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

- Dynamics
- Thermodynamics
- Structure
- Glass properties
- Transformation kinetics
- Glasses near the bottom of the potential energy landscape (vapor-deposited glasses)

#### Dynamics in SCLs depend strongly on temperature

R. Richert / Physica A 287 (2000) 26-36



Lunkenheimer et al., in Structural Glasses and Supercooled Liquids: Edited by Peter G. Wolynes and Vassiliy Lubchenko. 2012

Plazek and Magill, J. Chem. Phys. 49, 3678 (1968)



#### Strong and fragile glassformers

J. Phys. Chem., Vol. 100, No. 31, 1996 13201



- Strong limit = Arrhenius
- Structure is strong or fragile (with respect to temperature)
- kinetic fragility "m"

# Relaxation times from different techniques that measure SCL dynamics often show good agreement



Rossler, ...J. Non-Cryst. Solids 1994, 172-4, 113.

- α relaxation: dielectric relaxation, dynamic Kerr effect, light scattering, NMR, probe rotation
- β relaxation: dielectric relaxation, partial probe reorientation



Wu, ...J. Non-Cryst. Solids 1991, 131-3, 32

 α relaxation: Comparison of dielectric relaxation and heat capacity spectroscopy for glycerol, propylene glycol, salol, and o-terphenyl/o-phenylphenol

# Dynamics in SCLs continued: Self-diffusion has a weaker temperature-dependence



Swallen et al., J. Phys. Chem. B, (2009)

#### Thermodynamics



Molar volume data from Plazek and Magill, JCP 1966 6

#### Kauzmann entropy crisis



Yamamuro et al, J. Phys. Chem. B 1998, 102, 1605-1609 Tatsumi, et al. PRL 109, 045701 (2012); 7

# Kauzmann entropy crisis and the potential energy landscape



Angell, et al., J. Appl. Physics (2002)

# Are simulated systems good mimics of experimental glassformers?

	Propene	Butene	Pentene	3MP	MTHF	ETB	Toluene	PC
$T_{g}(\mathbf{K})$	56.0	60.0	71.7	79.0	93	115	119	158
$T_{\mathbf{K}}^{\circ}(\mathbf{K})$	49.8	49.3	55.9	59.8	73	101	108	135
$T_g/T_{\rm K} - 1$	0.12	0.22	0.28	0.32	0.27	0.14	0.10	0.17
$T_b/T_m - 1$	1.56	2.04	1.82	2.05	1.57	1.30	1.15	1.35
$S_{\rm res}({\rm J}{\rm K}^{-1}{\rm mol}^{-1})$	6.09	13.1	18.1	20.4	15.6	9.25	5.43	9.29
$z^{*}(0)$	7.26	4.76	3.82	3.41	3.20	5.99	7.12	5.05

TABLE I. Parameters related to glass transitions.

Tatsumi et al. PRL 109. 045701 (2012)

# Structure of supercooled liquids and glasses: Can you find the origin of slow dynamics



#### Structure of supercooled liquids and glasses: Can you find T<sub>g</sub>?



Eckstein, et al, JCP (2000)

#### Metallic glasses show correlation between temperaturedependent structural evolution and fragility



### Deep connections between thermodynamics and dynamics?



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.

Wolynes and Lubchenko, Annu. Rev. Phys. Chem. (2007)