Identifying the material time

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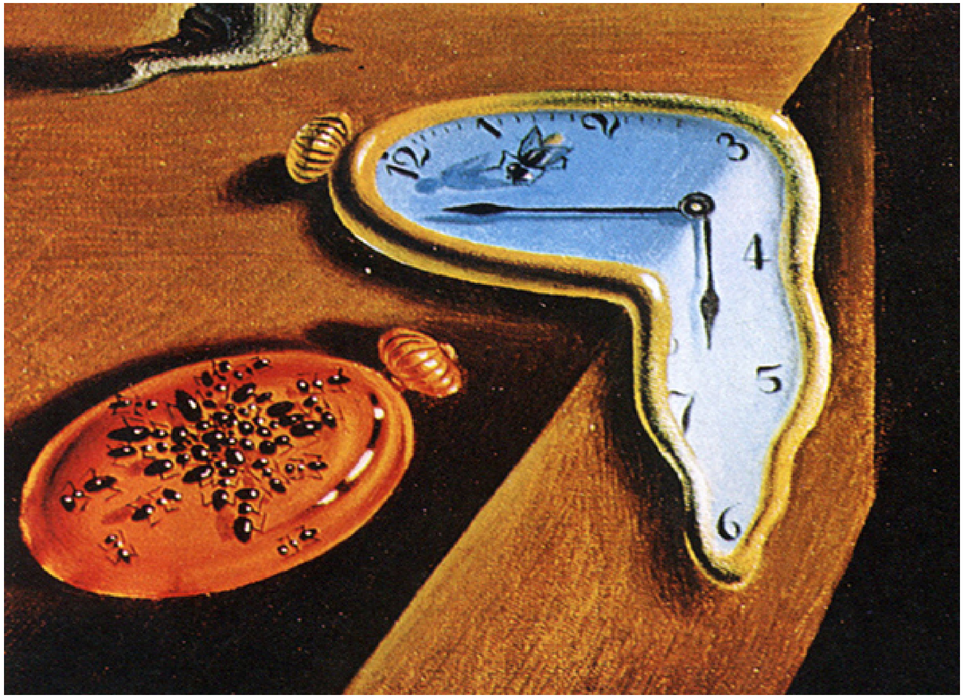

”The persistence of memory”
(Salvador Dali, 1931)

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Simplest physical aging experiment

”Ideal” temperature-jump experiment:

- Start and end in thermal equilibrium
- New temperature established throughout entire sample before any relaxation has taken place
- Monitor some quantity with high accuracy
- Keep temperature stable with high accuracy
- Have enough time to fully reach thermal equilibrium

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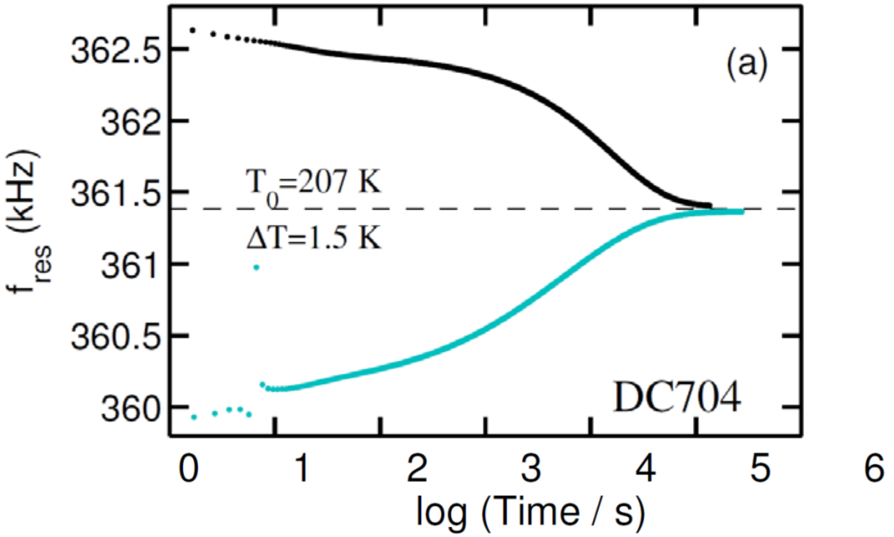
Resonance-frequency setup

Shear transducer

[Christensen & Olsen (1995)]
[Jakobsen *et al* (2005)]
[Maggi *et al* (2008)]

Microregulator
($\delta T < 100 \mu$K)

[Bauer *et al* (2000)]
[Hecksher *et al* (2010)]
[Niss *et al* (2012)]



205.5 K to 207.0 K
Up jump:
Self-accelerated

208.5 K to 207.0 K
Down jump:
Self-retarded

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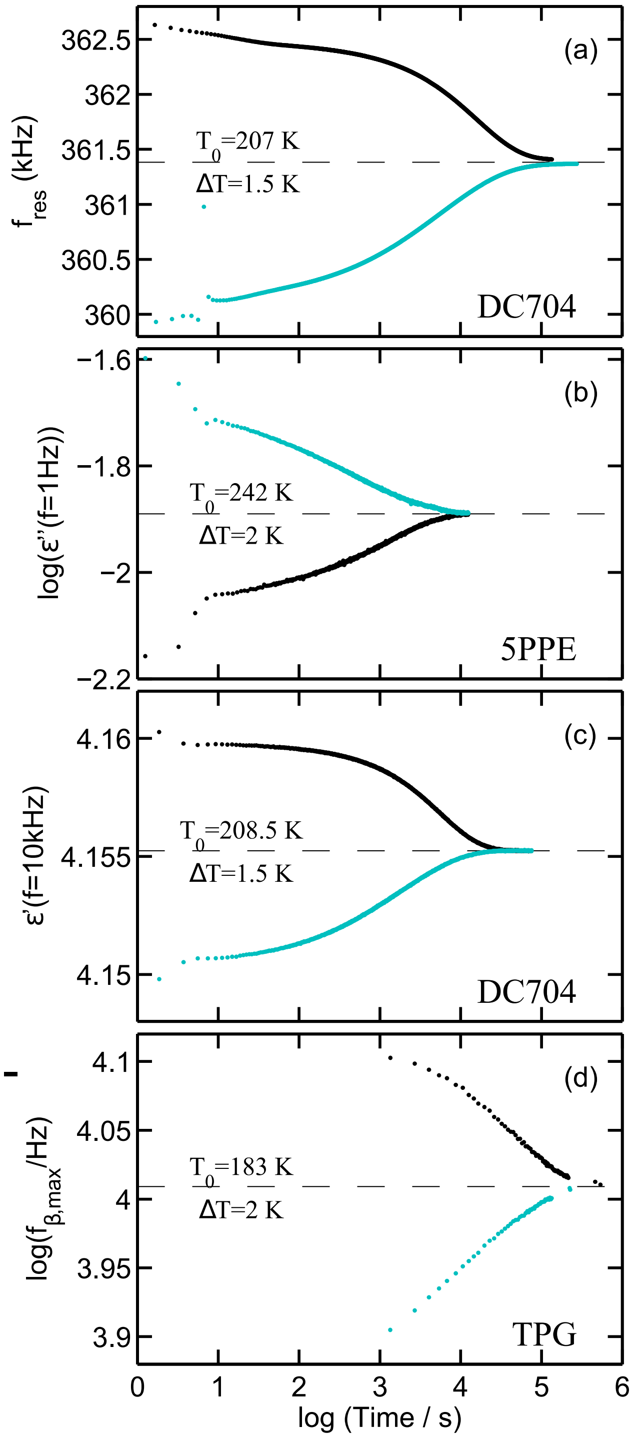
Mechanical resonance frequency

Dielectric loss (1 Hz)

Dielectric constant (10 kHz)

Beta relaxation loss-peak frequency
[PRL **91**, 155703 (2003)]



Up jumps: Black

Down jumps: Light blue

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From Narayanaswamy to a differential equation

A Model of Structural Relaxation in Glass

O. S. NARAYANASWAMY
Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121

October 1971 Journal of The American Ceramic Society—Narayanaswamy Vol. 54, No. 10

$$R(t) = \phi(\xi)$$

$$R(t) \equiv \frac{\Delta X(t)}{\Delta X(0)}$$

$$\dot{R} = \phi'(\xi)\gamma(t)$$

$$d\xi = \gamma(t)\, dt$$

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

<u>Single-parameter assumption:</u>
Aging rate activation energy proportional to $\Delta X(t)$

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

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

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

Referred to as ”Eq. (8)” on next slide

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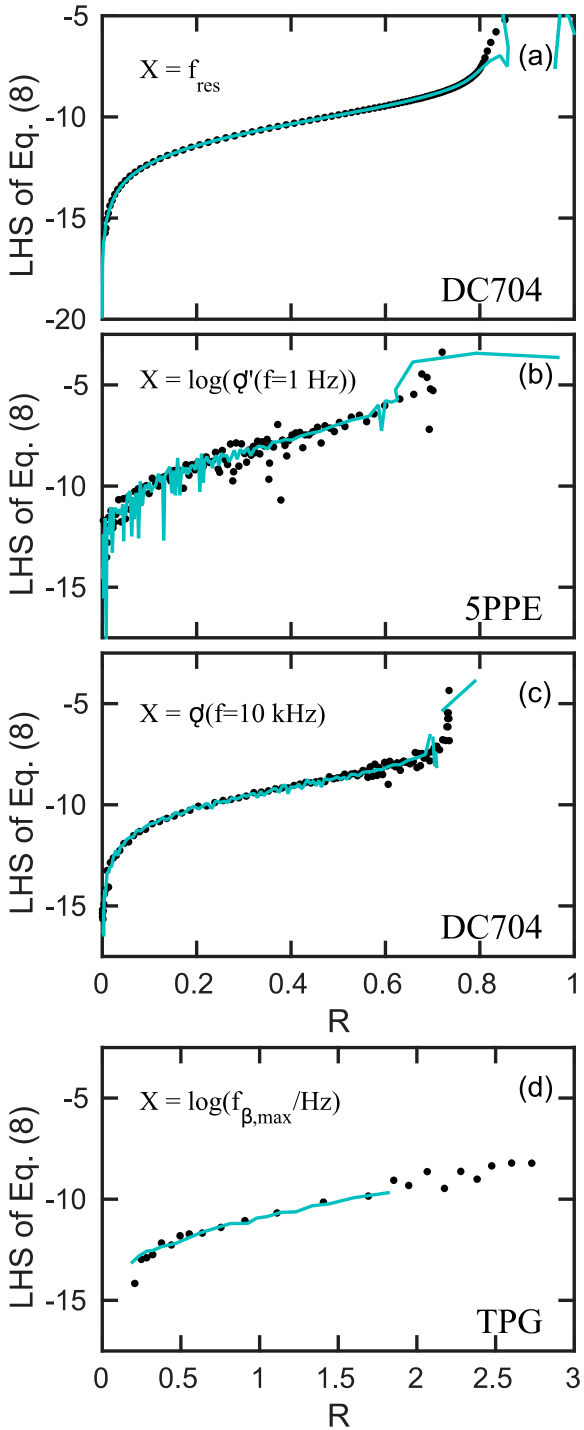

THE JOURNAL OF CHEMICAL PHYSICS **142**, 241103 (2015)

Communication: Direct tests of single-parameter aging

Tina Hecksher, Niels Boye Olsen, and Jeppe C. Dyre[a)]
DNRF Center "Glass and Time," IMFUFA, Department of Sciences, Roskilde University, P.O. Box 260, DK-4000 Roskilde, Denmark

(Received 23 May 2015; accepted 15 June 2015; published online 30 June 2015)

Calculating one temperature jump relaxation curve from another

Recalling that $d\xi = \gamma dt$, comparing two jumps leads to

$$\gamma_1(t_1)dt_1 = \gamma_2(t_2)dt_2$$

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

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

$$\Lambda_{12} \equiv a(\Delta X_1(0) - \Delta X_2(0))/X_{\mathrm{eq}}$$

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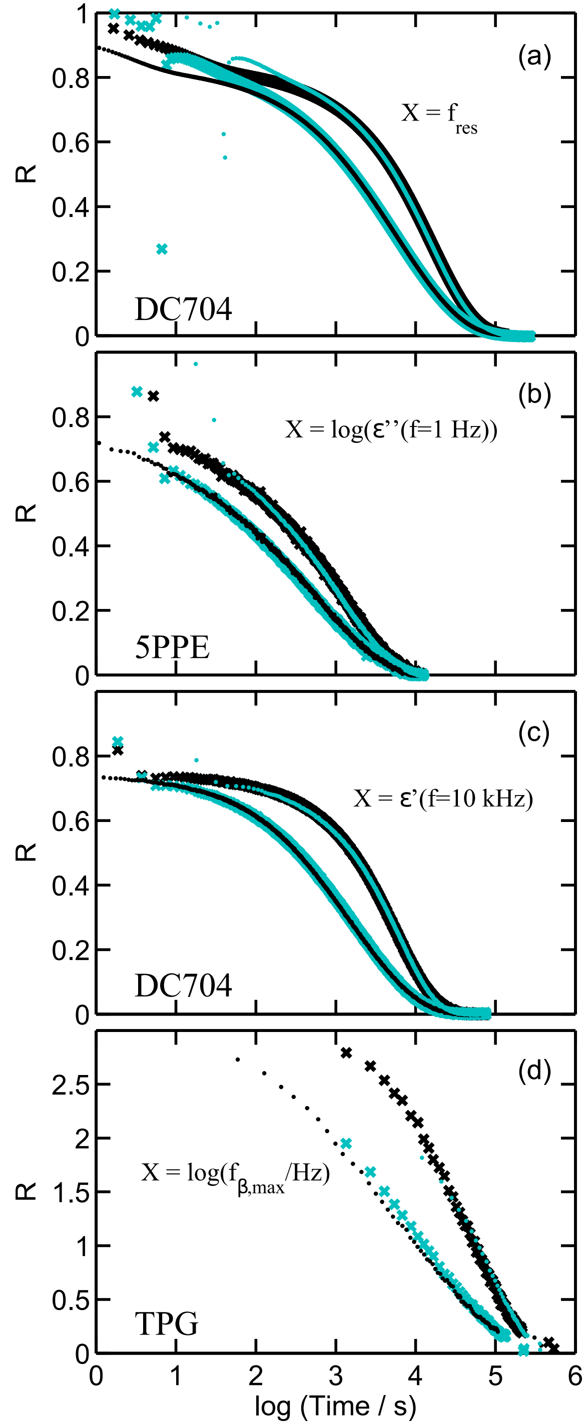

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Identifying the material time in computer simulations

If a system obeys the Narayanaswamy theory, the material time is – except for constants - given by the squared distance to a configuration of the distant past:

$$\xi(t) \equiv R_{0t}^2$$

THE JOURNAL OF CHEMICAL PHYSICS **143**, 114507 (2015)

Narayanaswamy's 1971 aging theory and material time

Jeppe C. Dyre[a)]
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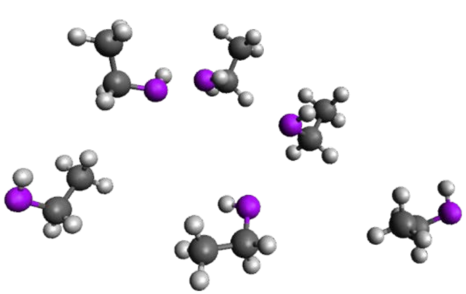
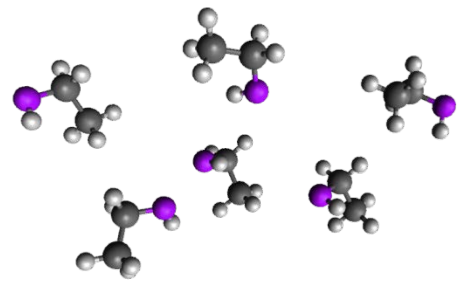
(Received 24 April 2015; accepted 27 August 2015; published online 17 September 2015)

”Hidden” scale invariance

[J. Chem. Phys. **141**, 204502 (2014)]

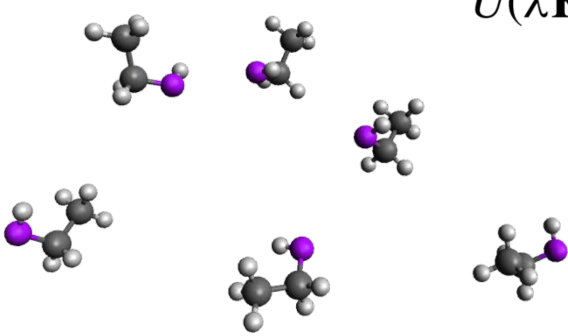


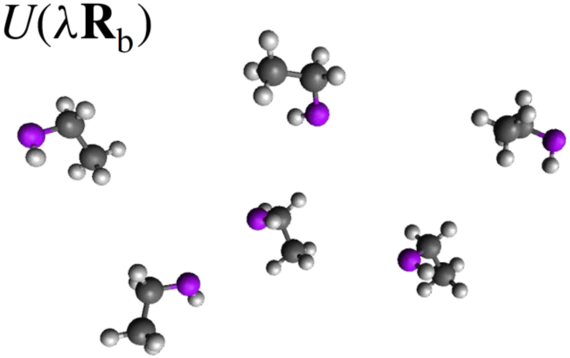


$$U(\mathbf{R}_\mathrm{a}) < U(\mathbf{R}_\mathrm{b})$$

$$\Downarrow$$

$$U(\lambda\mathbf{R}_\mathrm{a}) < U(\lambda\mathbf{R}_\mathrm{b})$$





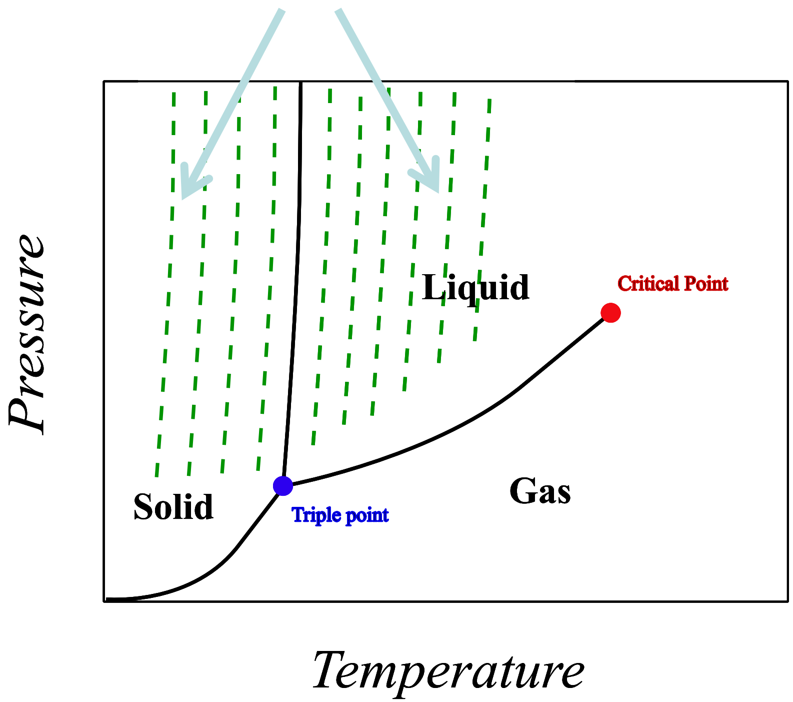
Isomorphs present in:

- Crystals
- Polymers
- Metals
- Plasmas
- Nanoconfined systems
- Plastic flows
- Fluids in 4 dimensions
- Biomembranes
- Mixtures

....

Thermodynamic phase diagram

Isomorphs



Explains rules, e.g.:

- ”Entropy controls viscosity”
- ”A solid melts when vibrations exceed 10%” (Lindemann, 1910)
- ”…”

- **and their exceptions!**

<u>R-simple systems:</u>

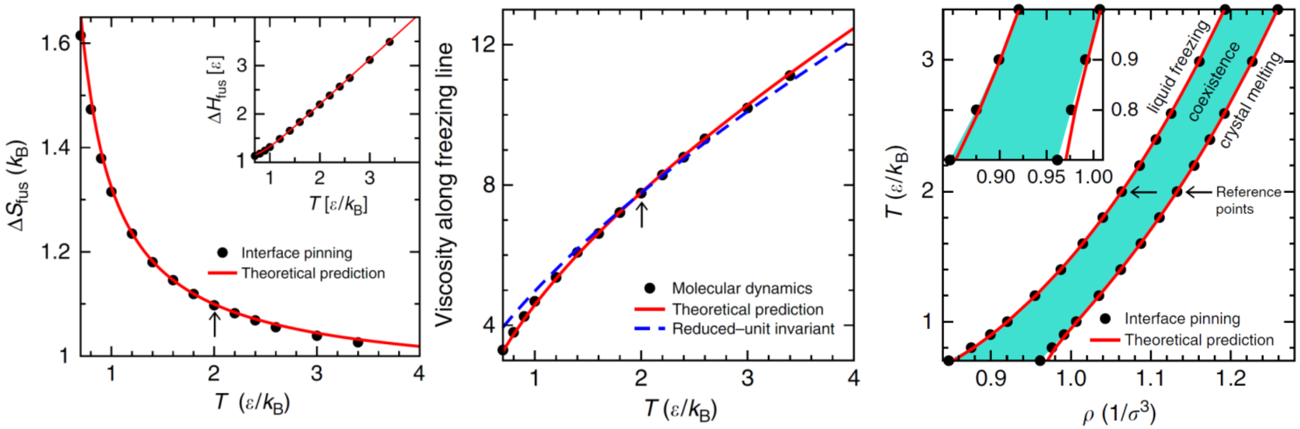
- van der Waals bonded
- metals
- weakly ionic/dipolar

<u>Complex systems:</u>

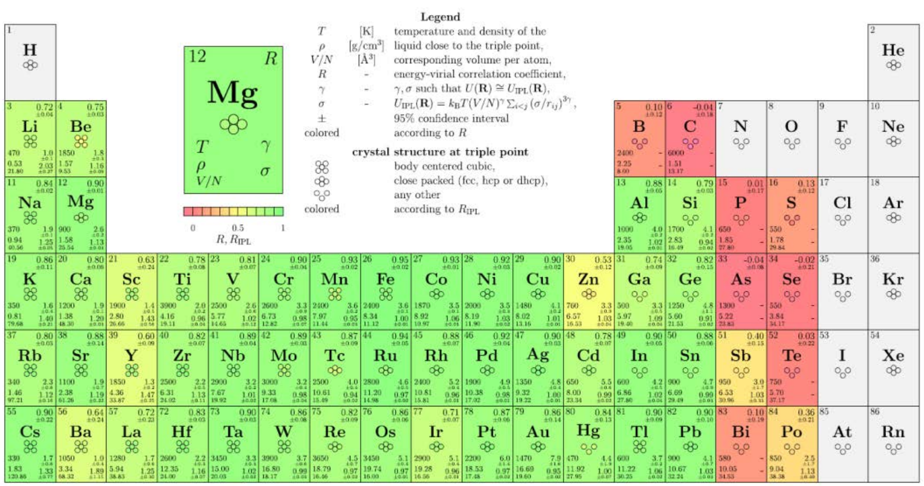
- hydrogen bonded
- covalently bonded
- strongly ionic/dipolar

<u>Reviews</u>:
Phys. Rev. X **2**, 011011 (2012);
J. Phys. Chem. B **118**, 10007 (2014);
J. Phys.: Cond. Mat. **28**, 323001 (2016).

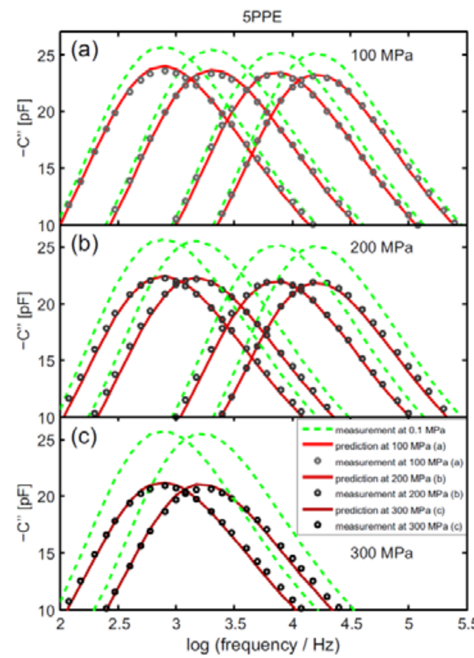
Examples



Melting of the Lennard-Jones system
[Nature Com. **7**, 12386 (2016)]



Ab initio DFT [Phys. Rev. B **92**, 174116 (2015)]



In-house experiments

[J. Non-Cryst. Solids **407**, 190 (2015)]

Isomorph theory of physical aging

Hidden scale invariance: $U(\mathbf{R}_\mathrm{a}) < U(\mathbf{R}_\mathrm{b}) \;\Rightarrow\; U(\lambda\mathbf{R}_\mathrm{a}) < U(\lambda\mathbf{R}_\mathrm{b})$

If a system is R-simple, it obeys if one assumes Langevin (Brownian) dynamics

$$\dot{\tilde{\mathbf{R}}} \;=\; -\frac{T_{\mathrm{eq}}(\rho, U)}{T}\tilde{\nabla}\tilde{S}_{\mathrm{ex}}(\tilde{\mathbf{R}}) \;+\; \tilde{\boldsymbol{\eta}}(\tilde{t}) \qquad \tilde{\mathbf{R}} \equiv \rho^{1/3}\mathbf{R}$$

$$\langle \tilde{\boldsymbol{\eta}}_i(\tilde{t})\boldsymbol{\eta}_j(\tilde{t}')\rangle \;=\; 2\,\delta_{ij}\delta(\tilde{t}-\tilde{t}')$$

- Connects to the ”potential energy clock model” of Adolf *et al.* (2004, 2007).
- Predicts unity Prigogine-Defay ratio [compare JCP **126**, 074502 (2007)]

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Conclusions

- Single-parameter aging describes small temperature jumps for the three systems studied, with an aging rate that depends exponentially on the quantity probed (Tool).

- From general differential equations describing aging to Narayanaswamy – and back to a differential equation for temperature jumps:

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

- The function $\boldsymbol{F}(\boldsymbol{R})$ may be determined from a linear-response experiment.

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