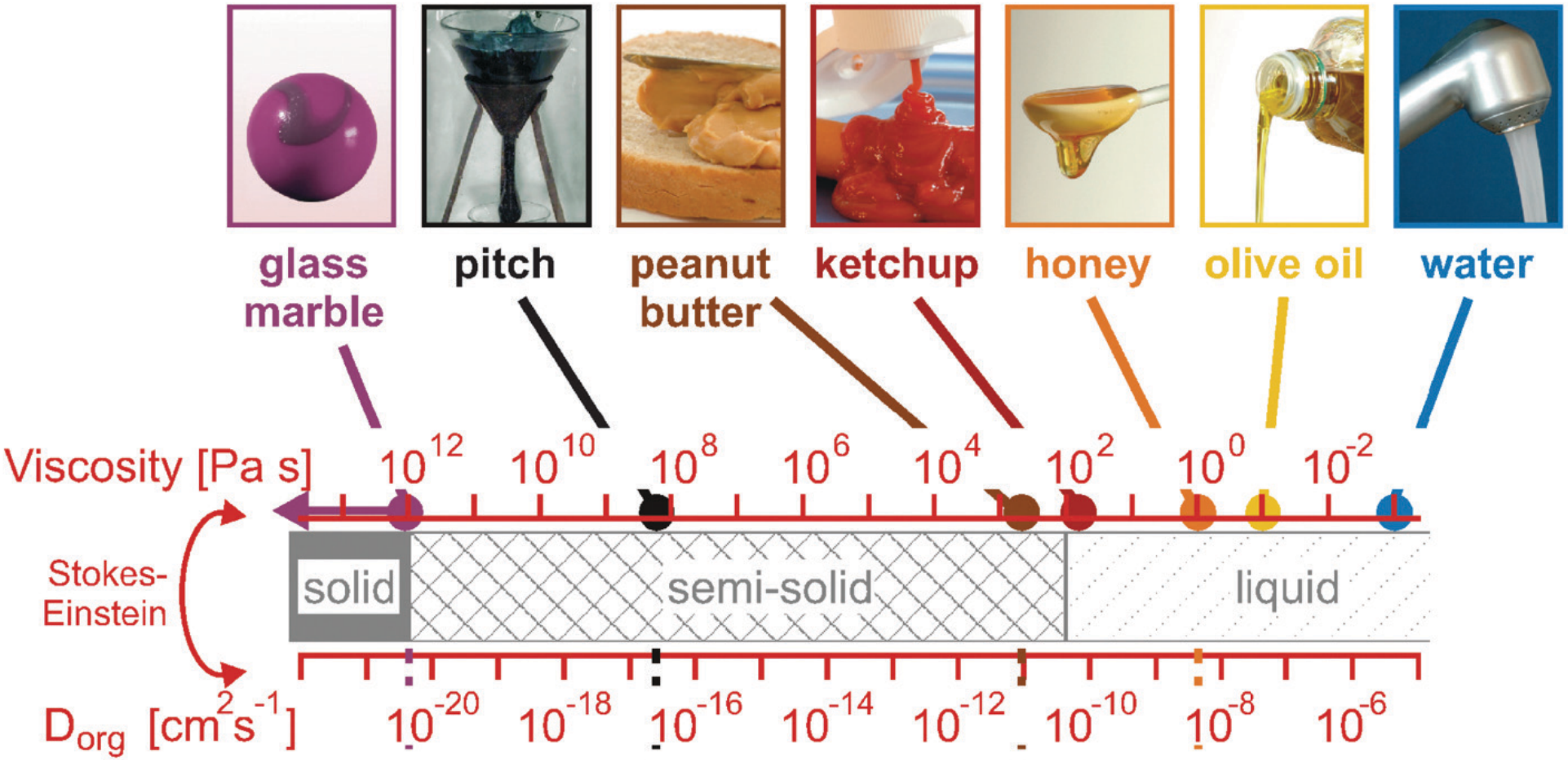
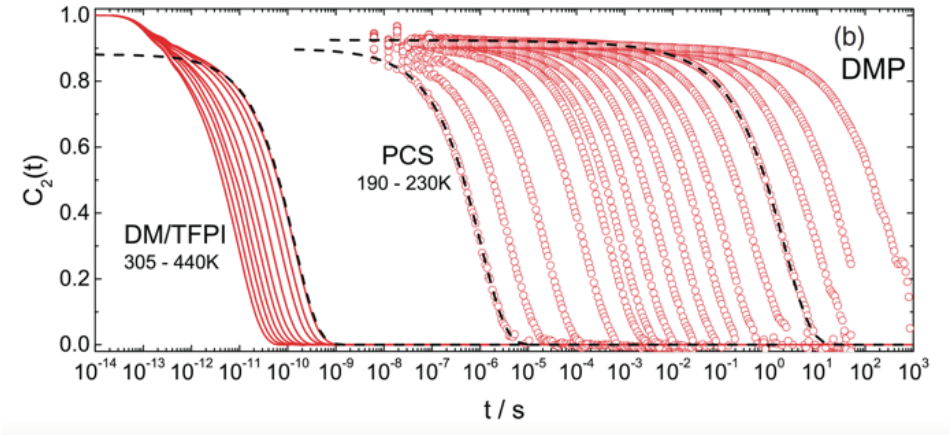



Koop et al., PCCP (2011)

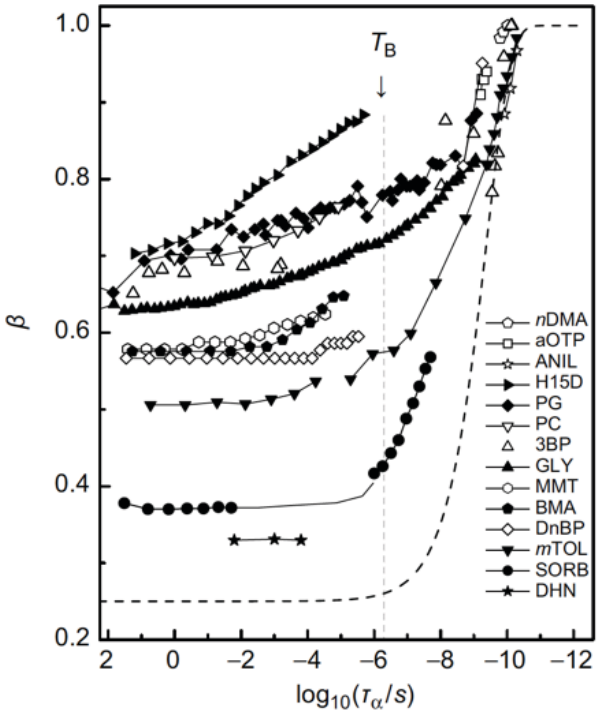
# Experimental perspective on supercooled liquids and glasses (molecular and atomic systems)

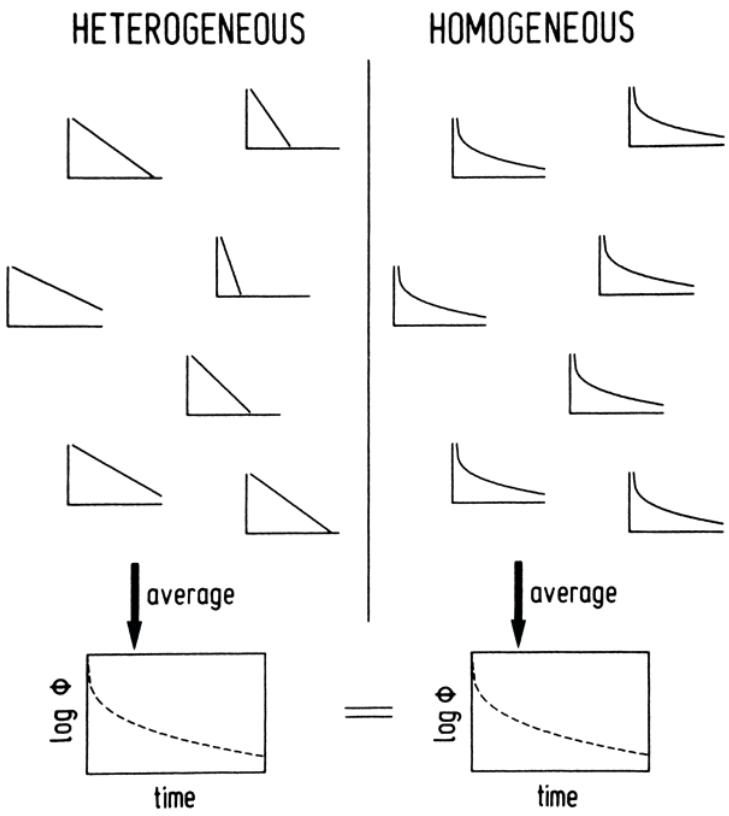
- Dynamics
- Thermodynamics
- Structure
- Heterogeneous dynamics in SCL
- Glass properties
- Transformation kinetics (glass -> SCL)
- Glasses near the bottom of the potential energy landscape (vapor-deposited glasses)

# Dynamics in SCLs continued: Nonexponential correlation functions




Schmidtke, … J. Chem. Phys 139, 084504 (2013)




Richert (1994)

Richert in: Structural Glasses and Supercooled Liquids: Theory, Experiment, and Applications, First Edition. Edited by Peter G. Wolynes and Vassiliy Lubchenko. 2012 John Wiley & Sons, Inc.

# Dynamics in SCLs are heterogeneous in space and time – single molecule optical experiments

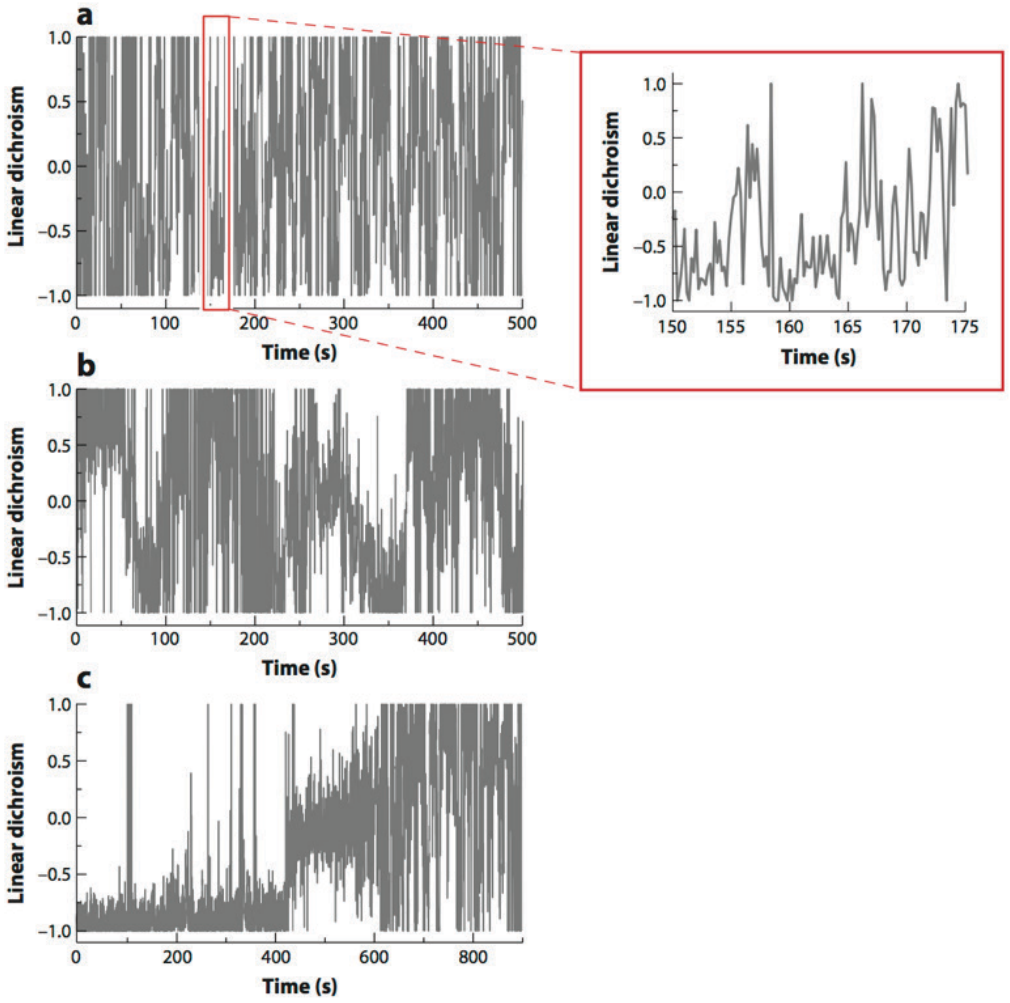
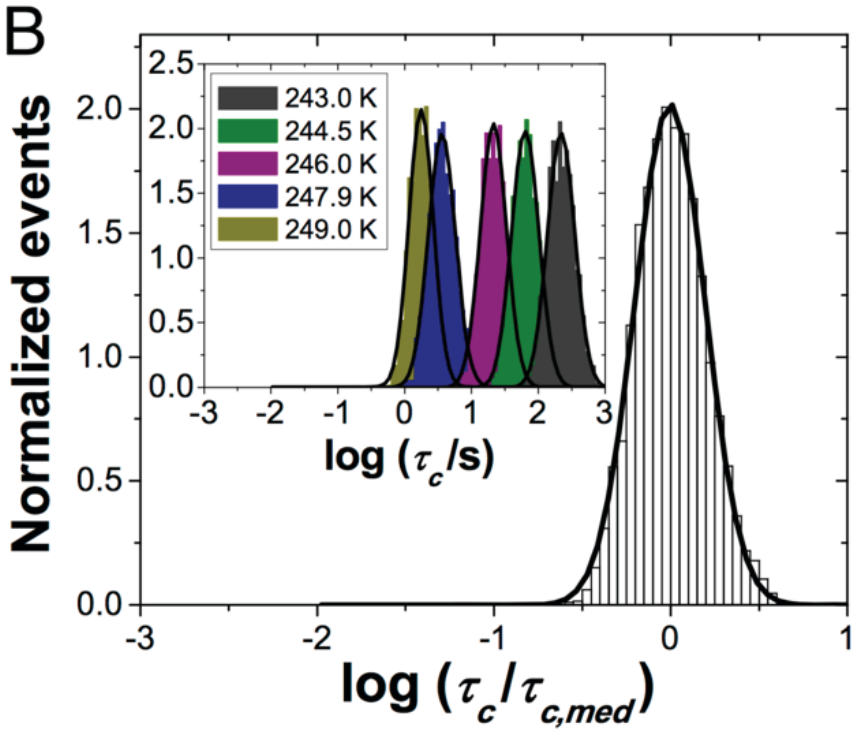



**Figure 3**

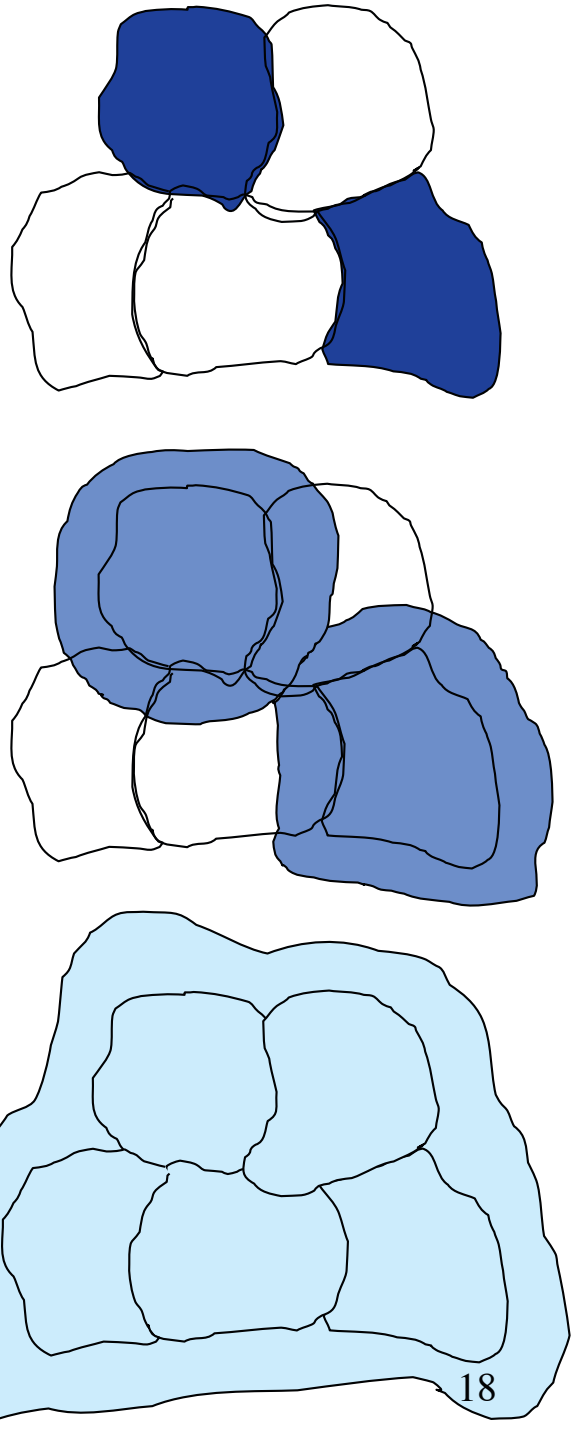
Linear-dichroism trajectory of a (*a*) fast, (*b*) slow, and (*c*) heterogeneous rubrene probe in glycerol at 204 K ($1.07T_g$). Figure adapted with permission from Reference 70. Copyright American Institute of Physics.

Kaufman, Annu. Rev. Phys. Chem. (2013)

# Dynamics in SCLs are spatially heterogeneous

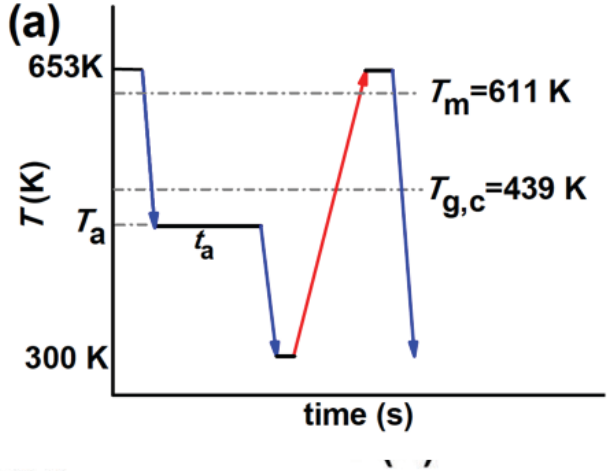


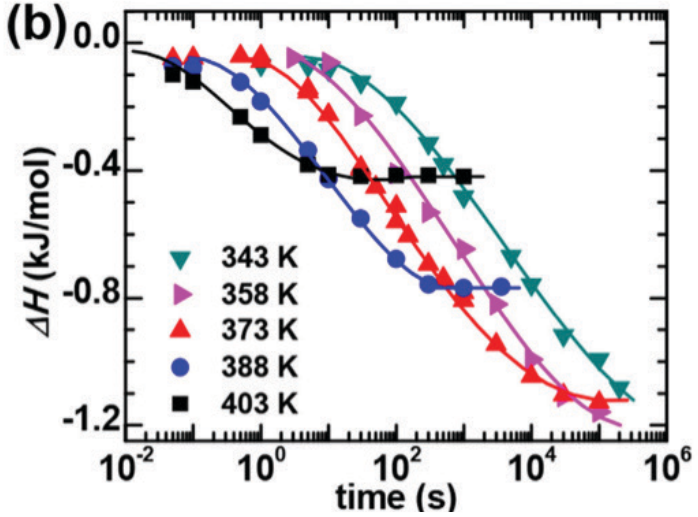

Paeng et al, … PNAS (2015)

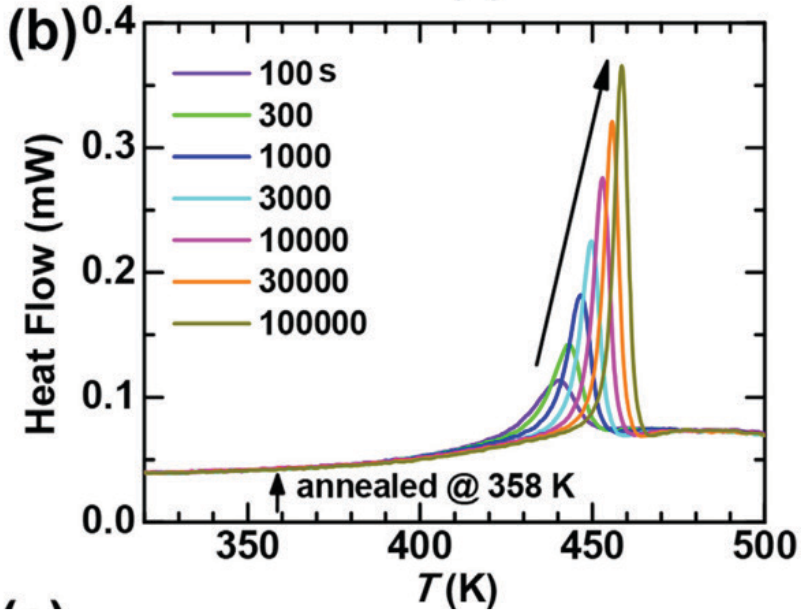


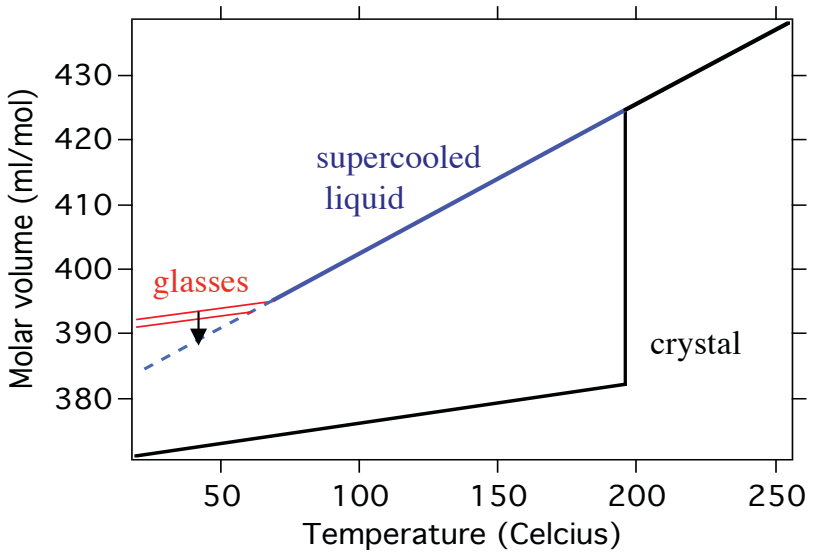
- Single molecule experiments
- 200 $\tau_\alpha$ for one molecule to sample representative environments
- Multidimensional NMR
- $\xi_{het}$ = 1.5 – 4 nm near $T_g$
- Connection to weaker T dependence of D

# Glasses age: Cooling a liquid to just below $T_g$ forms a barely stable glass whose properties change with time



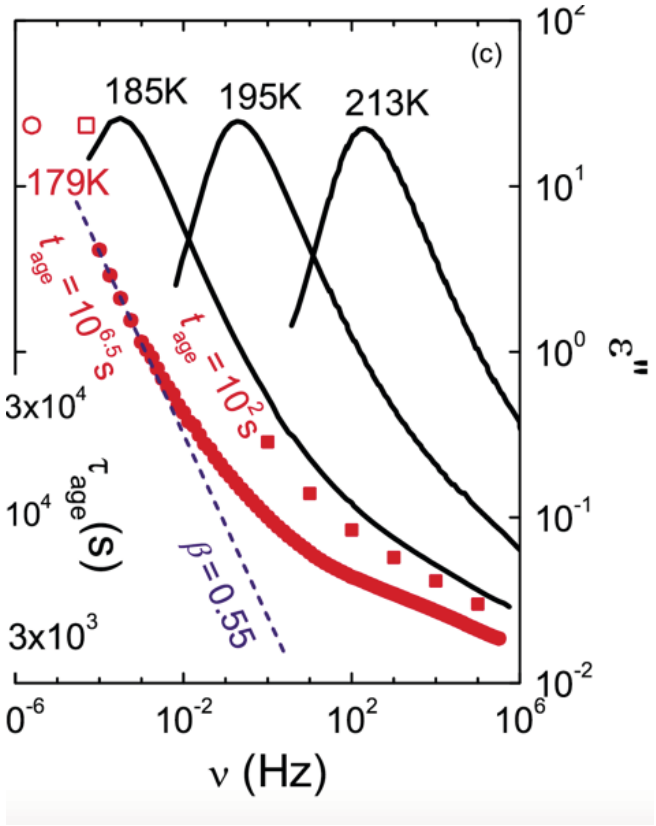



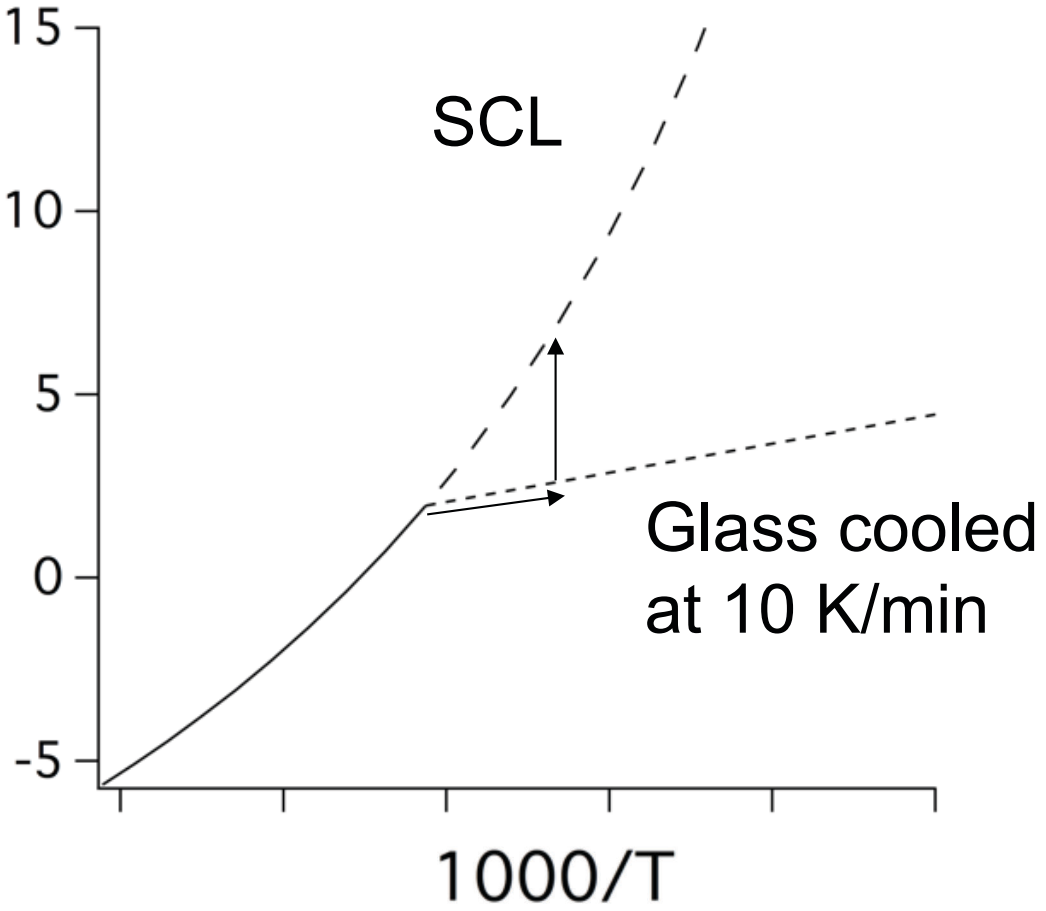




J.Q. Wang et al. / Acta Materialia 104 (2016); $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$

# Structural relaxation time of a glass changes during aging




Lunkenheimer et al. PRL 95, 055702 (2005); glycerol

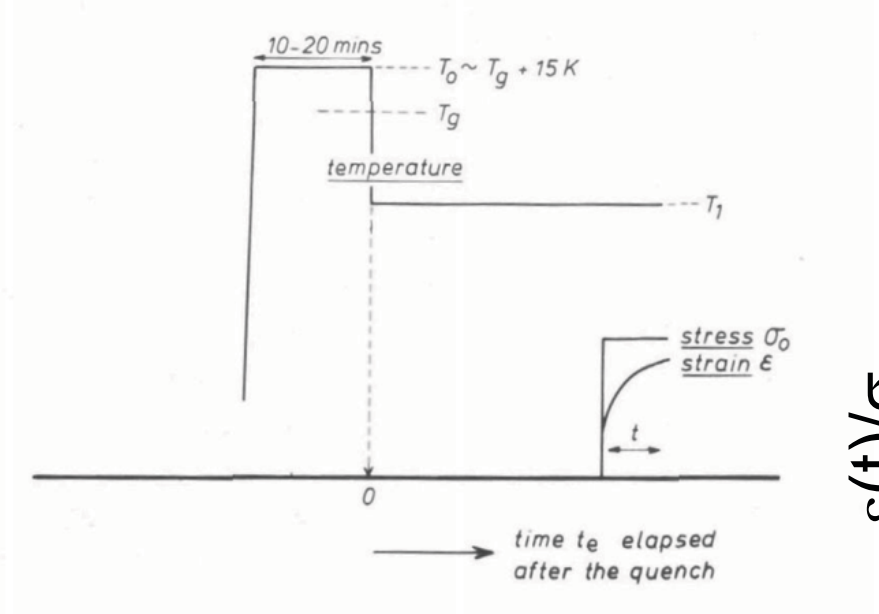
Glass relaxation line extrapolates back to ~ $10^{-12}$ s

# Homework: Do cathedral glasses flow appreciably in ~ 500 years?

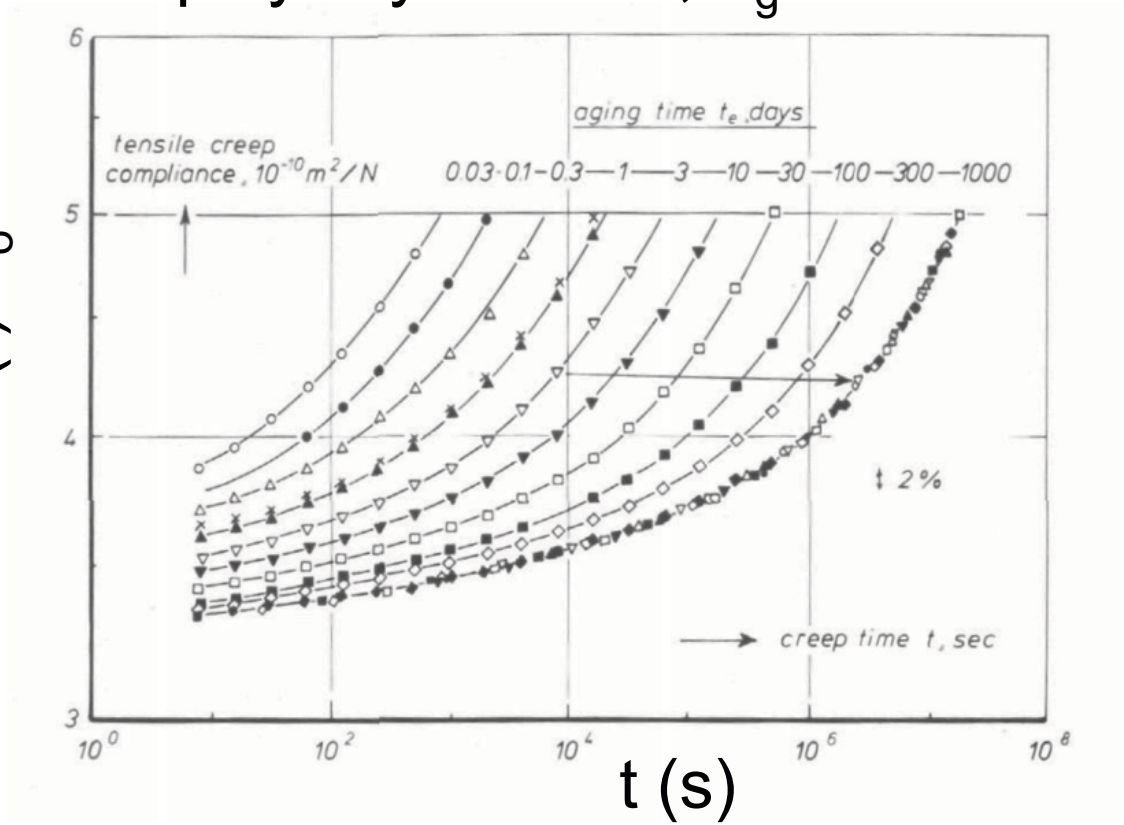
Assume:
$T_g$ = 800 K
$T_{aging}$ = 300 K

One approach:
Calculate structural relaxation time in the glass immediately upon cooling to $T_{aging}$.

# Perhaps we can isothermally age to reach equilibrium at $T_K$? Progress towards equilibrium slows logarithmically…



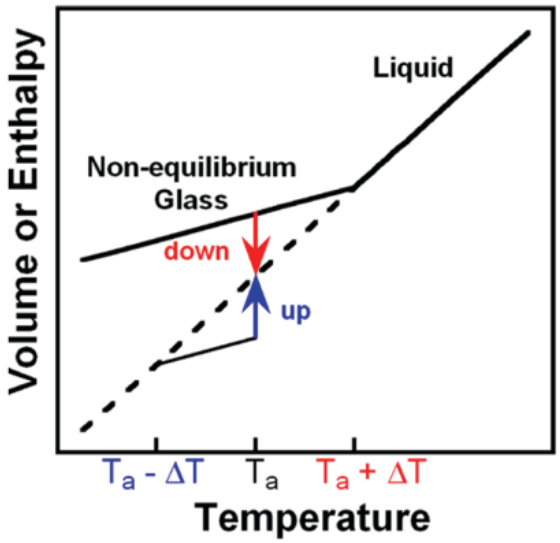

polyvinylchloride, $T_g$ – 40 K

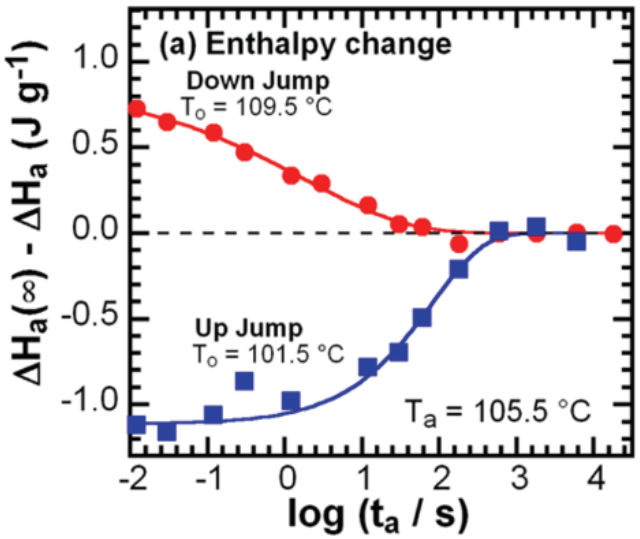


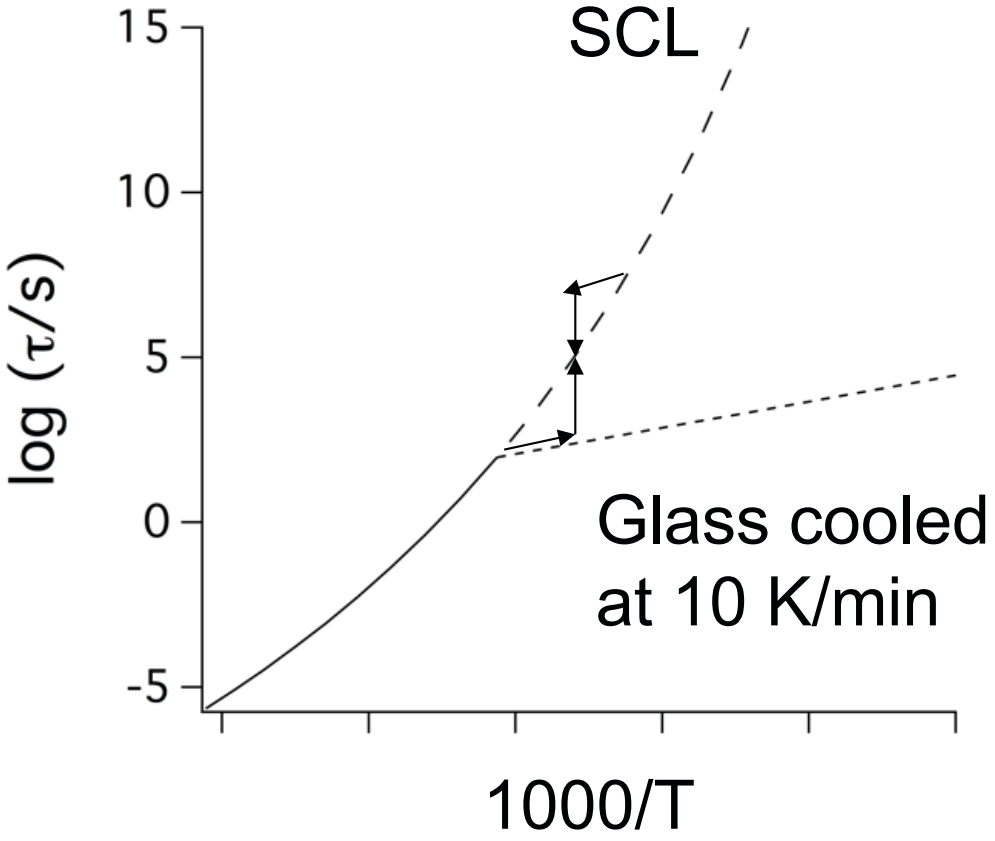

Struik, *Physical aging in amorphous polymers and other materials* (1978)

$\tau_{equilibration} \sim \tau_{\alpha,equilibrium}$

# Response of glass to perturbations is usually highly non-linear: “asymmetry of approach” experiment



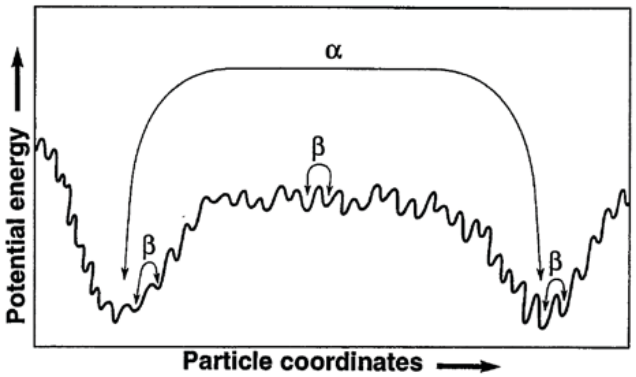



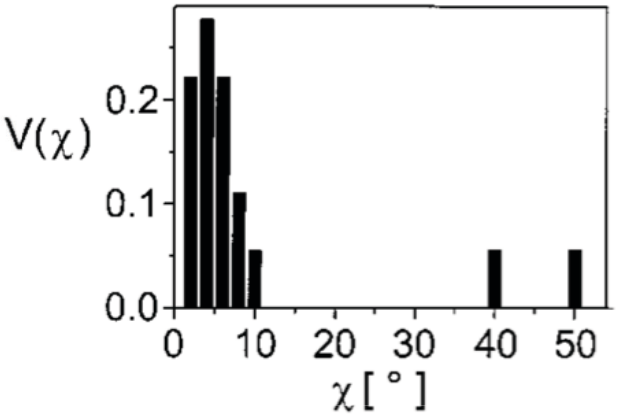

Lopez and Simon, Macromolecules 2016, 49, 2365−2374; polystyrene

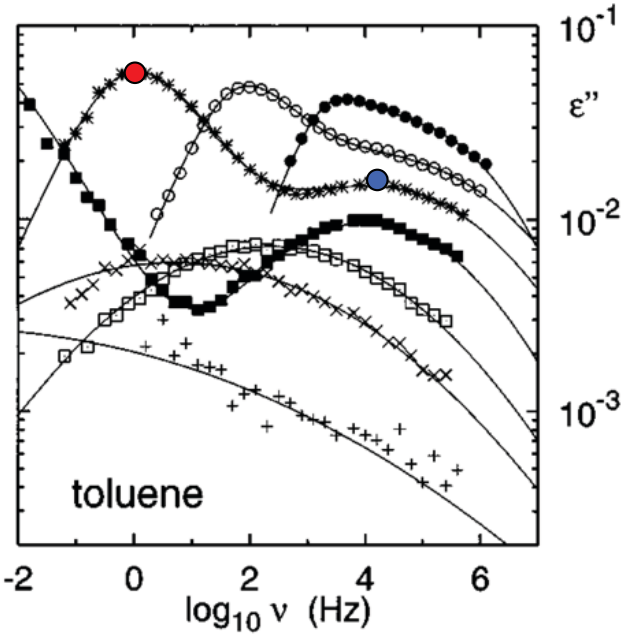
# β relaxation process (slow β process)

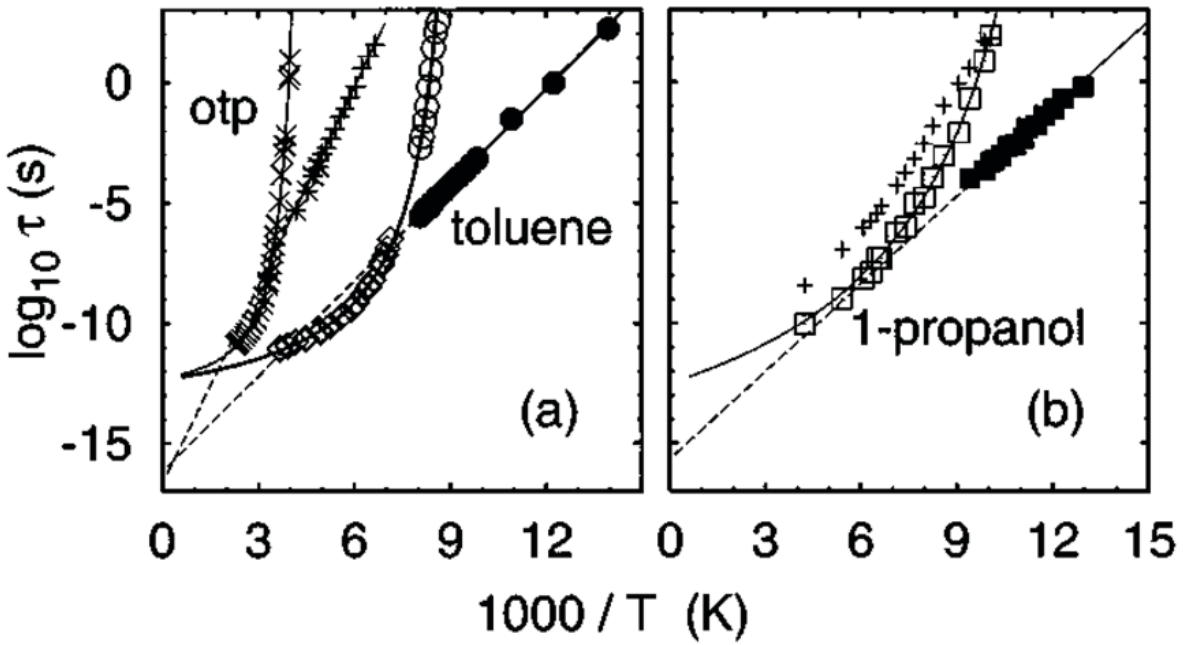
Stillinger, Science (1995)




Vogel, JCP (2001)




Kudlik et al., Europhys. Lett., 40 (6), pp. 649-654 (1997)

Beta relaxation time extrapolates back to ~ $10^{-16}$ s

# Low temperature properties of glasses: Interpretation as quantum tunneling two-level systems

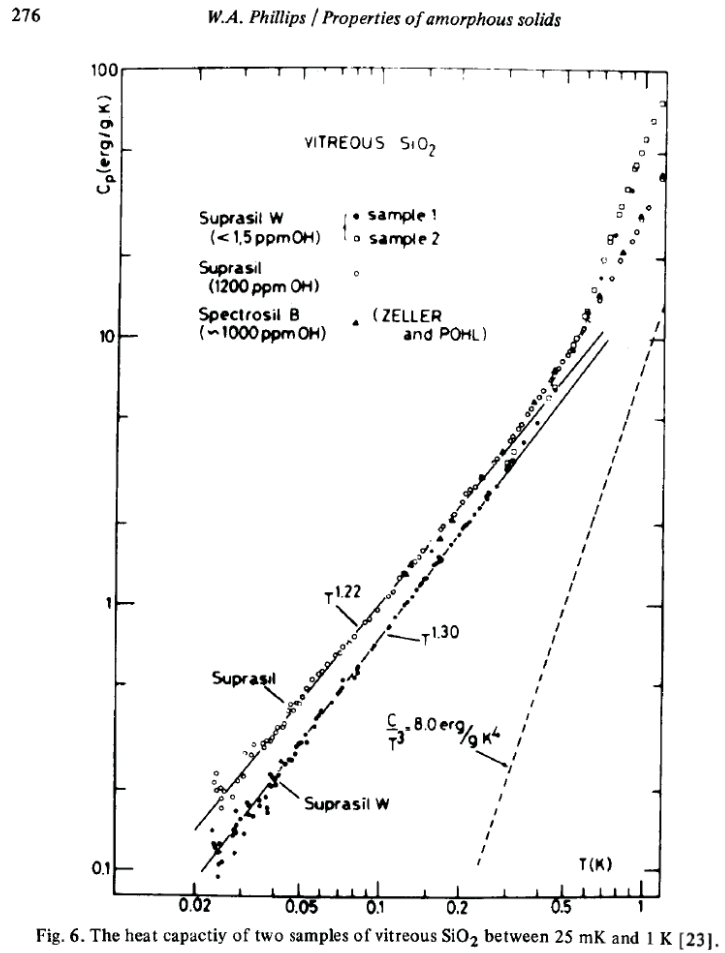
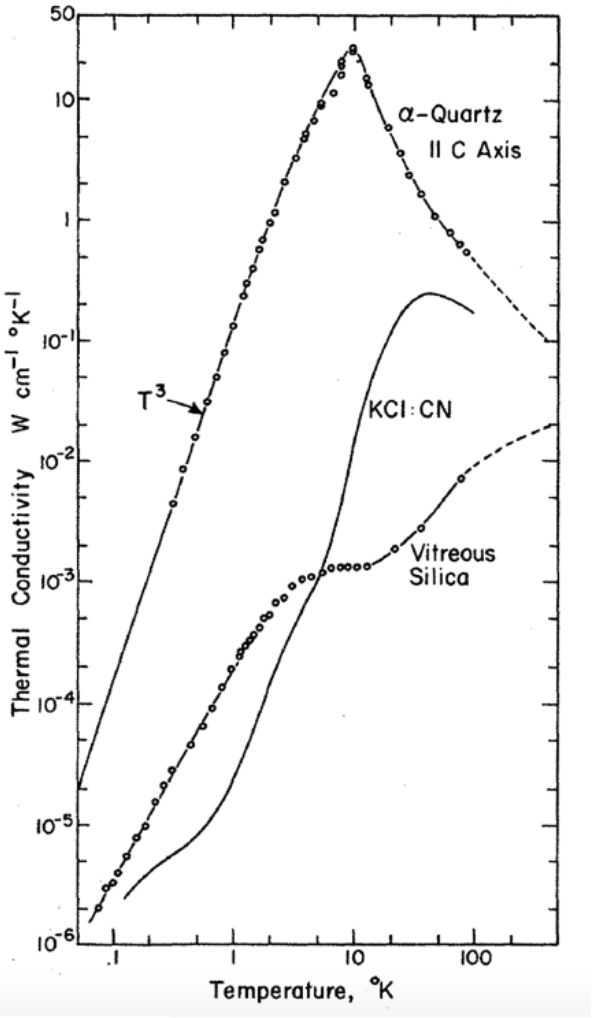
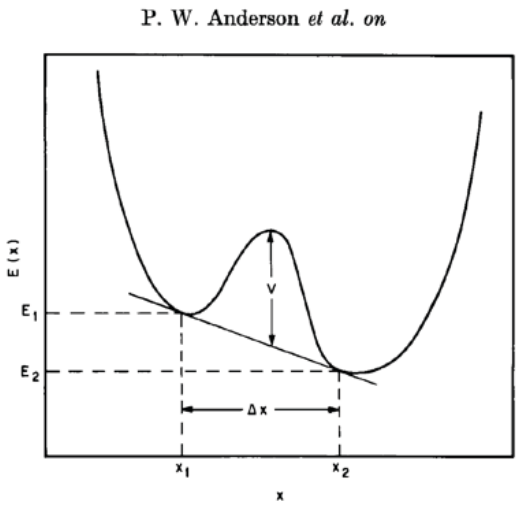



Fig. 6. The heat capactiy of two samples of vitreous $SiO_2$ between 25 mK and 1 K [23].




Anderson, Halperin, and Varma, Philo. Mag. (1972)

Data from: Lasjaunias et al., SolidState Commun. (1975)

Zeller and Pohl, Phys. Rev. B (1971)