Dynamical Heterogeneity of Glasses

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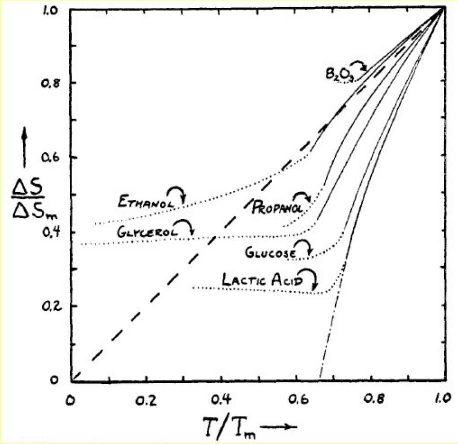
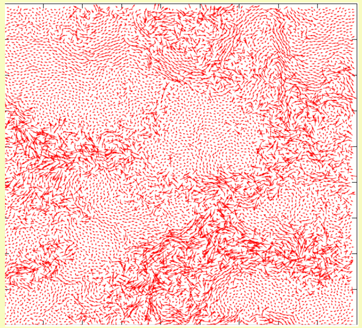
Outline

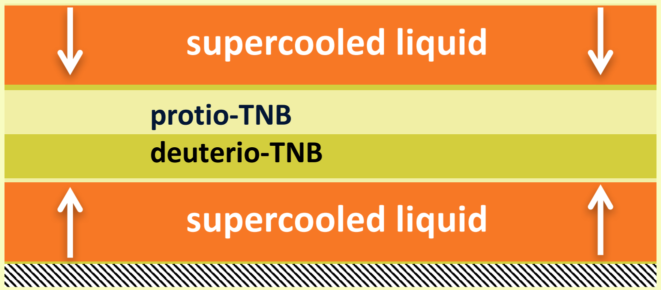
Thermodynamics & kinetics of glasses



Dynamical heterogeneity of the glassy state



Surface mobility of glasses



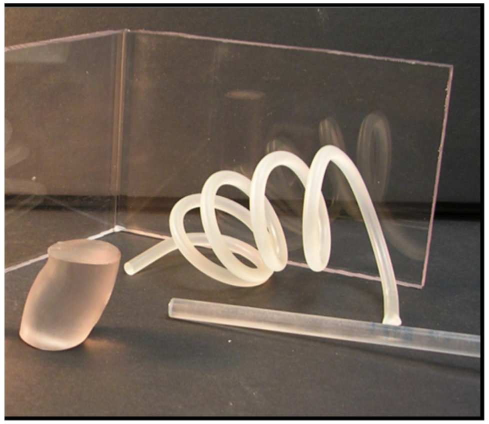
Mechanical behavior of glasses

Many Types of Glasses

Roman glass

Moldavite – a natural glass formed by meteorite impact

Trinitite – a glass made by the Trinity nuclear-weapon test



Polymer glasses – PC, PS, etc.

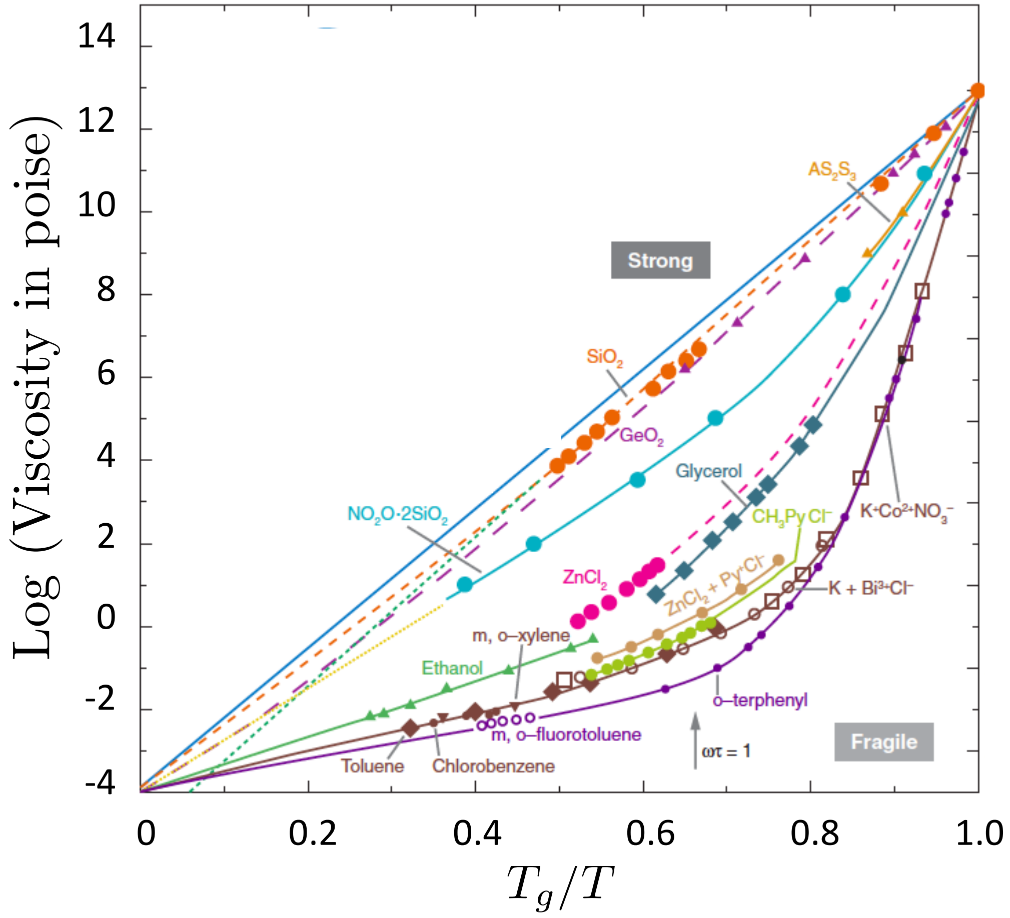
Metallic glasses

Nuclear waste

https://en.wikipedia.org/wiki/Glass, https://ediger.chem.wisc.edu/content/dynamics-actively-deformed-glasses

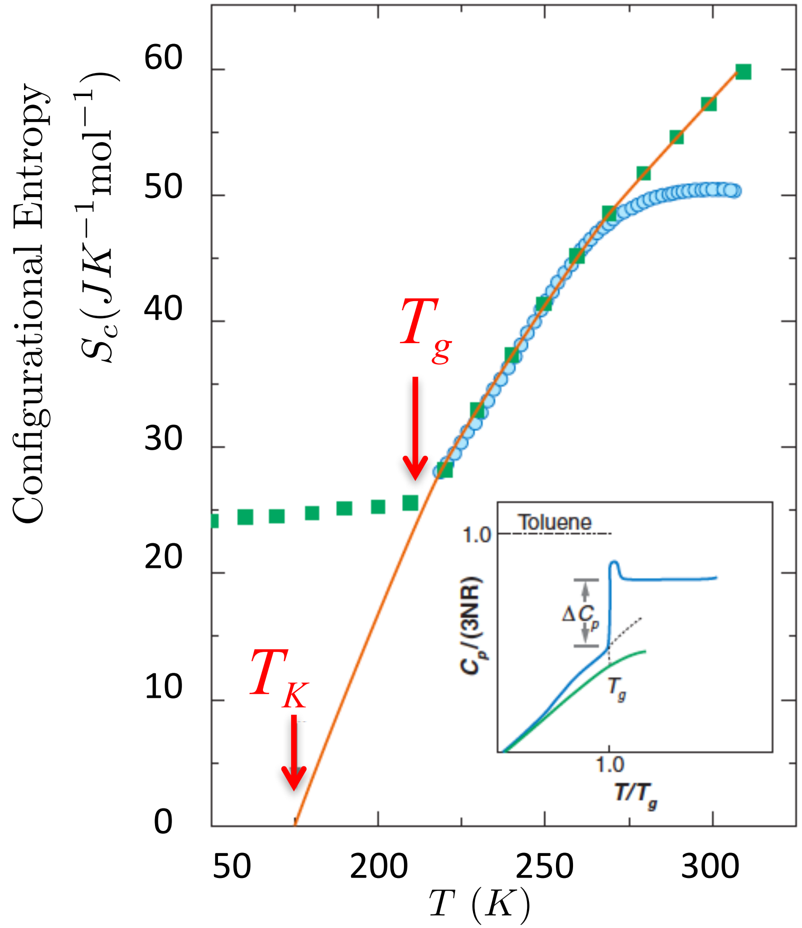
Thermodynamics and Kinetics of Glasses

Kinetics



Thermodynamics

Salol



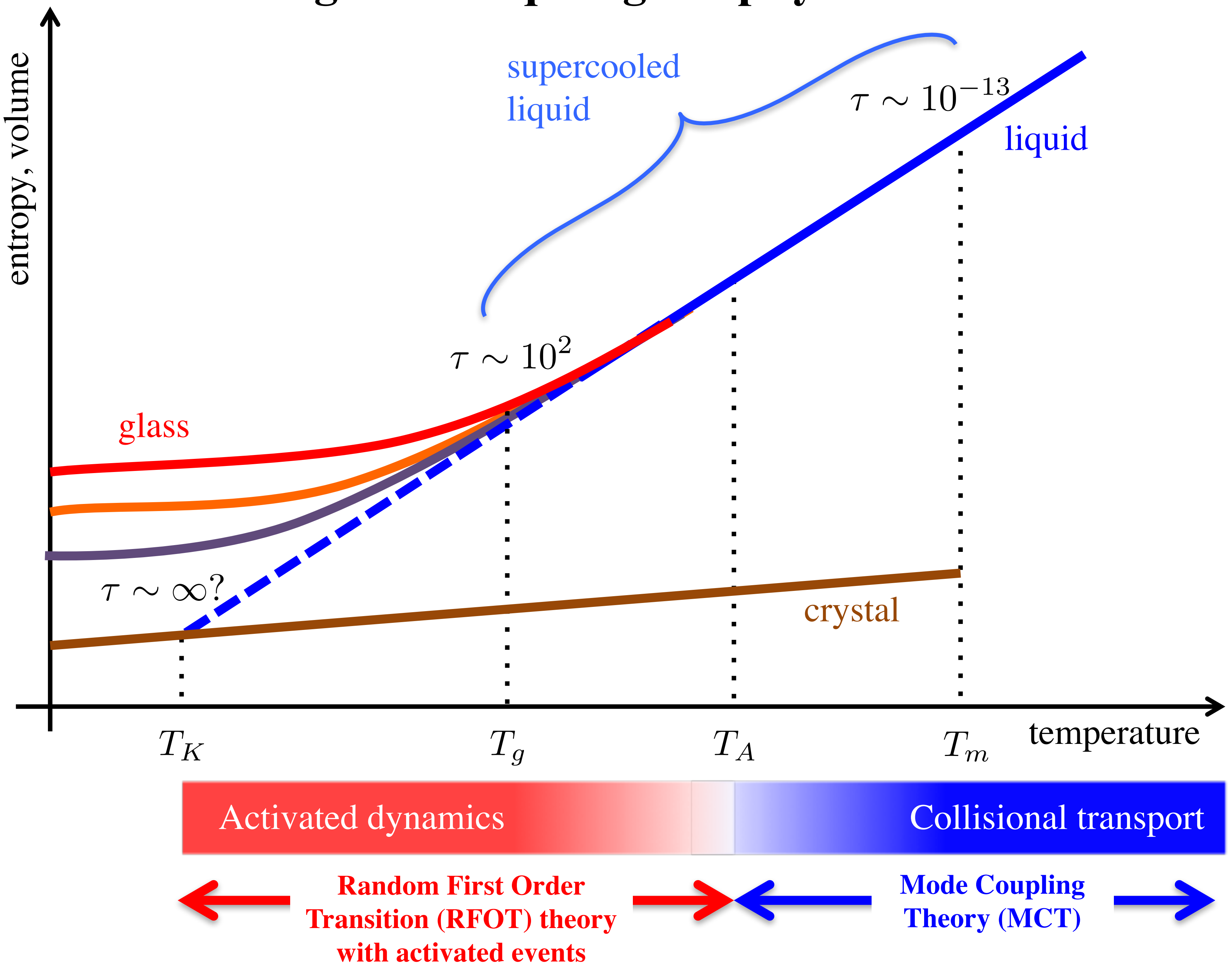
Volgel–Fulcher Law: $\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right)$

$$S = \int \frac{C_p}{T} dT$$

$$S_c \equiv S_{\text{liquid}} - S_{\text{crystal}}$$

[1] Angell CA. 1997. J. Res. Natl. Inst. Stand. Technol. 102:171–85. [2] Richert R, Angell CA. 1998. J. Chem. Phys. 108:9016–26. [3] Kauzmann (1948) Chem. Rev. 43(2), pp 219-256

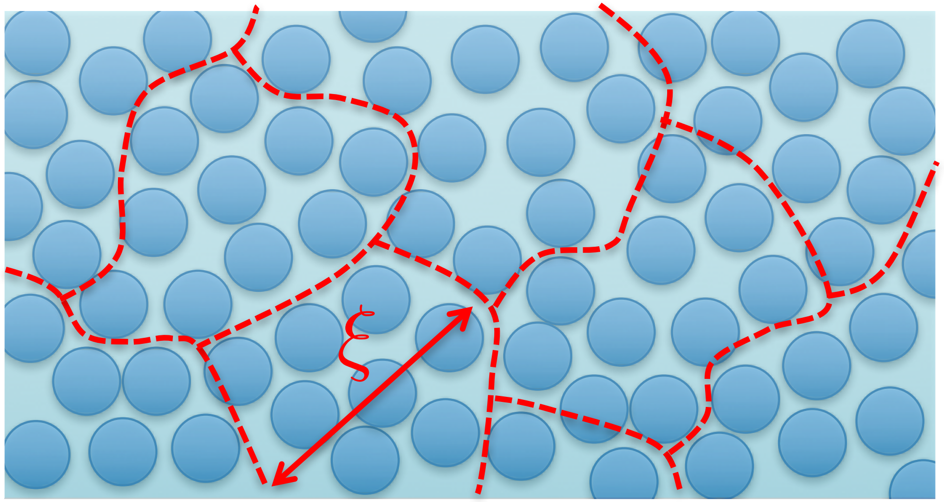
Regime of liquid/glass physics



Lubchenko and Wolynes (2007) Annu. Rev. Phys. Chem. 58:235-66

Random First-Order Transition (RFOT) theory

- At Low $T<T_A$, system decomposes into patches that correspond to a local of minimum of the free energy. The driving force is configurational entropy.
- There is an interface between these patches which costs energy



$$F(r) = -\frac{4}{3}\pi T s_c r^3 + 4\pi\sigma(r) r^2$$

- The size of of the patches given by the condition

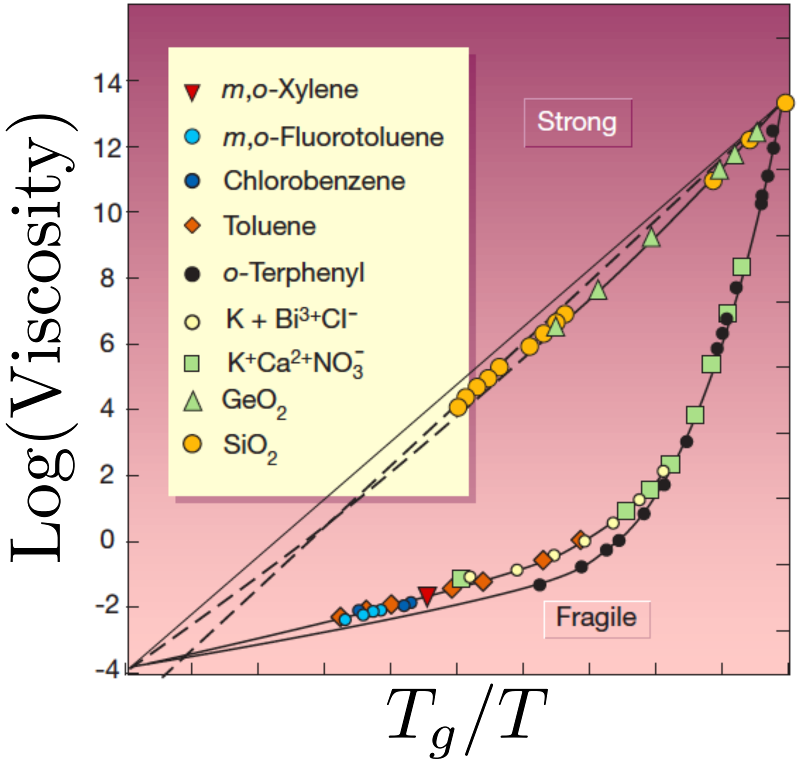
$$F(r^*) = 0; \qquad \frac{r^*}{a} = 2\left(\frac{2}{3\pi\ln(\alpha_L a^2/\pi e)}\right)^{2/3}\left(\frac{DT_K}{T-T_K}\right)^{2/3}$$

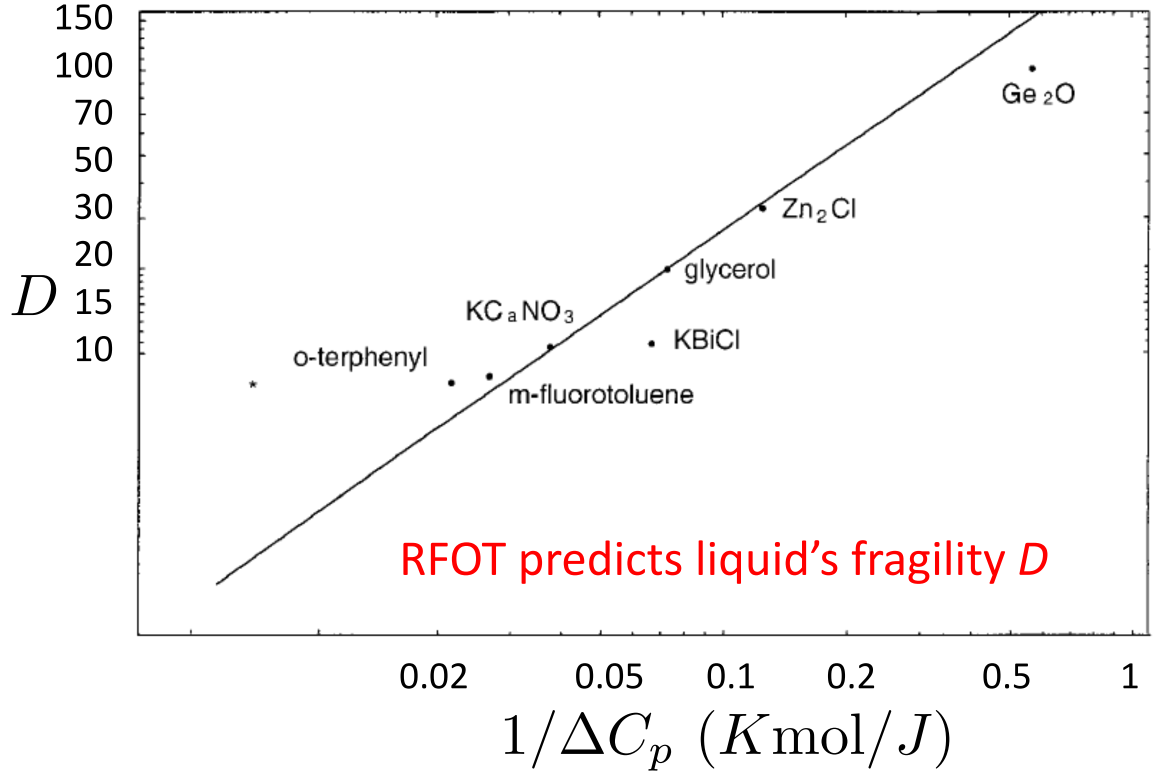
- The process is activated. The relaxation time is given by

$$F(r^\ddagger) = 0; \qquad \tau = \tau_0 \exp\left(\frac{F^\ddagger}{k_B T}\right) = \tau_0 \exp\left(\frac{DT_K}{T-T_K}\right)$$

Lubchenko & Wolynes, Annu. Rev. Phys. Chem. **58**, 235 (2007)

Glassy dynamics from mosaic of energy landscapes





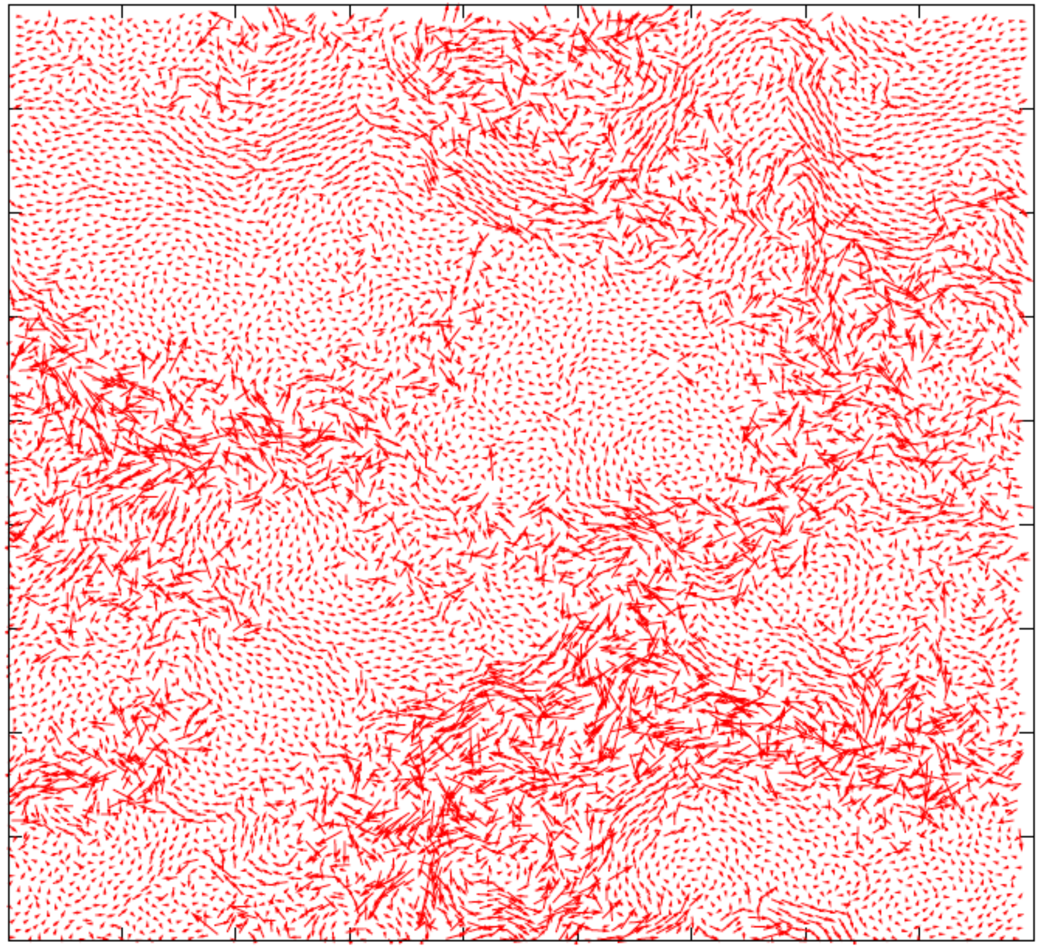
Volgel–Fulcher Law:

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right)$$

$$D = 32k_B/\Delta c_p^{\text{bead}}$$

Xia and Wolynes (2000) PNAS, Debenedetti and Stillinger (2001) Nature; Berthier et al. Science (2005) 310, 1797

DYNAMICAL HETEROGENEITY OF THE GLASSY STATE



- Non-Gaussian distribution of free energy barrier
- Stretching exponent β
- Asymmetric of thermodynamics response (calorimetric experiments)
- Growing length scale
- Two-step relaxation of enthalpy in aging glasses

Berthier (2005)

Mode coupling theory (MCT)

- Mori-Zwanzig projection operator formalism is a method to derive exact equations of motions for the slow degree of freedom

- Glasses: vibration (inside the cages) = fast
  alpha-relaxation = slow

MZ formalism + Approximations = MCT equations

$$\ddot{\Phi}(q,t) + \Omega^2(q)\Phi(q,t) + \int_0^t M(q,t-s)\dot{\Phi}(q,s)ds = 0$$

$$\Omega^2(q) = \frac{q^2 k_B T}{m S(q)} \qquad \Phi(q,t) \equiv \frac{1}{N}\langle \rho_{-q}(0)\rho_q(t)\rangle$$

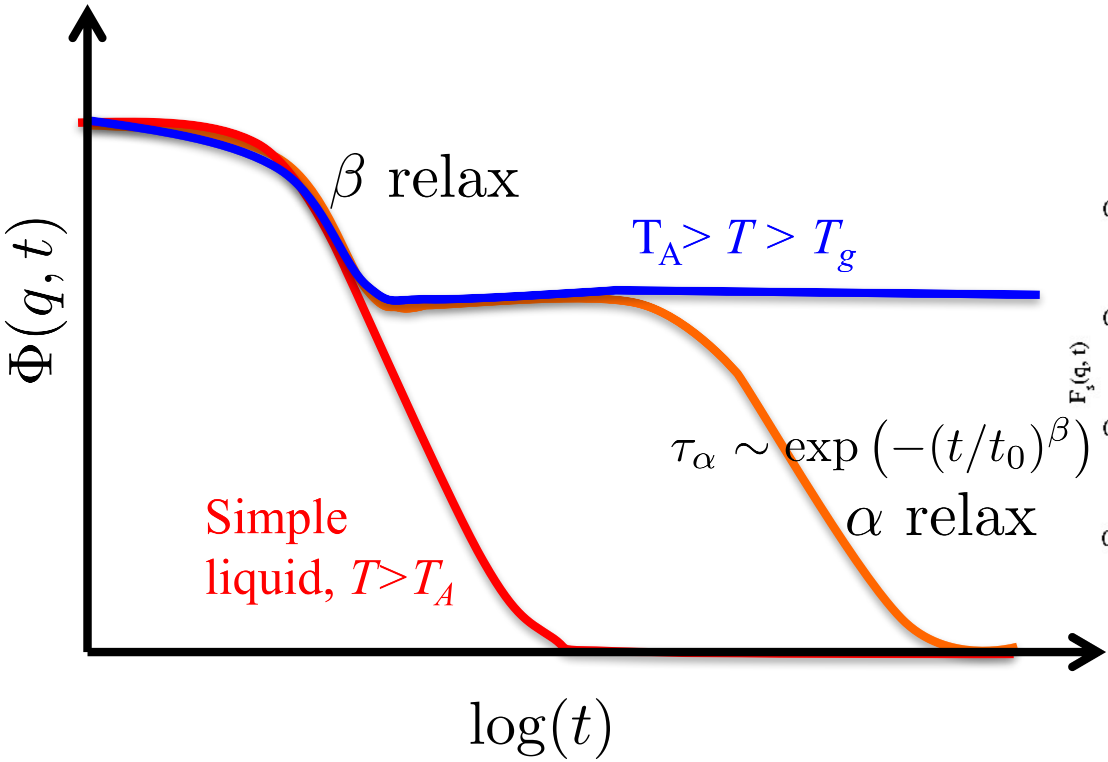
$$M(q,t) = \int d^3q' V(q,q')\Phi(q',t)\Phi(q,t)$$

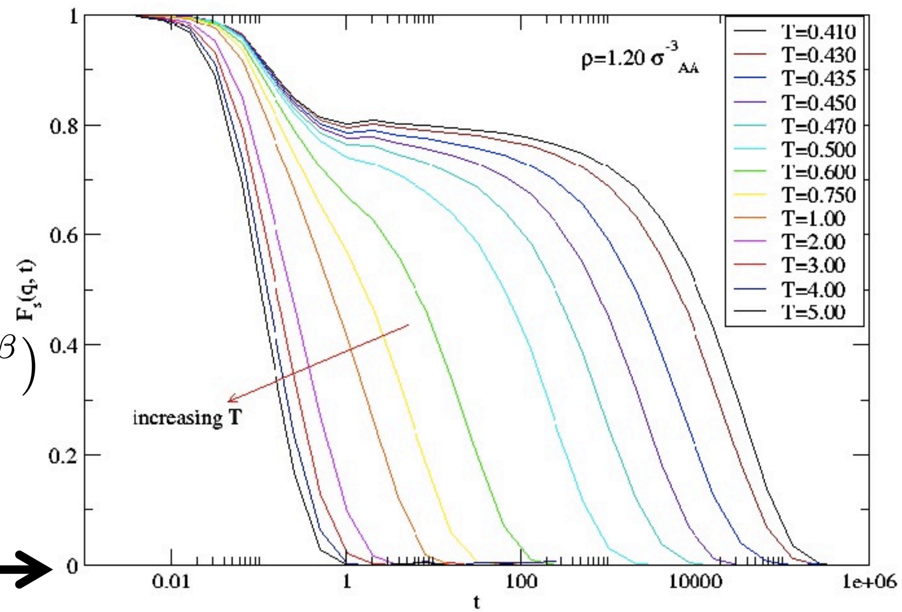
W Götze, Complex Dynamics of Glass-Forming Liquids (2009)

Idealized Mode Coupling Theory

$$\Phi(q,t) = \langle e^{i\vec{q}\cdot(\vec{r}(t)-\vec{r}(0))} \rangle$$

$$\ddot{\Phi}(q,t) + \Omega^2(q)\Phi(q,t) + \int_0^t M(q,t-s)\dot{\Phi}(q,s)ds = 0$$





Bridging the gap between Idealized MCT and RFOT

- A formal way of bridging the gap between MCT and activated transitions is to include an activated event vertex in the self-consistent MCT

$$\Phi(q,z) = \frac{1}{z + M_{\mathrm{hop}}(q,z) + M_{\mathrm{mct}}(q,z)}$$

$$M_{\mathrm{mct}} = \frac{\langle \omega_q^2 \rangle}{z + \eta_l(q,z)}, \qquad M_{\mathrm{hop}} = P_{\mathrm{hop}} \frac{v_0}{v_p} \left(G(q,z) - 1\right)$$

$$\eta_l(q,z) = \gamma + 4\lambda\Omega_0^2 \mathcal{L}\left[\Phi^2\right], \qquad P_{\mathrm{hop}} = \frac{1}{\tau_0} \exp\left(-\frac{\Delta F}{k_B T}\right)$$

- Dynamical heterogeneity is not made explicit in their work

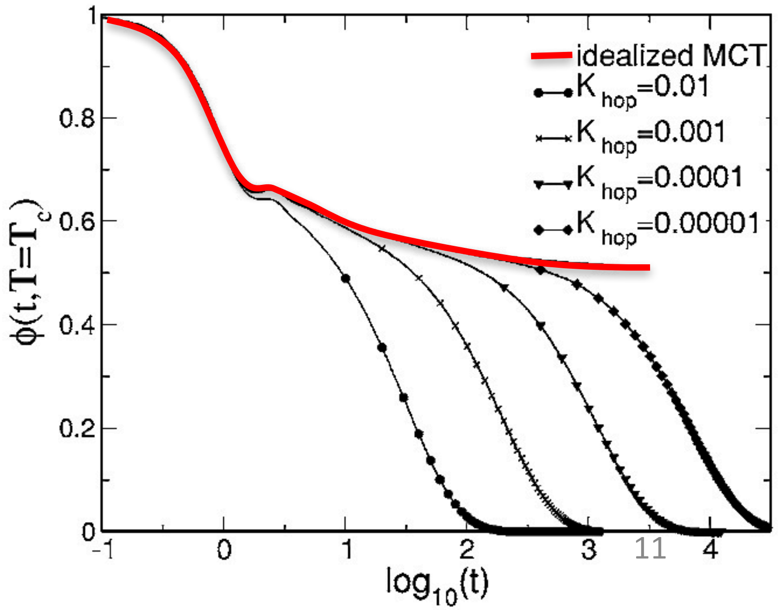
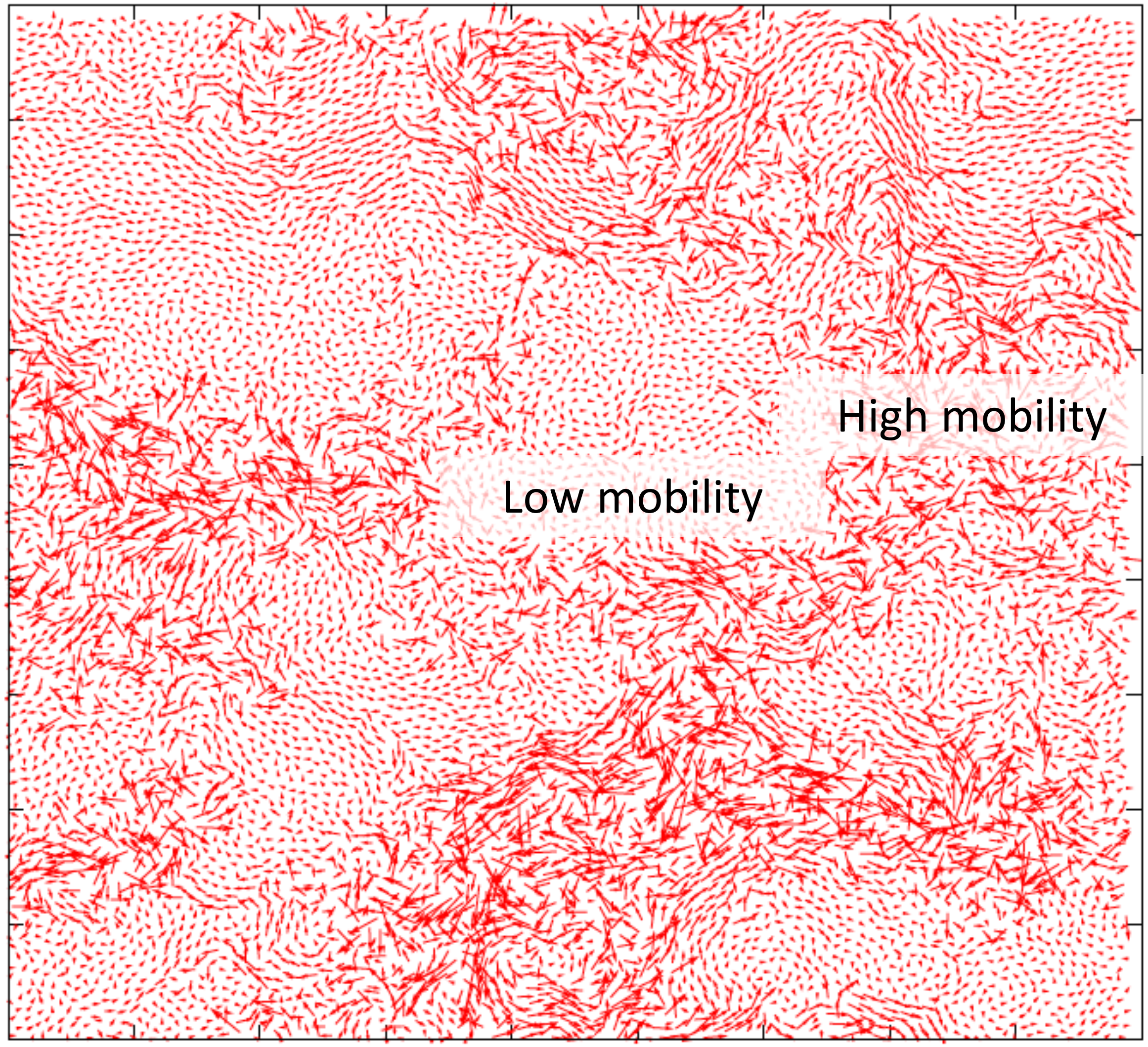


Figure: The idealized MCT result and the modified full *Φ(t)* have been plotted against *log(t)*. Time is scaled by picosecond. All the plots are at $T=T_c$.

S Bhattacharyya, B Bagchi, & PG Wolynes, PRE **72**, 031509 (2005)



$$M_{total}(q;t,t') = M_{mct}(q;t,t') + M_{hop}(q;t,t')$$

Mobility field: $$\mu(r,t) = \int_{-\infty}^{t} dt' \int_{-\infty}^{\infty} dq e^{-iq\cdot r} M_{total}(q;t,t')$$

Berthier (2005)

Continuum equation of the mobility field

Mobility field: $$\mu(r,t) = \mu_{hop}(r,t) + \mu_{mct}(r,t)$$

$$\frac{\partial \mu_{mct}}{\partial t} = \vec{\nabla} \cdot \left(\frac{2\mu^2 \xi^2}{\bar{\mu}_{mct}} \vec{\nabla} \mu_{mct} \right) - \frac{2\mu^2}{\bar{\mu}_{mct}} \left(\mu_{mct} - \bar{\mu}_{mct} \right) + \delta g + \vec{\nabla} \cdot \delta \vec{j}$$

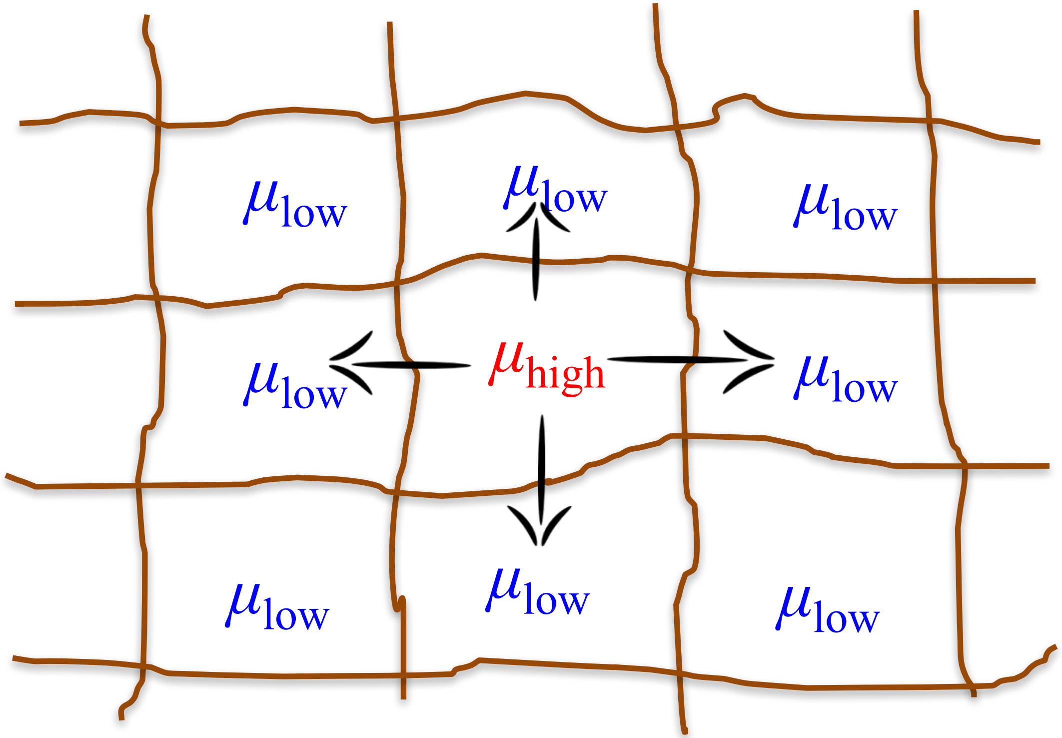
$$\mu_{hop} = \lambda \bar{\mu} \approx 0.25 \bar{\mu}$$

Uniform solution of MCT with activated events: $$\bar{\mu} = \mu_0 \exp \left\{ - \frac{\gamma^2}{4 k_B T \Delta c_p T_g \left(\frac{T - T_K}{T_K} - \ln \frac{T}{T_f} \right)} \right\}$$

Fictive temperature field: $$\frac{\partial T_f}{\partial t} = -\mu \left(T_f - T \right) + \delta T_f$$

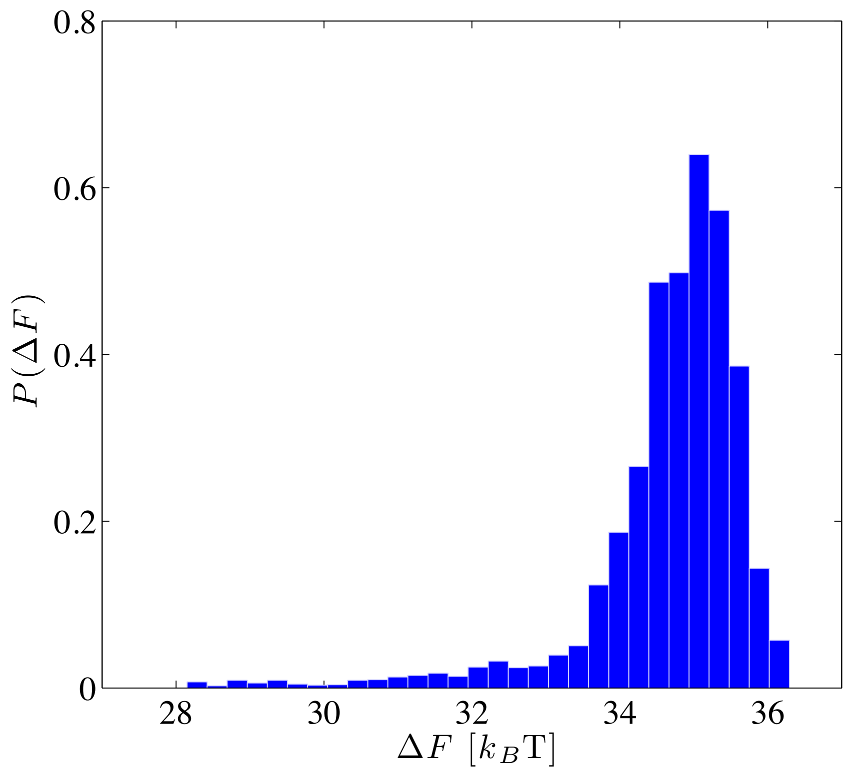
A Wisitsorasak, PG Wolynes, PRE (2013) 88: 022308;
A Wisitsorasak, PG Wolynes, JPCB (2014) 118: 7835 - 7847

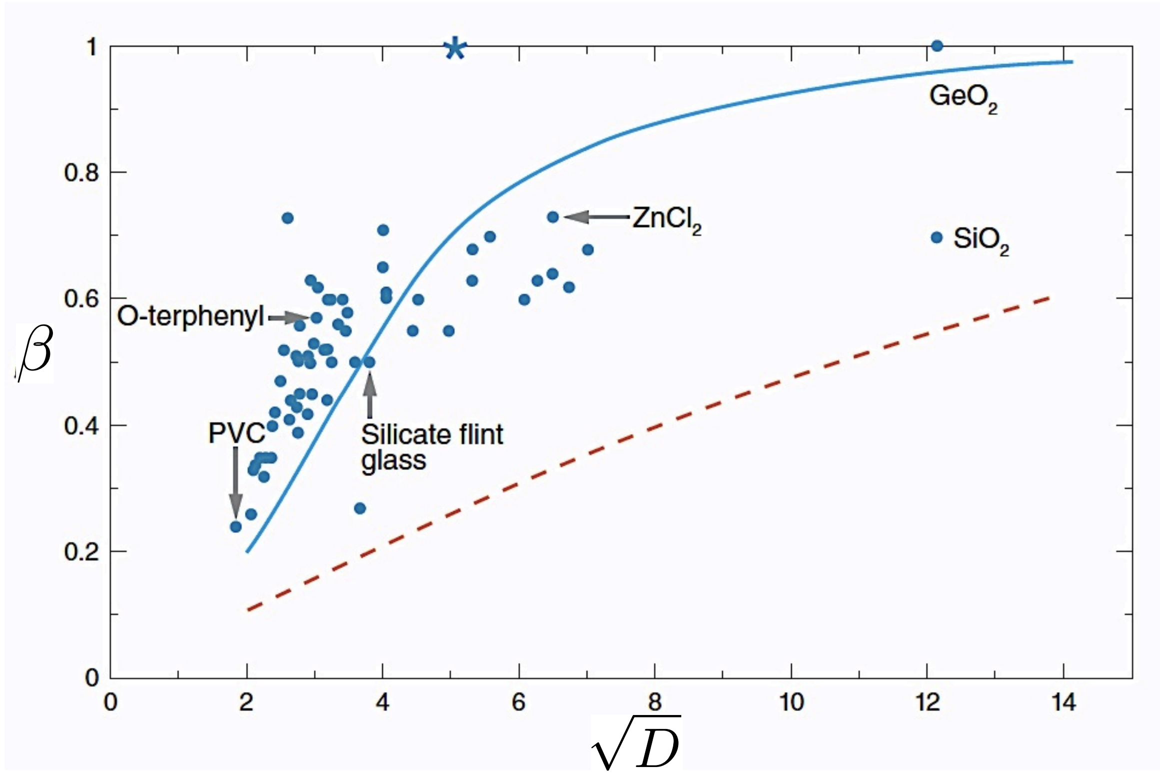
Facilitation effect



$$\mu = \tau^{-1} = \tau_0^{-1} \exp\left(-\frac{\Delta F^{\ddagger}}{k_B T}\right)$$

Activation Free Energy Barrier Distribution





Cutoff distribution for activation barrier

$$P(\Delta F^{\ddagger}) = \begin{cases} P_f(\Delta F^{\ddagger}), & \text{for} \Delta F^{\ddagger} < \Delta F_0^{\ddagger} \\ C\delta(\Delta F^{\ddagger} - \Delta F_0^{\ddagger}). & \end{cases}$$

Stretching exponent:

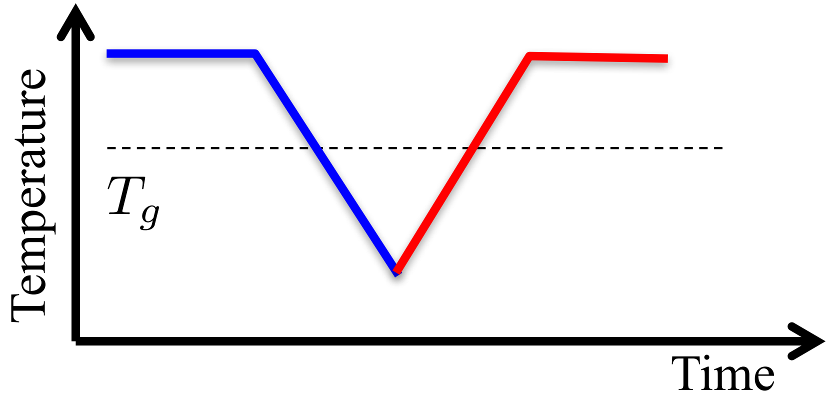
$$\beta \approx \frac{1}{\sqrt{1 + (\delta F^{\ddagger}/k_B T)^2}}$$

$$\frac{\delta F^{\ddagger}}{F^{\ddagger}_{mp}} \approx \frac{1}{2\sqrt{D}}$$

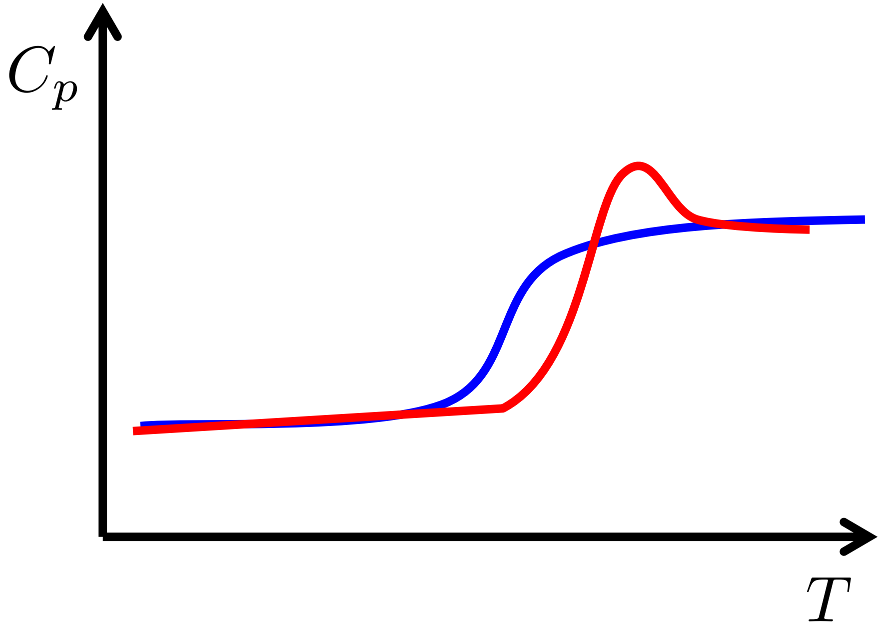
A Wisitsorasak, PG Wolynes, JPCB (2014) 118: 7835 - 7847

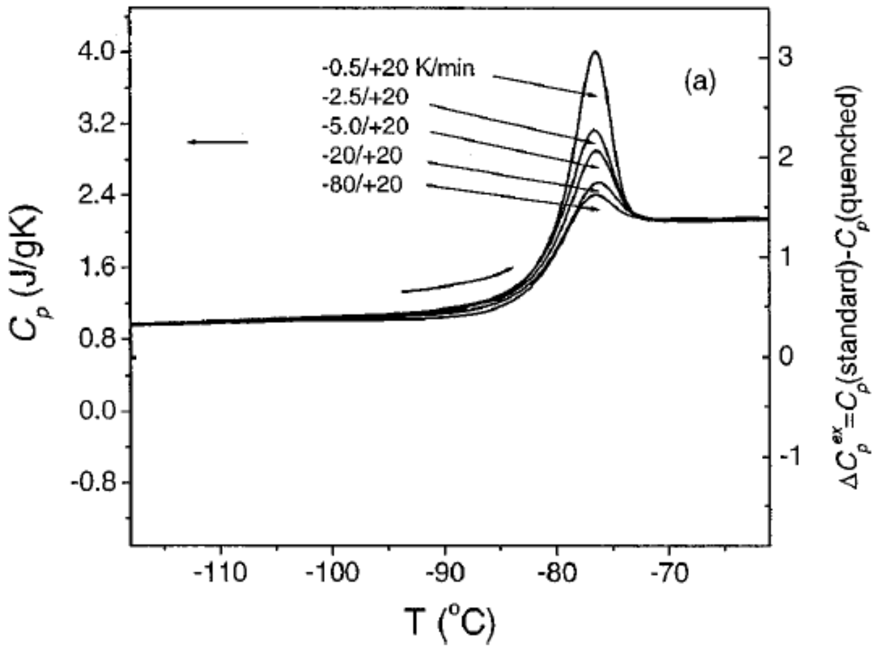
Xia and Wolynes (2000)

Calorimetric experiments



"If you would understand a phenomenon, but are allowed only a single type of measurement to study it, choose the heat capacity." *Einstein*

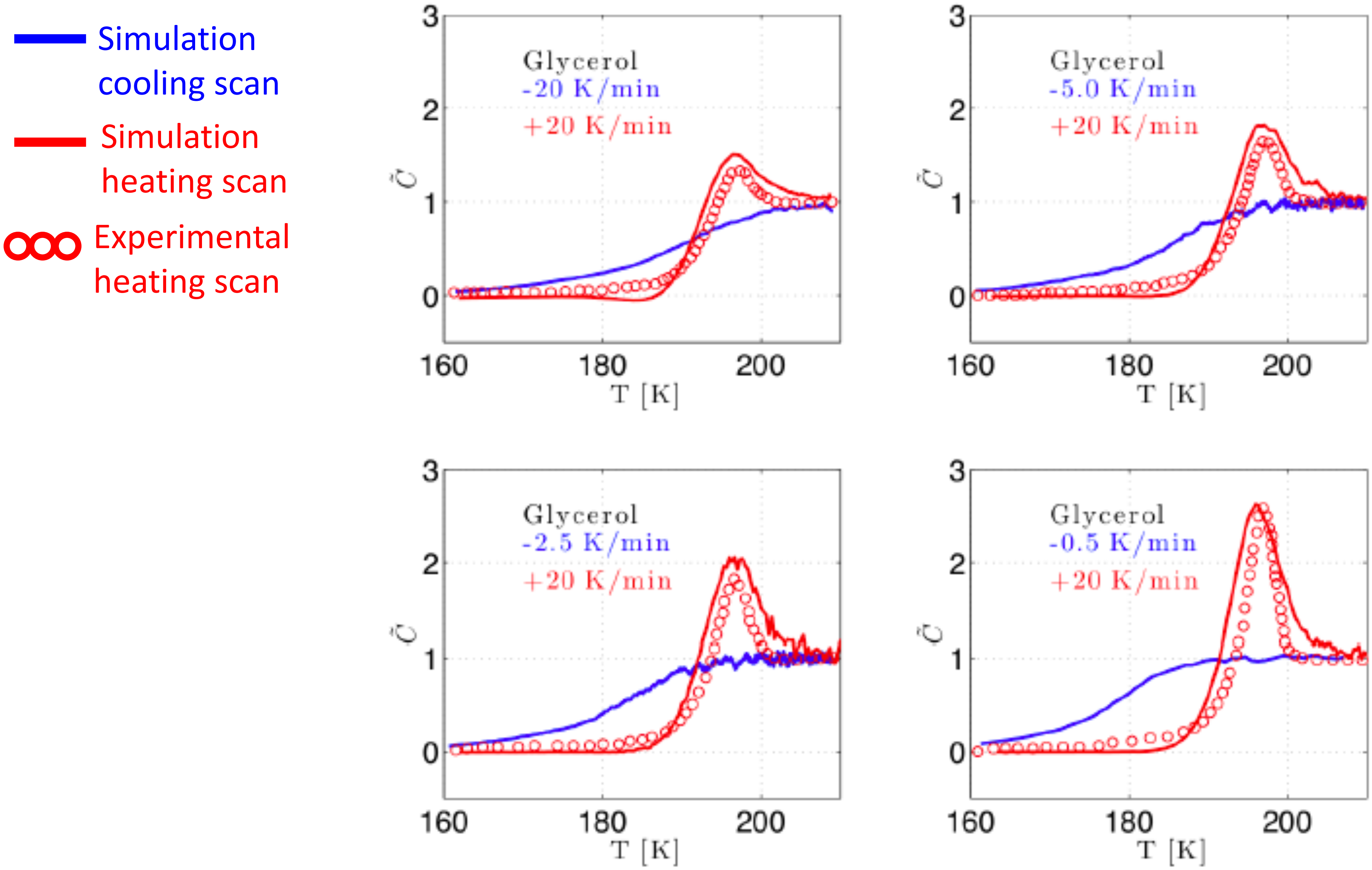




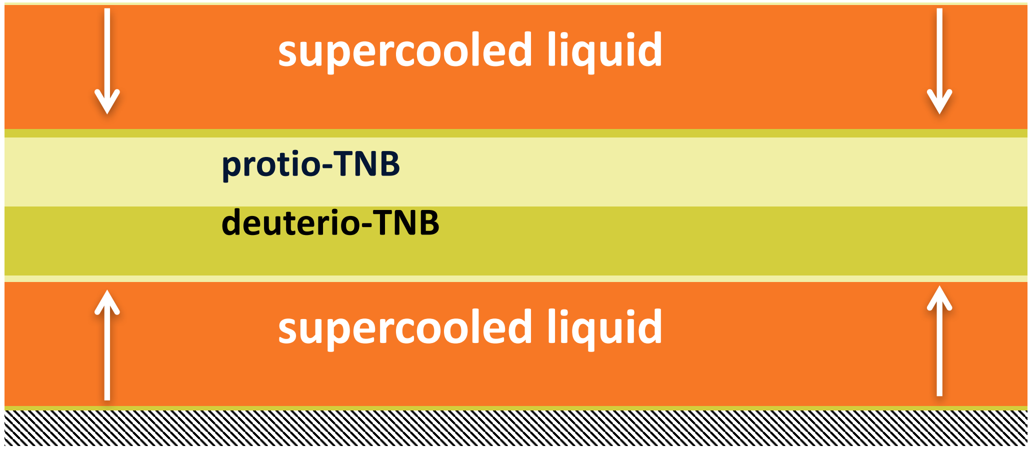
DSC upscans at the heating rate, 20 K/min, of glycerol glasses with different cooling rate

Wang, Velikov, and Angell, JCP 117, 10184 (2002)

Calorimetric experiments

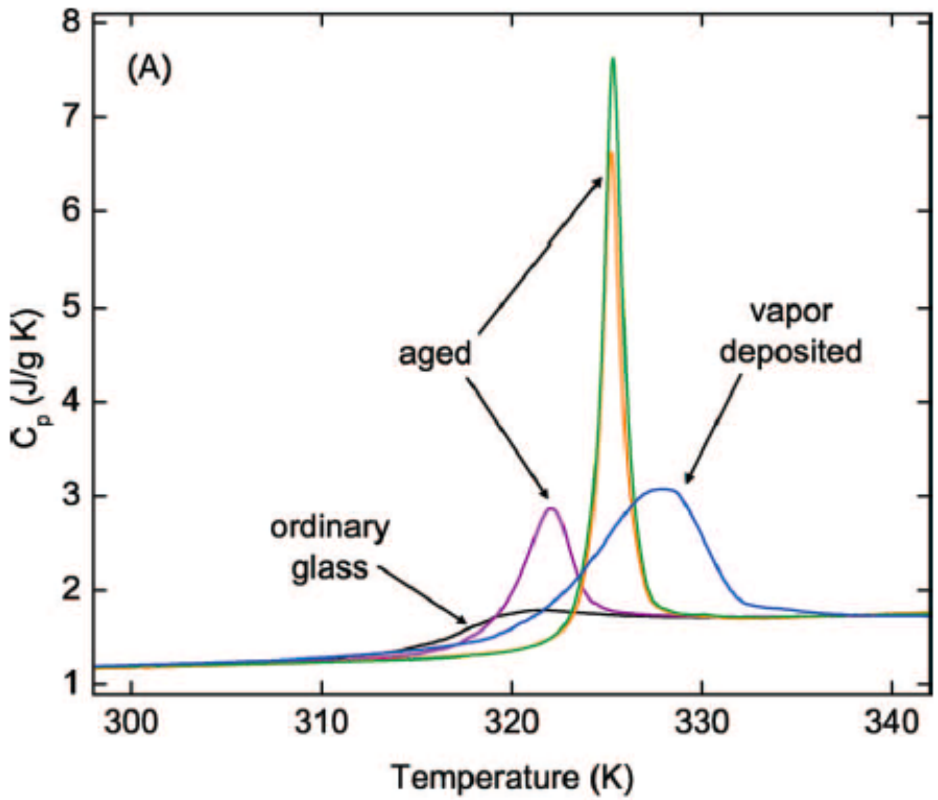


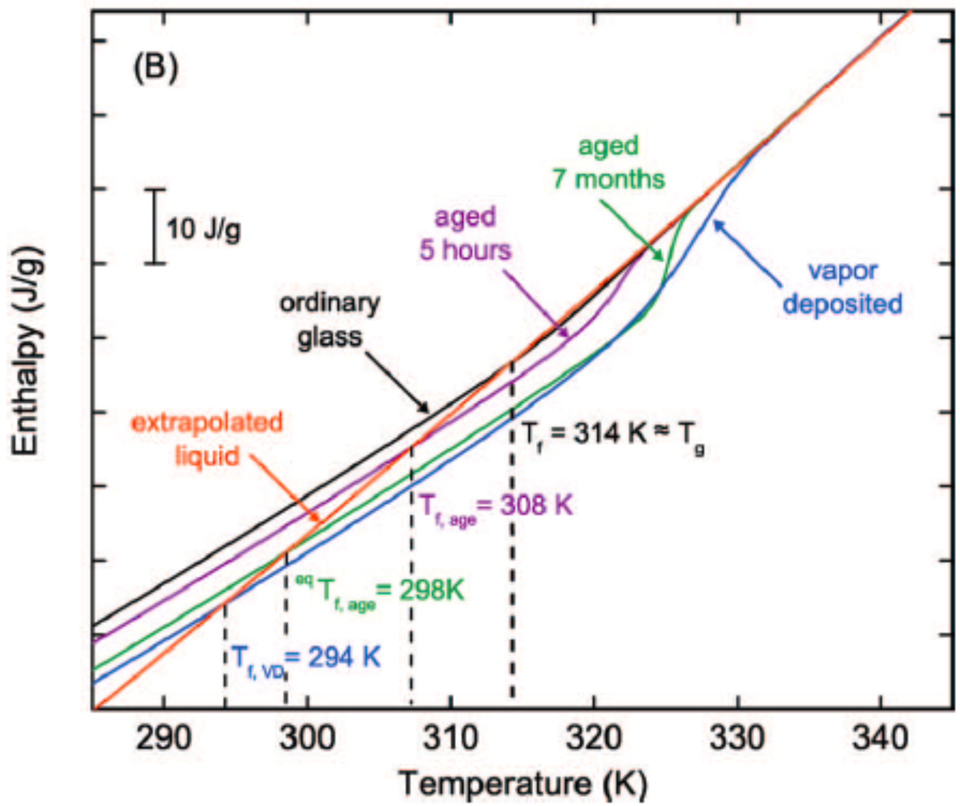
A Wisitsorasak, PG Wolynes, JPCB (2014) 118: 7835



TRANSFORMATION OF STABLE GLASSES INTO SUPERCOOLED LIQUIDS

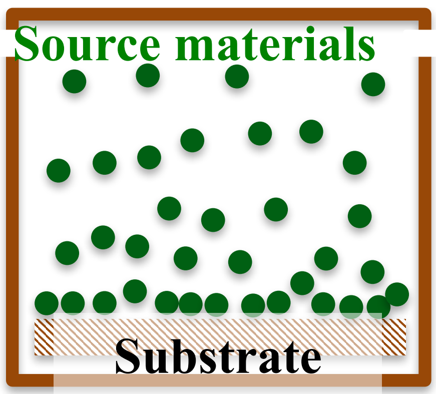
Ultrastable glasses: Vapor deposition method





(A) Observed C_p for aged and vapor-deposited samples. Ordinary glasses were aged for 5 h (purple), 5 months (orange), and 7 months (green). The vapor-deposited sample (blue) was prepared with a substrate temperature of 265 K.

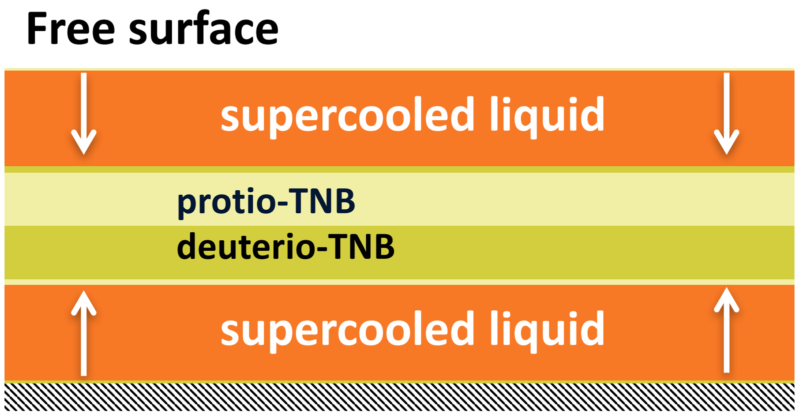
(B) Enthalpies from integrated C_p curves shown in (A). Dotted vertical lines indicates T_f for the various samples.



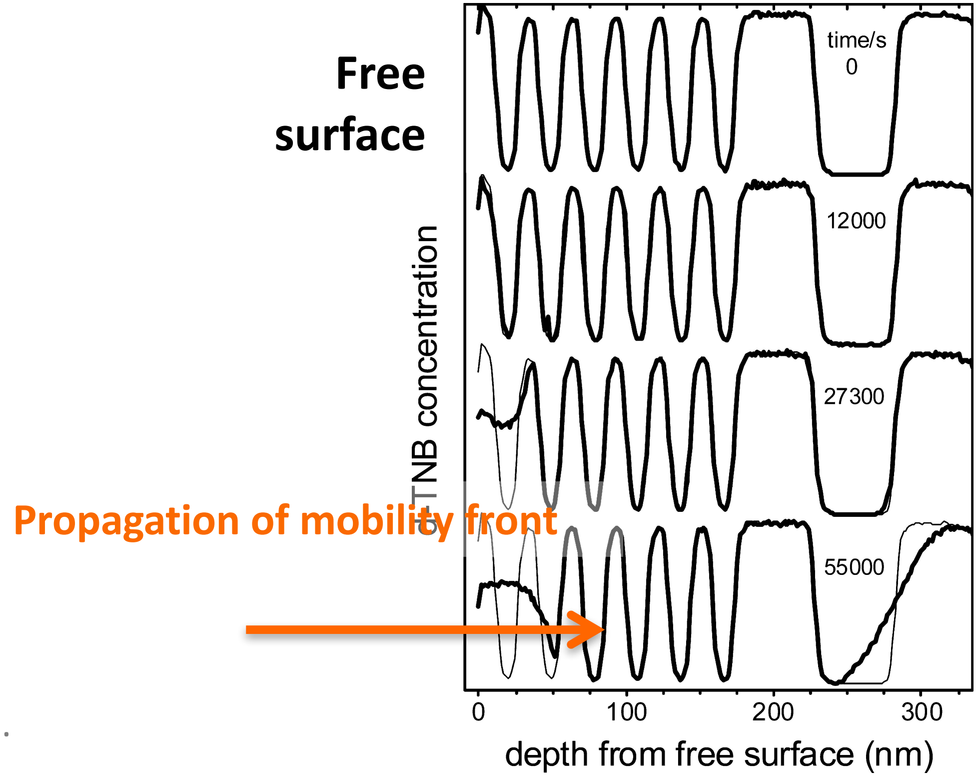
SF Swallen, et al., Science 315, p353 (2007); KL Kearns, et al., JCP 127, 154702 (2007)

Transformation of stable glasses into supercooled liquids

- Heat stable glasses to high *T*, they transform to a liquid via a growth front mechanism
- The speed of the front is measured from ion mass spectrometry
- Unusual high mobility in the liquid behind the front ?



Note: TNB = tris(naphthyl)benzene



SF Swallen, K Windsor, RJ McMahon, MD Ediger, TE Mates, J. Chem. Phys. B, **114**, 2635 (2010)

Front speed & Mobility behind the front

Front speed & Temperature

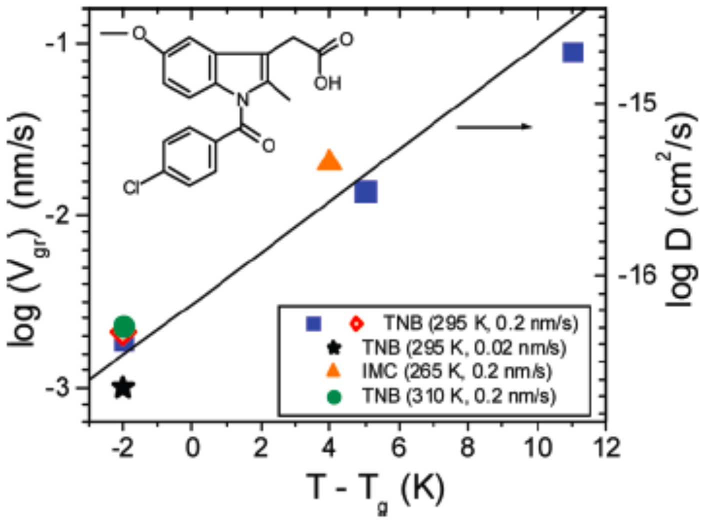


Figure 5. Growth front velocities measured from the free surface of stable IMC and TNB films at various annealing temperatures (relative to T_g for each material). Blue squares and open red diamond are for TNB deposited at 295 K at 0.2 nm/s determined from SIMS and neutron reflectivity, respectively. Other SIMS measurements shown are as follows: TNB deposited at 295 K at 0.02 nm/s (black star), TNB deposited at 310 K at 0.2 nm/s (green circle), and IMC deposited at 265 K at 0.2 nm/s (orange triangle). The solid line is the Fickian diffusion coefficient for the supercooled liquid of TNB.[22] Inset is a schematic of IMC.

Unusual high mobility behind the front?

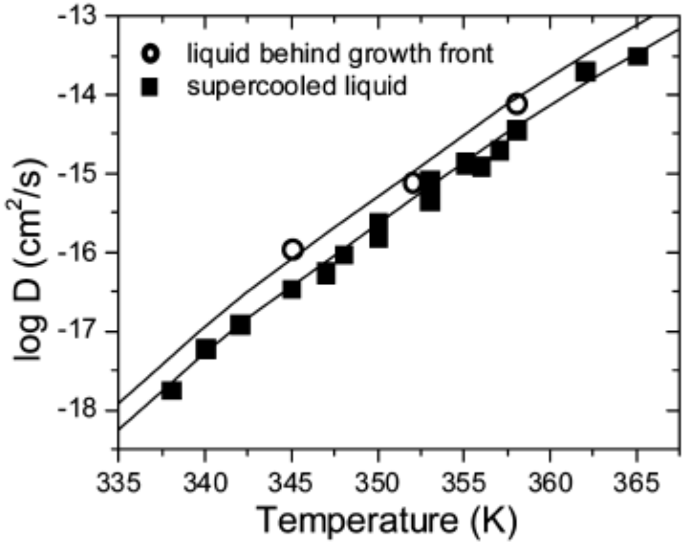
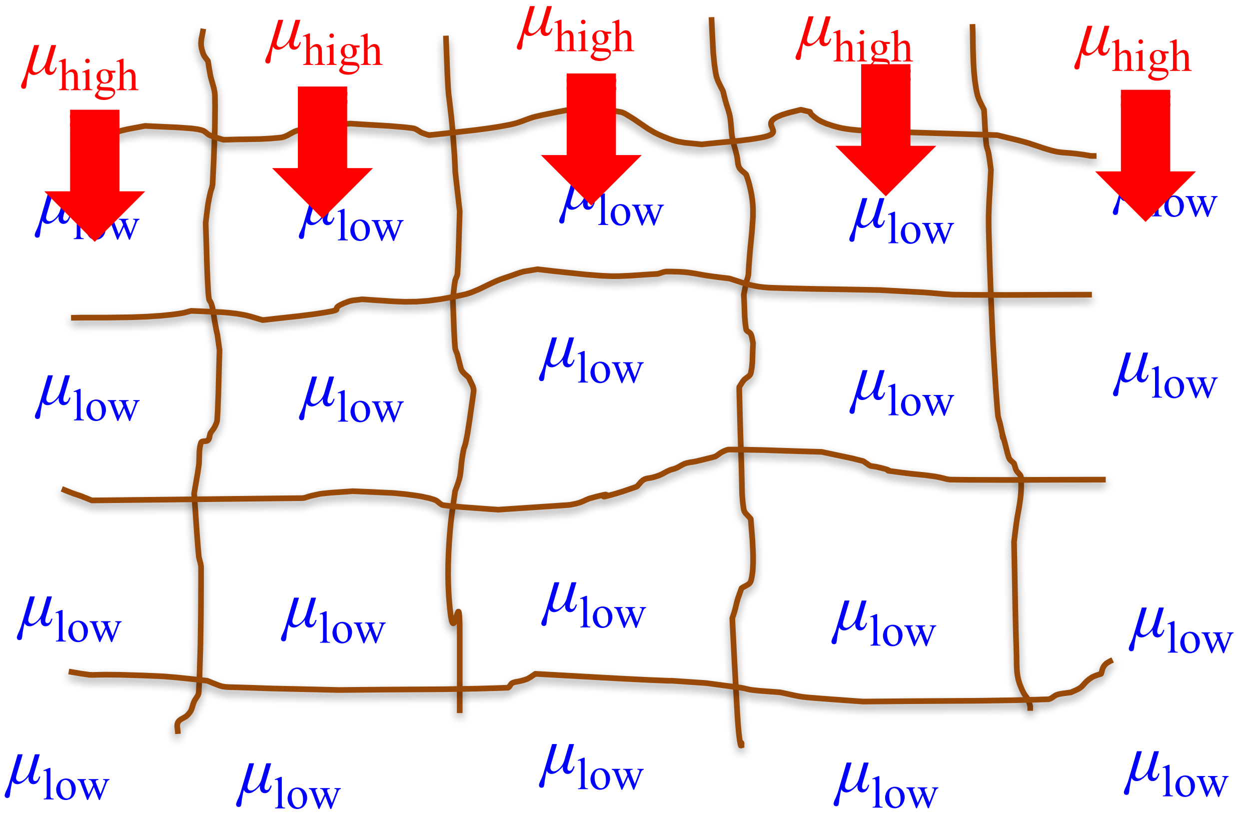


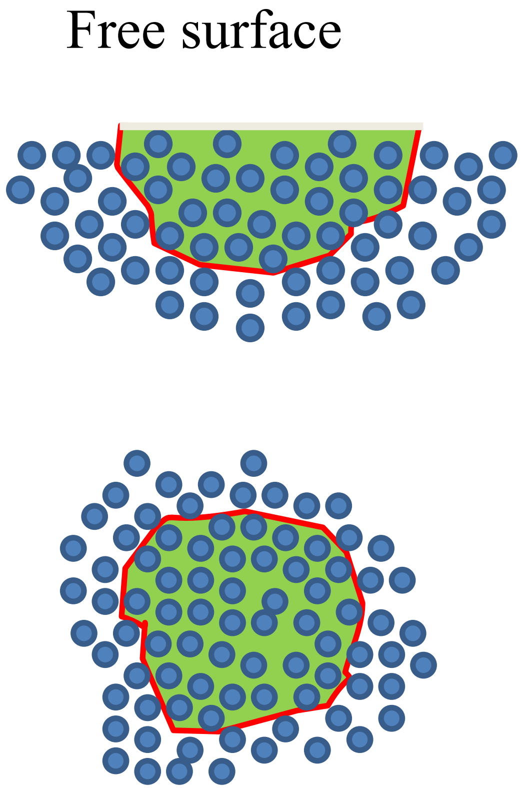
Figure 7. Self-diffusion coefficients for the supercooled liquid of TNB (squares, from ref 22) and the liquid prepared by transforming TNB stable glasses (open circles). Lines are guides to the eye.

A new liquid phase?

SF Swallen, K Windsor, RJ McMahon, MD Ediger, TE Mates, J. Chem. Phys. B, **114**, 2635 (2010)

Surface of Glasses



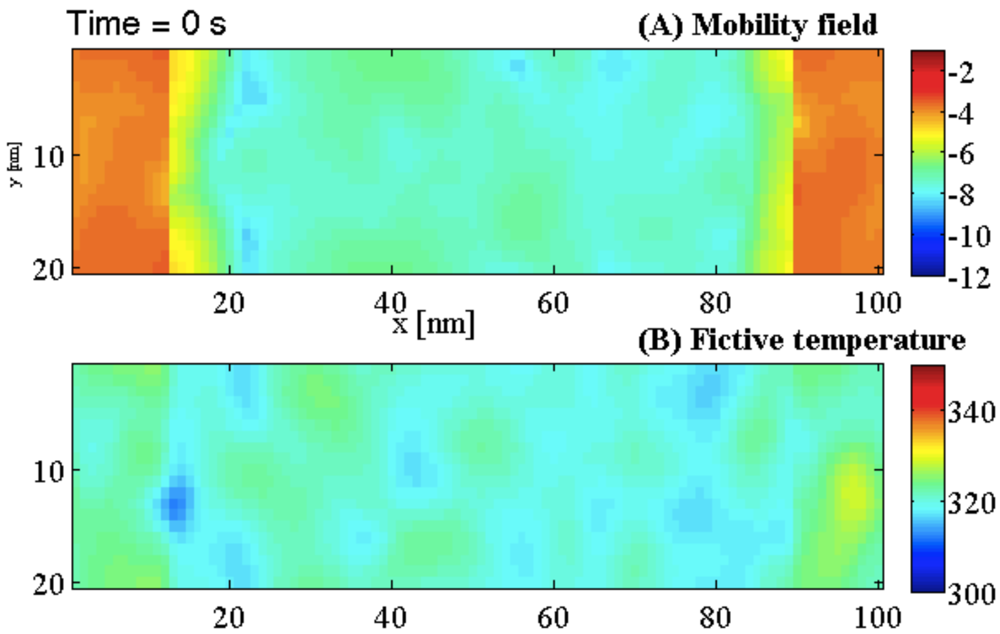


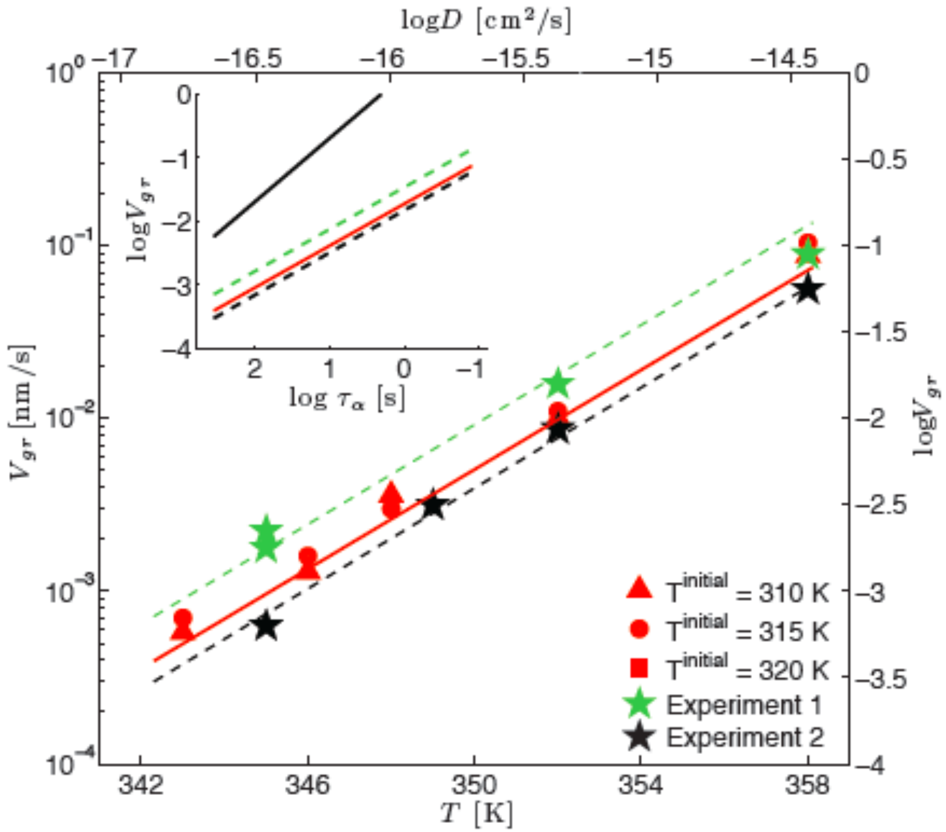
$$\mu = \tau^{-1} = \tau_0^{-1} \exp\left(-\frac{\Delta F^{\ddagger}}{k_B T}\right)$$

$$\tau_{\text{surf}} = \sqrt{\tau_0 \tau_{\text{bulk}}}$$

2D Stochastic dynamics

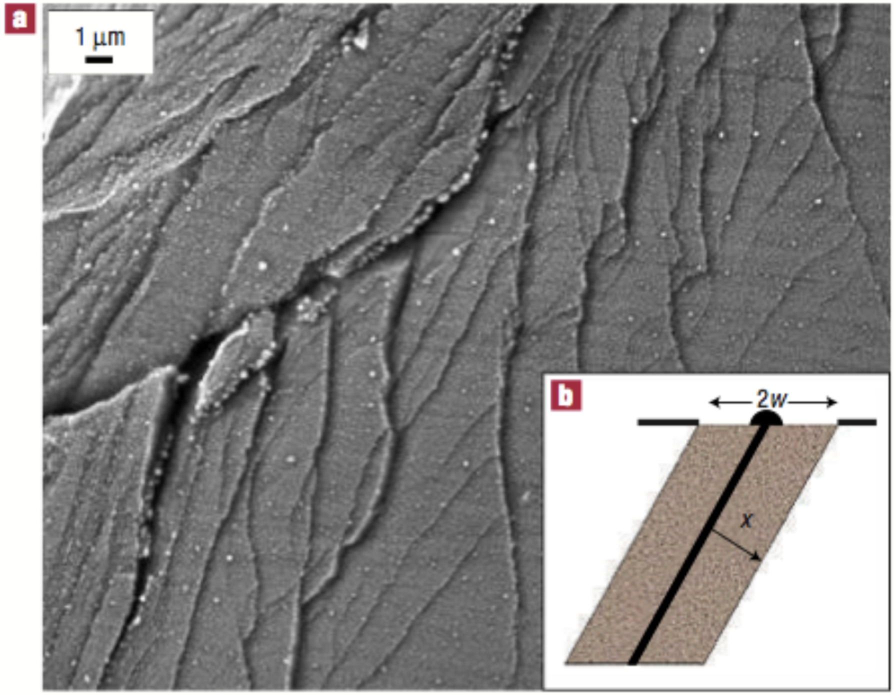
- Front speeds obtained from the stochastic dynamics are faster than those from deterministic by a factor of two
- Speed of the front is quite close with recent experiment

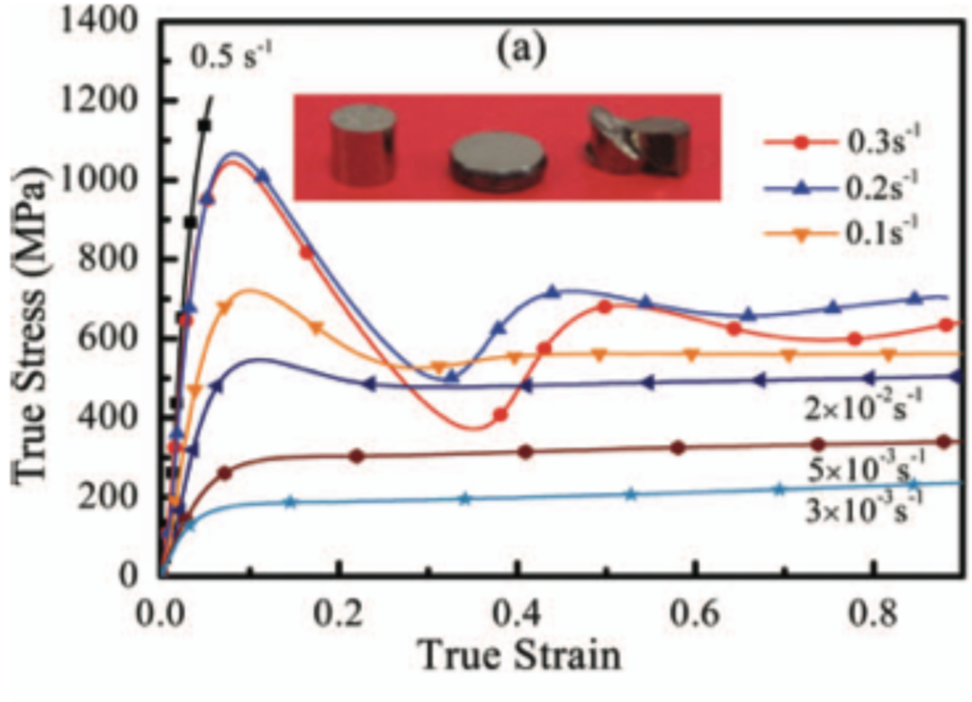




[Above figure]
Experiment 1: SF Swallen, K Windsor, RJ McMahon, MD Ediger, TE Mates, JCPB, **114**, 2635 (2010)
Experiment 2: A Sepulveda, SF Swallen, LA Kopff, RJ McMahon, MD Ediger , JCP **137**, 204508 (2012)

Shear Banding in Metallic Glasses





Top: Shear bands near a surface of Zr-based bulk metallic glass coated with tin. (a) Electron micrograph illustrating shear bands decorated with tin beads.

Top: Compressive stress-strain curves of supercooled liquid state of the bulk metallic glass Vitreloy 106a at various strain rates at T = 703 K.

Lewandowski and Greer, *Nature Materials*, 2011 (10), 823 – 837.
Zhang, Liu, and Wu, *JCP*, 2013 (139), 164508.

Dynamical shear bands in structural glasses

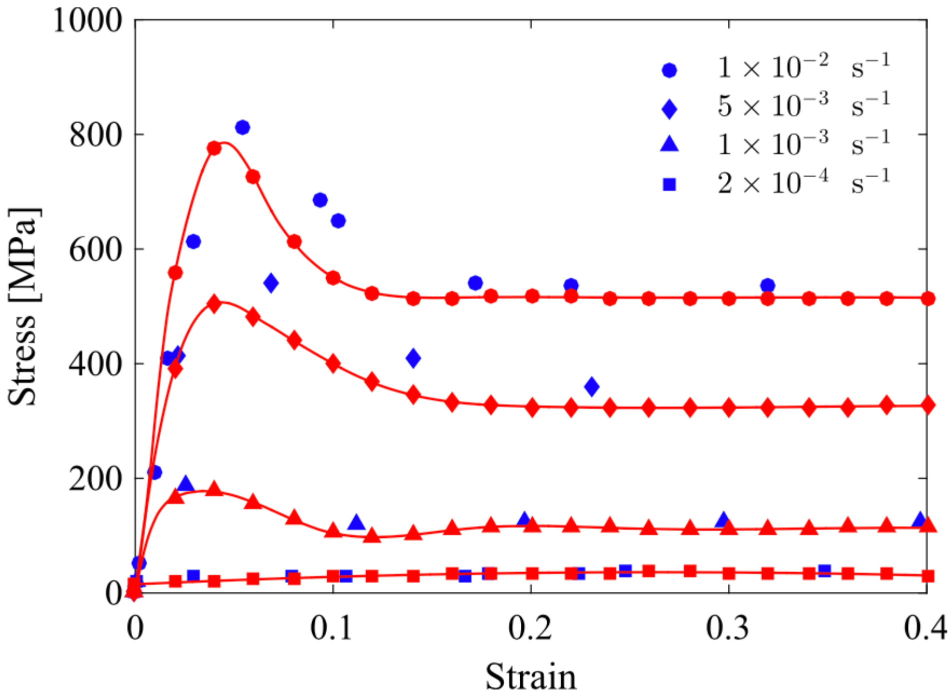
Mobility field: $\mu(r,t) = \mu_{hop}(r,t) + \mu_{mct}(r,t)$

$$\frac{\partial \mu_{mct}}{\partial t} = \vec{\nabla} \cdot \left(\frac{2\mu^2 \xi^2}{\bar{\mu}_{mct}} \vec{\nabla} \mu_{mct} \right) - \frac{2\mu^2}{\bar{\mu}_{mct}} \left(\mu_{mct} - \bar{\mu}_{mct} \right) + \delta g + \vec{\nabla} \cdot \delta \vec{j}$$

Fictive temperature field: $\frac{\partial T_f}{\partial t} = -\mu \left(T_f - T \right) + \delta T_f$

Maxwell model for viscoelasticity:

$$\frac{\partial \sigma_{ik}}{\partial t} = 2G\dot{u}_{ik} - \mu\sigma_{ik},$$



Wisitsorasak, Wolynes (2017)

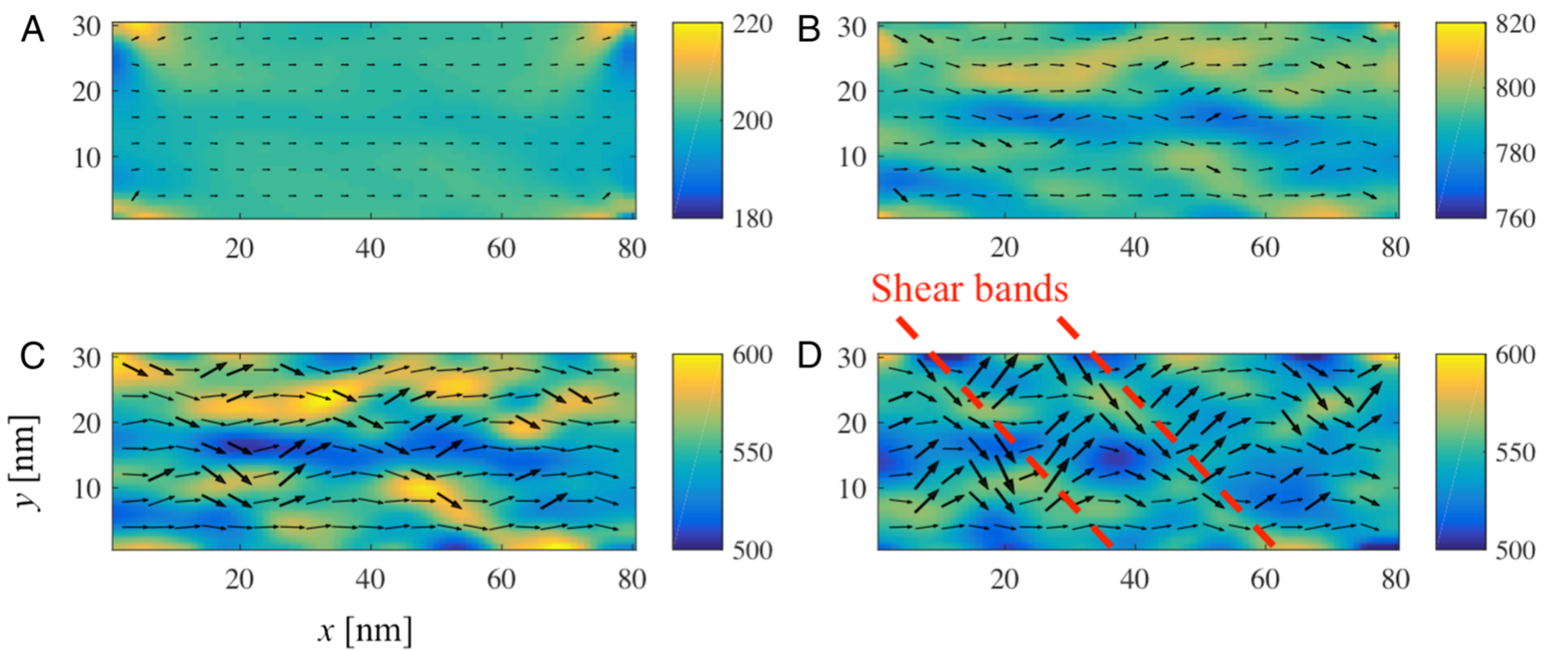


Fig. 3. Predictions of the various deformation fields in the Vitreloy 1 model under the applied strain rate of 0.01 s^{-1} at various stages of deformation. The ambient temperature $T = 643$ K. Each plot shows the equivalent stress overlaid with the strain field. The color bar on the right of each plot shows the magnitude of the stress in units of MPa. (*A*) The strain $\epsilon = 0.01$, (*B*) $\epsilon = 0.03$, (*C*) $\epsilon = 0.1$, and (*D*) $\epsilon = 0.2$.

Wisitsorasak, Wolynes (2017)

Confrontation of RFOT Theory with Observations

Lindemann Length	1984	☑	Neutron scattering plateau
Onset of Activated Behavior	1987	☑	Density from microscopic theory
Correlation Length	1987	☑	Absolute $\xi(T_g)$ vs particle size
	1989	☑	ξ vs T
Entropy Crisis	1987	☑	Density, temperature from microscopic theory
	2003	☑	Dependence on crosslinking follows from microscopics
	2007	☑	Pressure dependence of T_g, M_v vs M_p
VTF behavior in deeply supercooled regime	1989	☑	T_0 vs T_K
	2000	☑	$D = 32\, k_B/\Delta C_p$
	2000	☑	Universality of $S_c(T_g)$
Stretched Exponentiality	2001	☑	β vs D, β vs T

Aging Behavior	2003	☑	m vs x, β vs T_{eff}, Ultraslow relaxation
Network Glass	2003	☑	Crosslinking decreases fragility
Crossover Temperature	2006	☑	T_c vs T_g
	2006	☑	Relaxation time
Surface Glass Transitions	2008	☑	Diminished activation energy
Mobility Transport	2009	☑	Rejuvenation front dynamics predicted
Secondary Relaxations	2009	☑	Nearly Arrhenius, grow in amplitude as T_c is approached
Crystallization Dynamics near T_g	2010	☑	New mechanisms of crystal growth and nucleation
Strength of glasses	2012	☑	Strength is predicted
Transformation of stable glasses into supercooled liquids	2013	☑	Front speed of the transformation agree with experimental observations
Dynamical heterogeneity in the glassy state and its consequences	2014	☑	4-point correlator, calorimetry, ultraslow relaxation
Shear bands in glasses	2017	☑	Narrow shear bands arise in glasses
Nuclear waste glasses	2018	☐	

Acknowledgements – thanks!

- Prof.Peter G. Wolynes (Rice U)
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- Thailand Research Fund
- KMUTT

CTBP

RICE

KMUTT King Mongkut's University of Technology Thonburi

สกว TRF

ICTP The Abdus Salam International Centre for Theoretical Physics