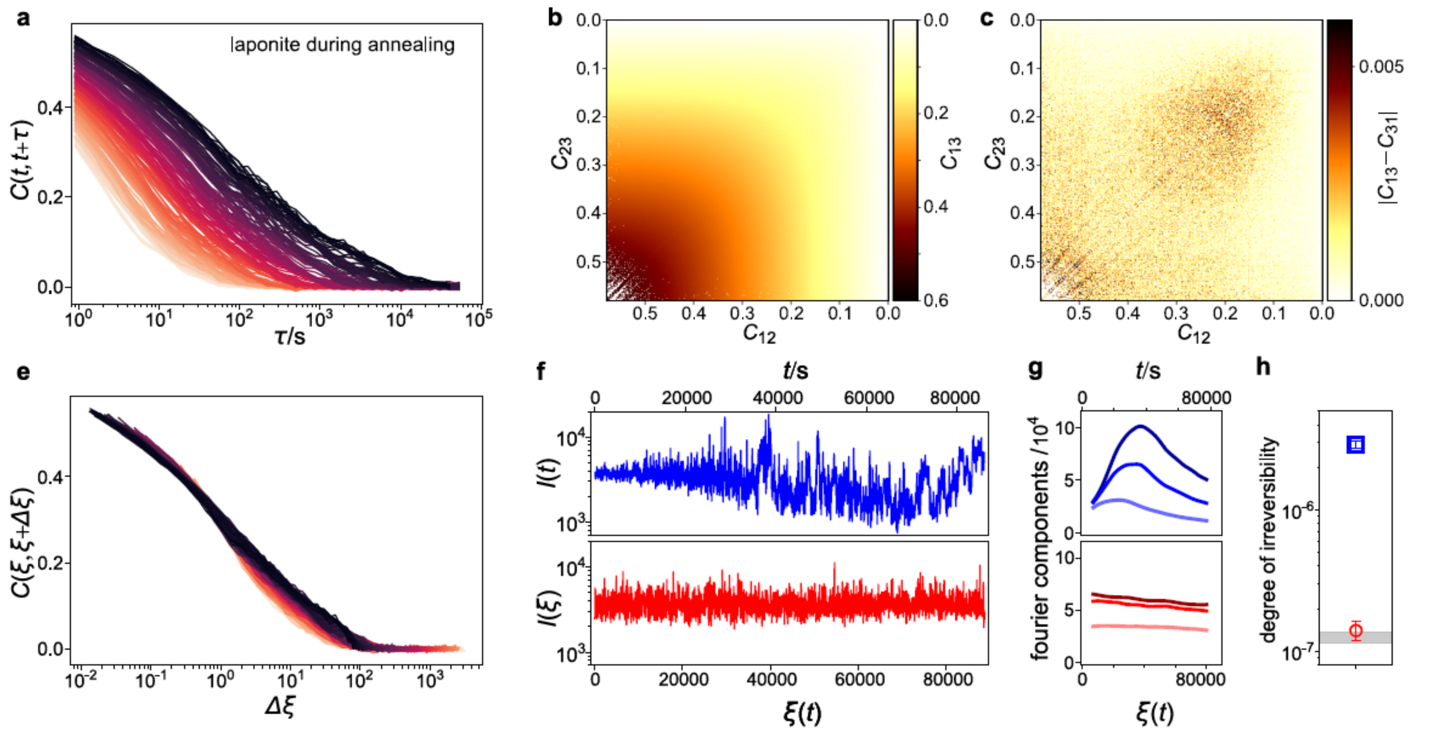
Testing the triangular relation for the intensity time-autocorrelation function:

$$C_{13} = F(C_{12}, C_{23})$$

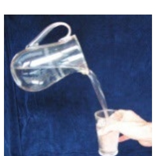


1-phenyl-1-propanol

Dynamic light scattering III



Laponite



Conclusions

- Single-parameter aging has been confirmed in experiments and simulations.
- Aging can be predicted from its linear limit.
- The implied fact that aging can be predicted from a knowledge of equilibrium fluctuations (FD theorem) has been confirmed in simulations [Mehri *et al*., J. Chem. Phys. **154**, 094504 (2021)], but await experimental confirmation.
- The reversibility condition and the triangular relation (Kurchan & Cugliandolo, 1994) has been confirmed in experiments and simulations.

Thanks!

TN, TTS, and time-scale coupling

[I. M. Douglass and JCD, Phys. Rev. E **106**, 054615 (2022)]

$$q_a(t) = \int_{-\infty}^{t} \phi_{ab}(t - t')\, \delta e_b(t')$$

$$d(t_0, t) = \alpha t + \beta \qquad q_a(t) = \int_{-\infty}^{t} \psi_{ab}[d(t_0, t) - d(t_0, t')]\, \delta e_b(t')$$

$$\xi(t) \equiv d(t_0, t)$$

$$q_a(t) = \int_{-\infty}^{\xi(t)} \psi_{ab}[\xi(t) - \xi']\, \delta e_b(\xi')$$

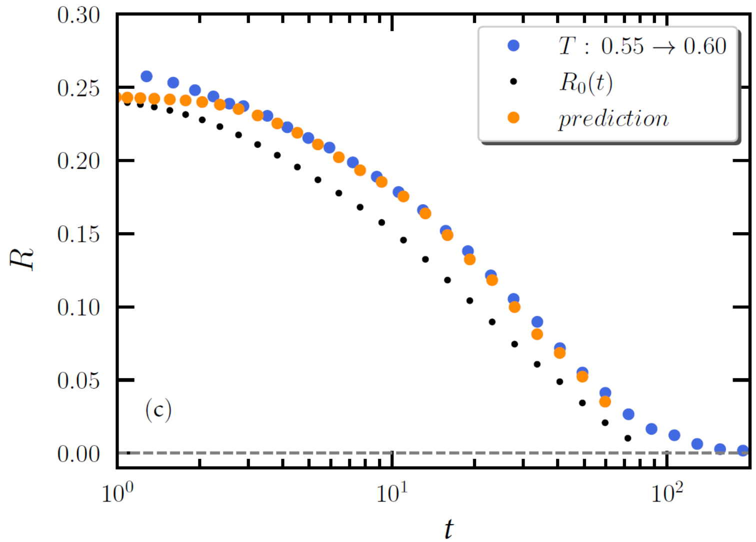
TN equation

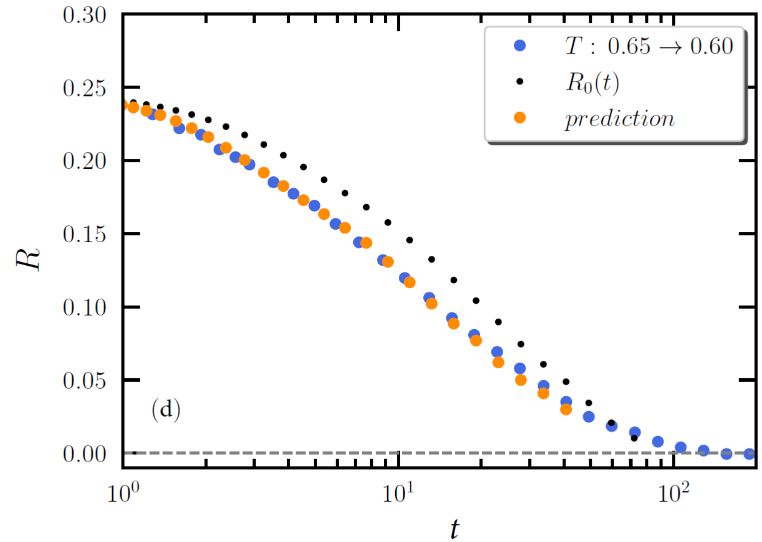
Single-parameter aging III

[S. Mehri *et al.*, Thermo. **142**, 241103 (2021)]

$$\dot{R} = -F(R)\, e^{\Lambda R}$$

$$R(t) = R_0(t) + \Lambda R_1(t) \qquad R_1(t) = \dot{R}_0(t) \int_0^t R_0(t')dt'$$





Kob-Andersen binary Lennard-Jones system