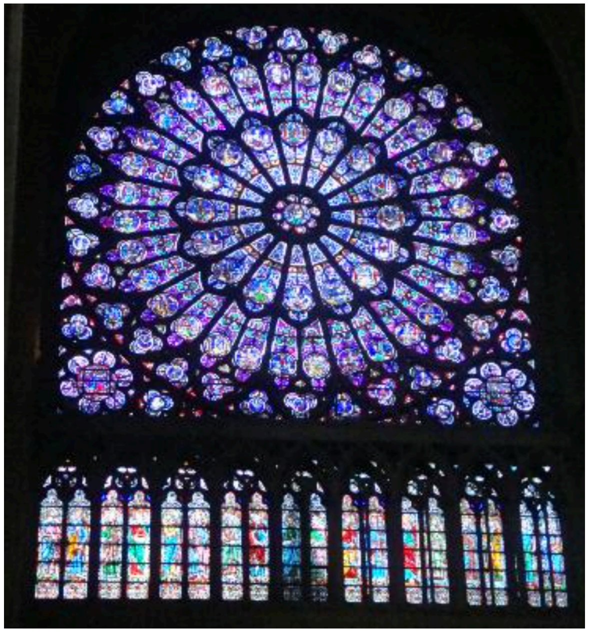
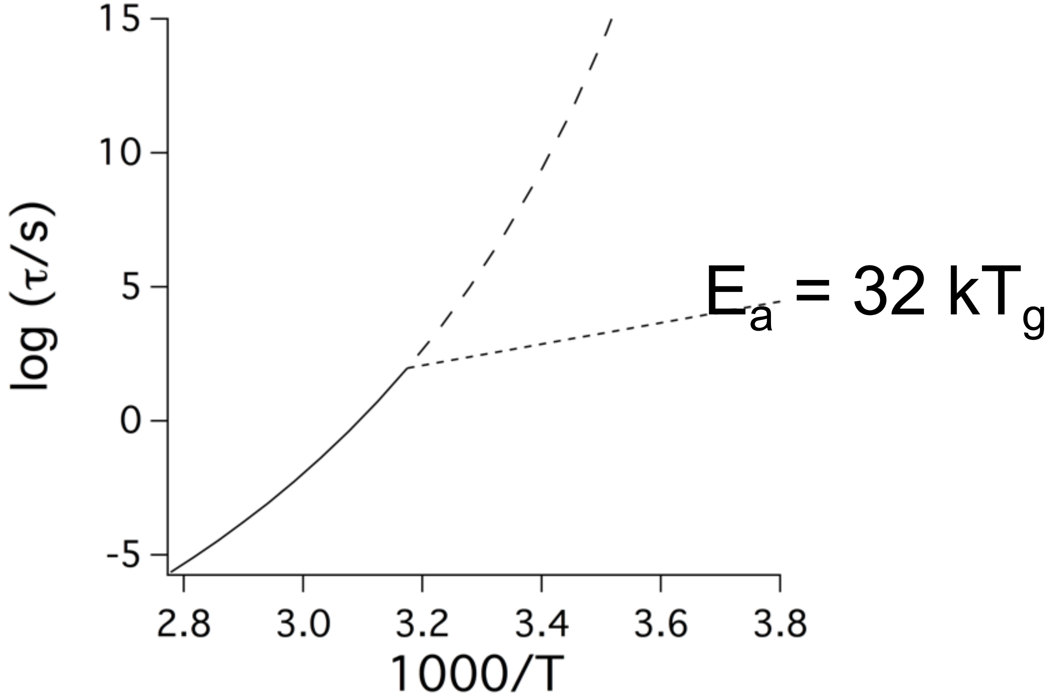
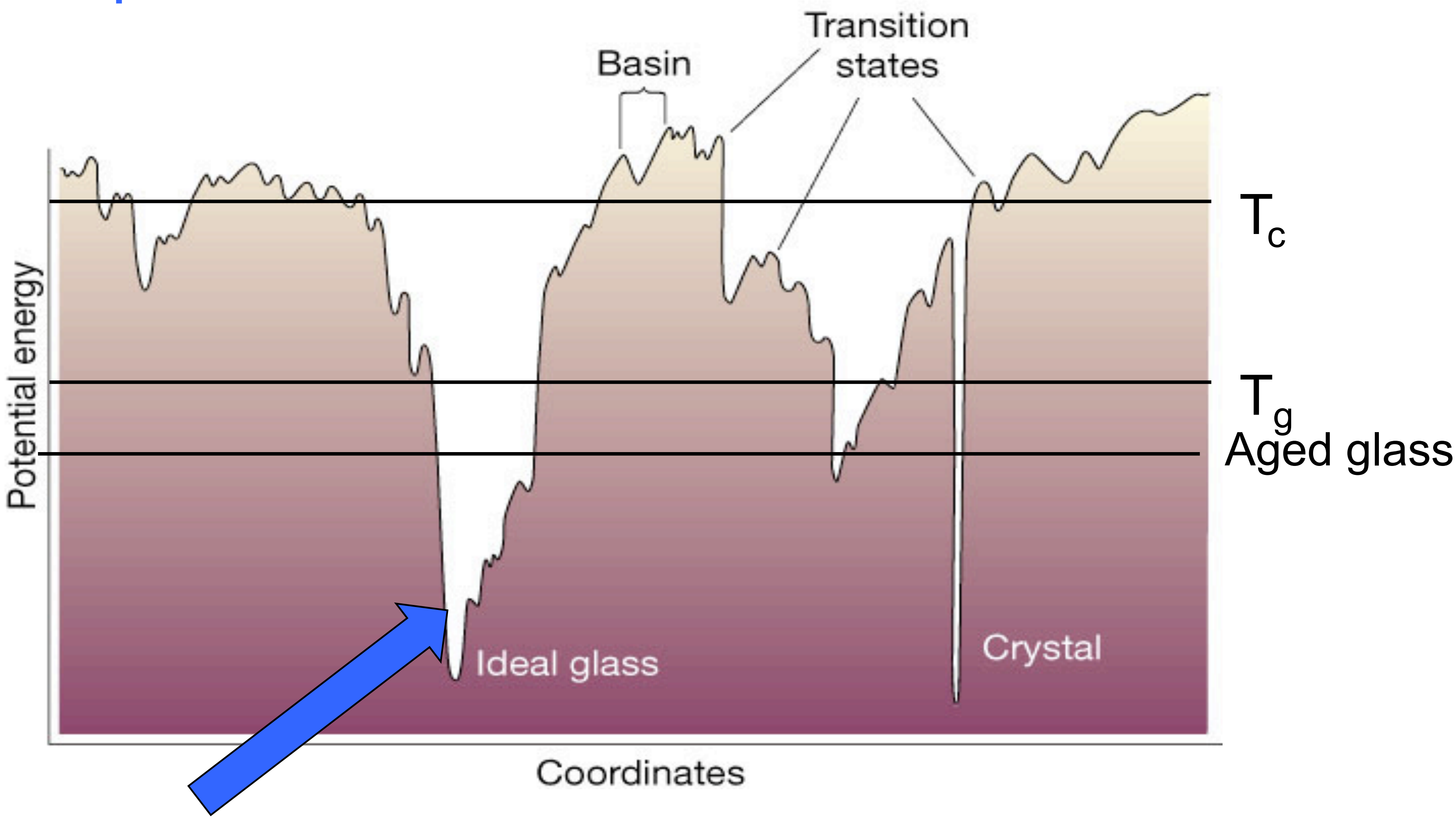
Homework: Do cathedral glasses flow appreciably in 500 years?





Assume: T_g = 800 K; T_{aging} = 300 K
One approach: Calculate structural relaxation time in the glass immediately upon cooling to T_{aging}.
My answer: Extrapolate along glass line from T_g to T_a; Initial (glassy) structural relaxation time = 10^{23} s = 10^{15} years. No flow expected. See: Zanotto and Gupta, Am. J. Phys. (1999) for a related calculation – and even larger time estimate.

Glasses near the bottom of the potential energy landscape



These states: Entropy crisis? Diverging relaxation times? Growing length scales? Properties of the "ideal glass". Ultimate material properties.

Energy landscape adapted from Debenedetti and Stillinger, Nature 2001

Why not try naturally aged glasses?

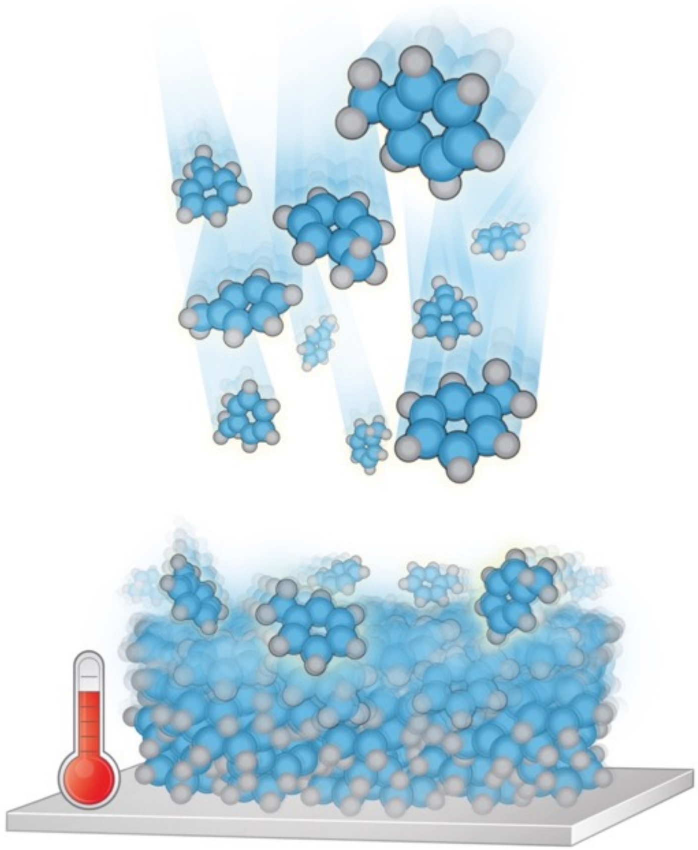
Images from Berthier and Ediger, Physics Today (2016)

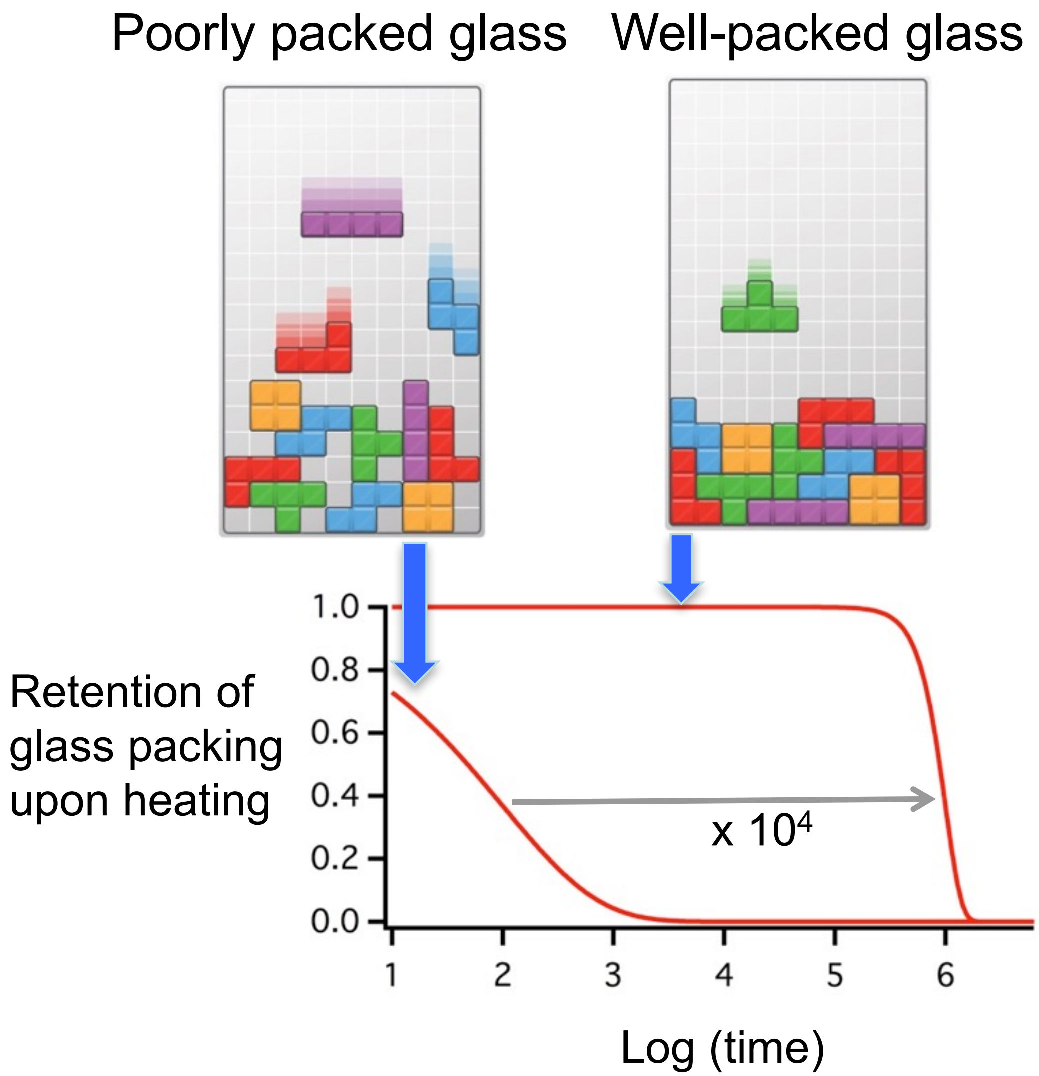
In class assignment: Suppose someone handed you an "ideal glass". What experiments would you do to determine its properties? (Hint: What is special about an ideal glass?)

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)
  - Thermodynamics
  - Dynamics/Transformation kinetics
  - Structure

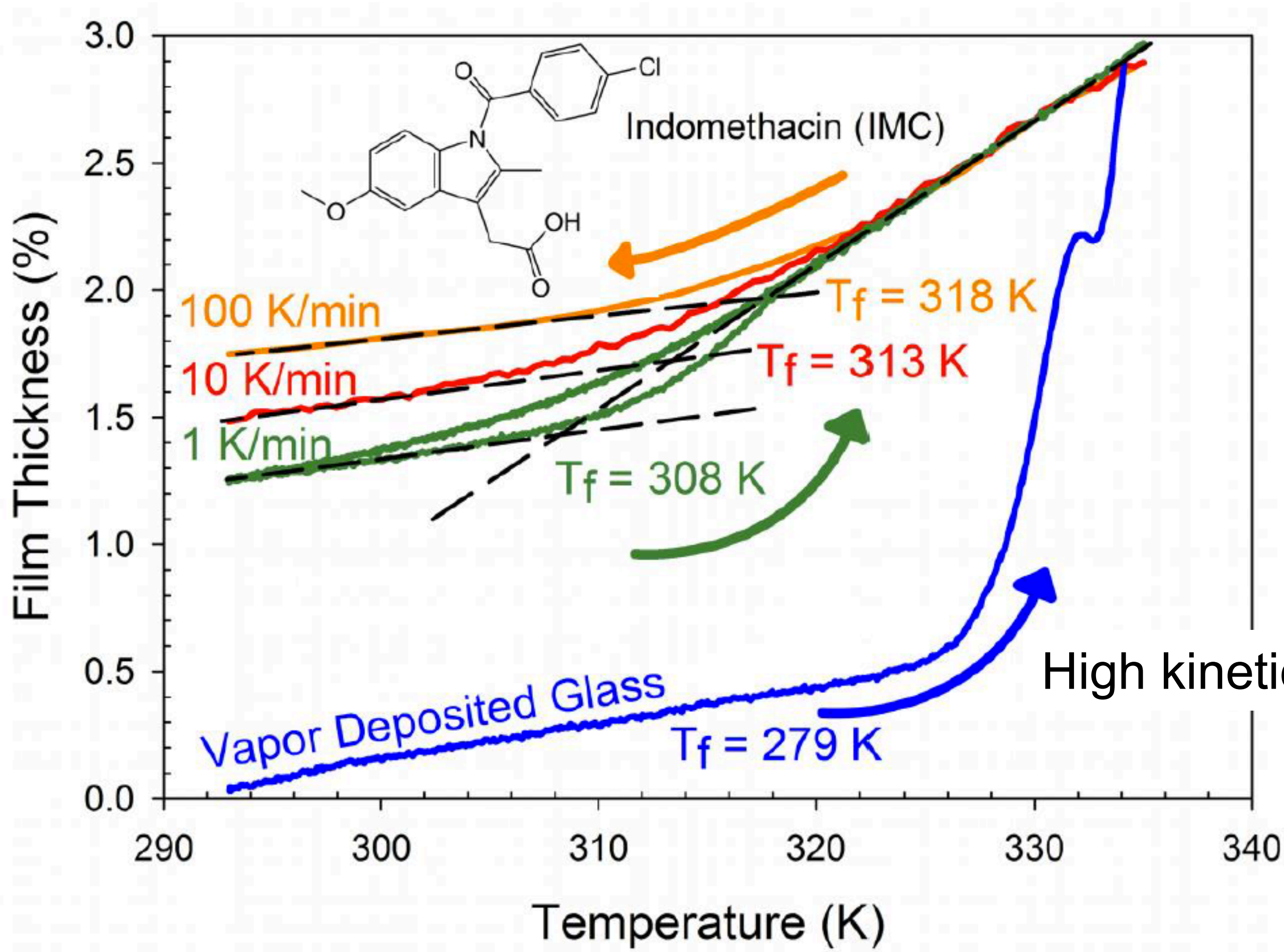
Physical vapor deposition allows the formation of glasses with low energy and high kinetic stability ("stable glasses")





Berthier and Ediger, Physics Today (2016)

PVD can prepare glasses of organic molecules with high density and high kinetic stability

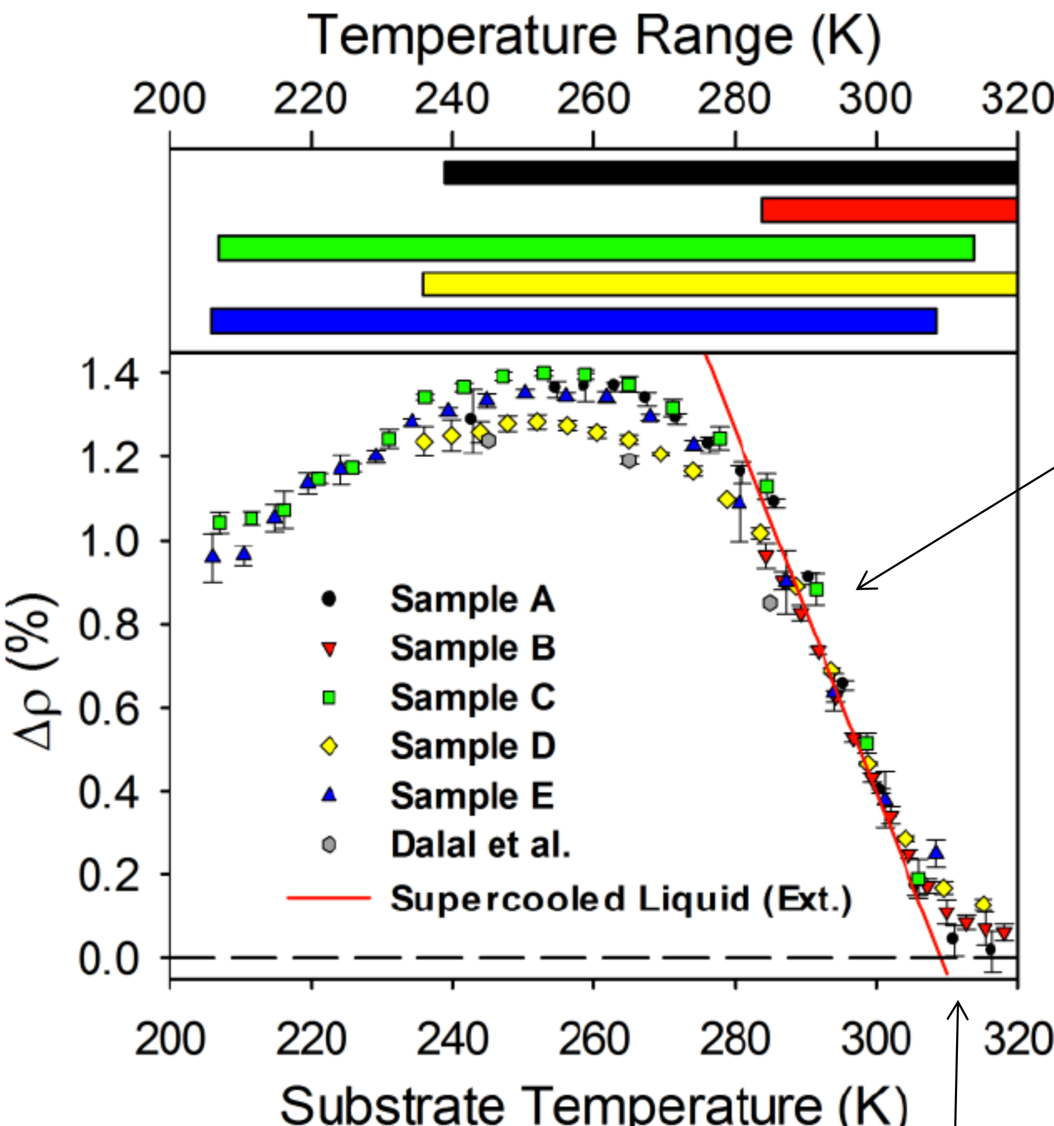


High kinetic stability

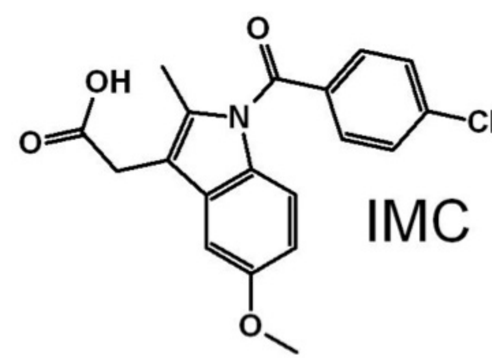
Dalal et al., JPC Lett. (2012)

Equivalent to 10^3 – 10^{10} years of aging

PVD glass densities match density expected for SCL down to 0.92 T_g.



Matches density expected for supercooled liquid down to T_g – 30 K (thermodynamic control – mobility is high enough to reach "equilibrium")

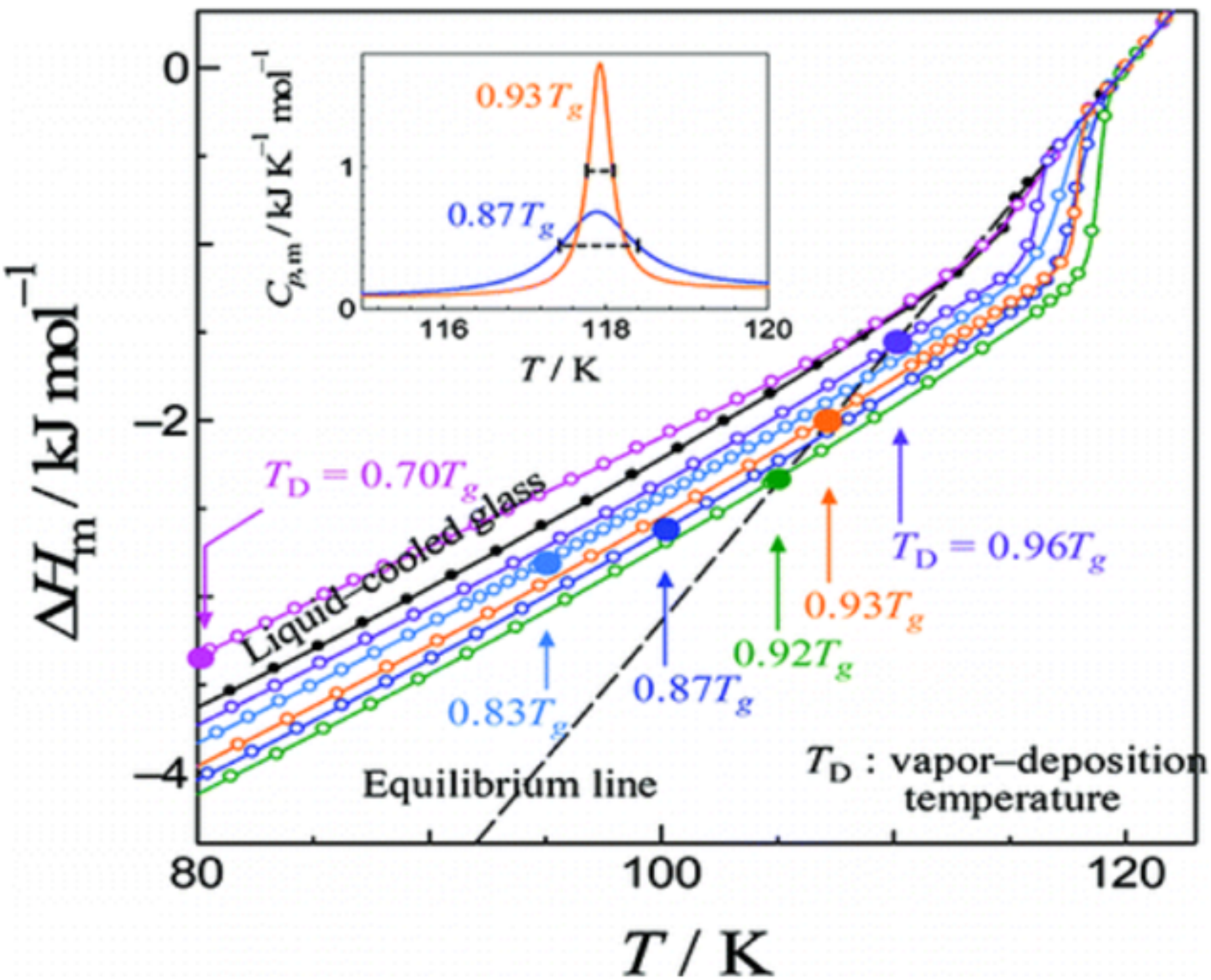


IMC

Dalal et al., J. Phys. Chem. B (2013)

T_g

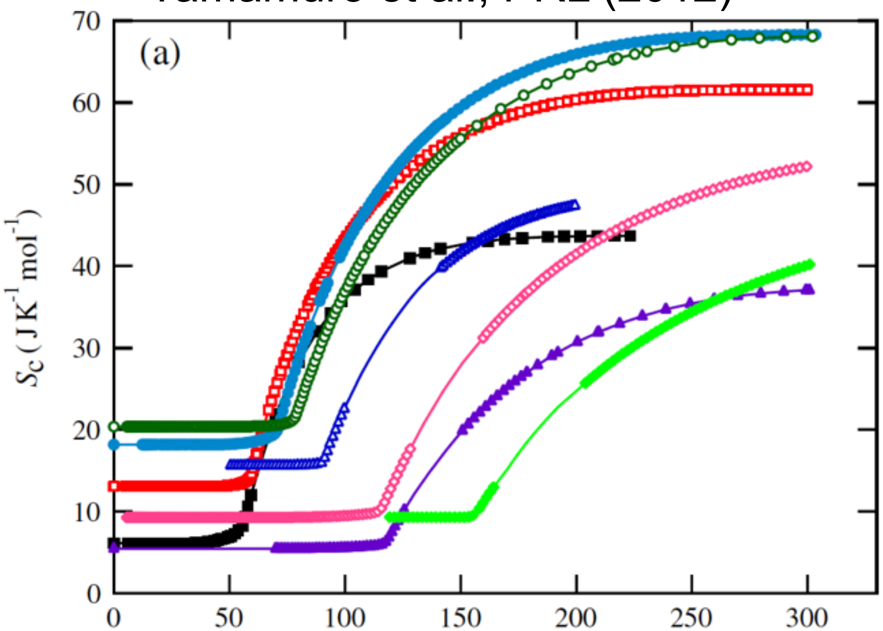
PVD glasses can be very low in the energy landscape with measured enthalpy matching extrapolated SCL



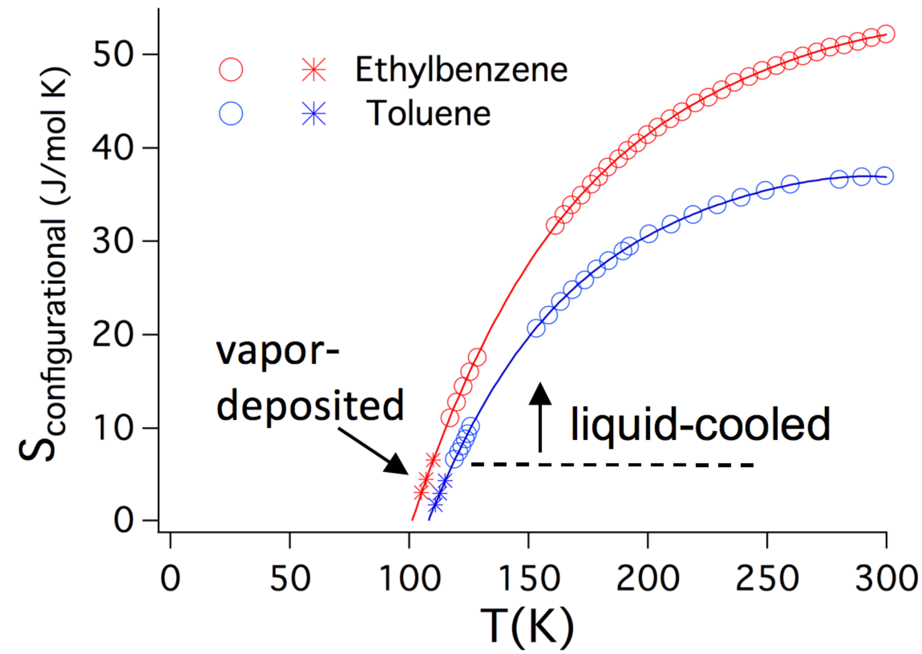
Ramos, Oguni, Ishii, Nakayama, J. Phys. Chem. B (2011); ethylbenzene

PVD glasses provide insight into resolution of entropy crisis

Yamamuro et al., PRL (2012)



PVD data from Ramos et al. and Rafols-Ribe et al.



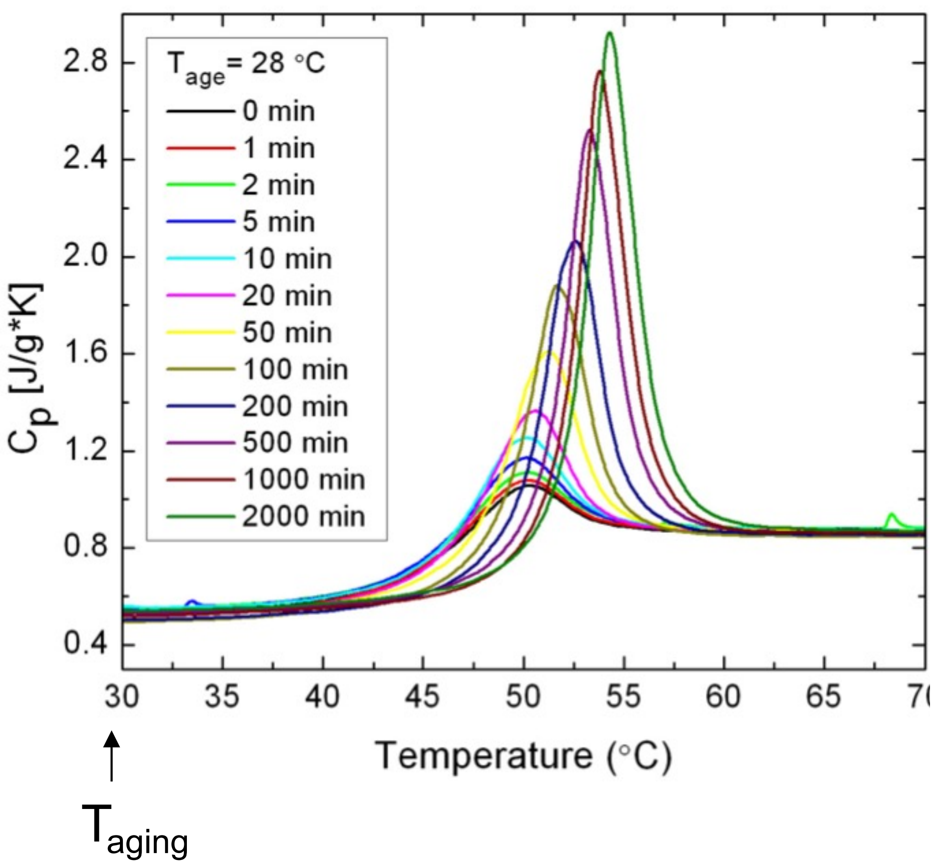
Argument:

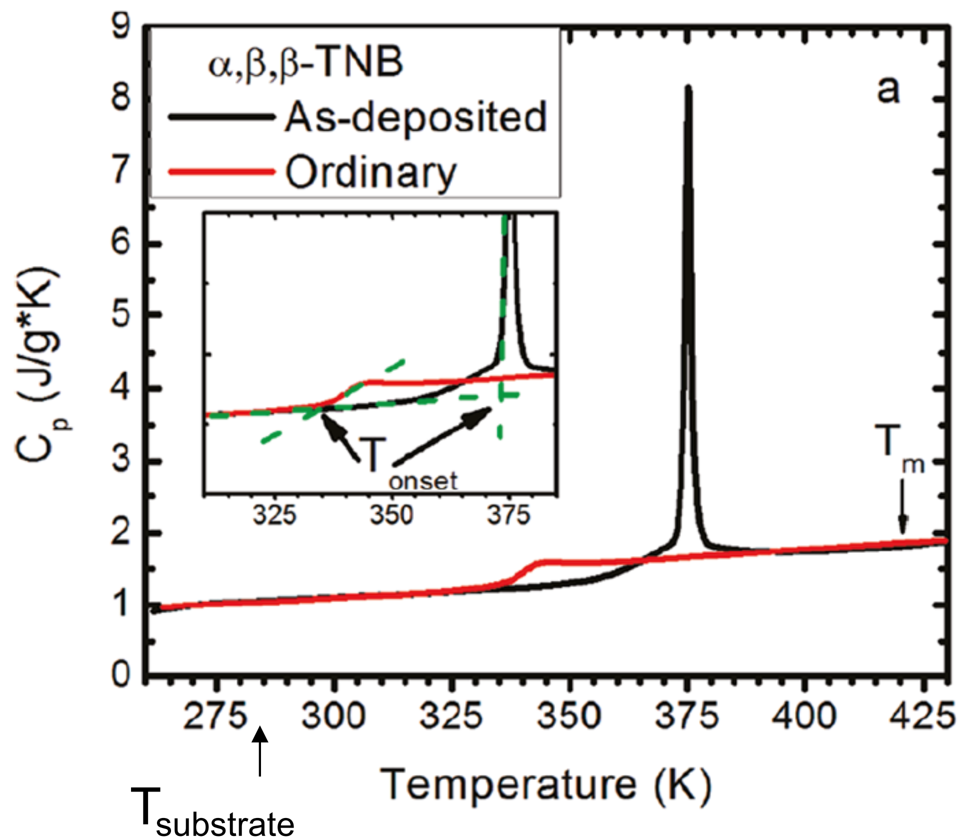
- H for PVD glasses of toluene and ethylbenzene matches extrapolated H for SCL, in “thermodynamic control regime”
- V for PVD glasses of indomethacin matches extrapolated V for SCL, in “thermodynamic control regime”
- This is not a coincidence and indicates that extrapolated SCL H is correct in “thermodynamic control regime.” (ASSUMPTION)
- If extrapolated H is correct, then extrapolated C_p is correct, then extrapolated S is correct in “thermodynamic control regime”.

Conclusion:

- Second-order phase transition at T_K is now 5 times more probable (toluene).
- If something else intervenes, it happens between T_K and 1.03 T_K (toluene).

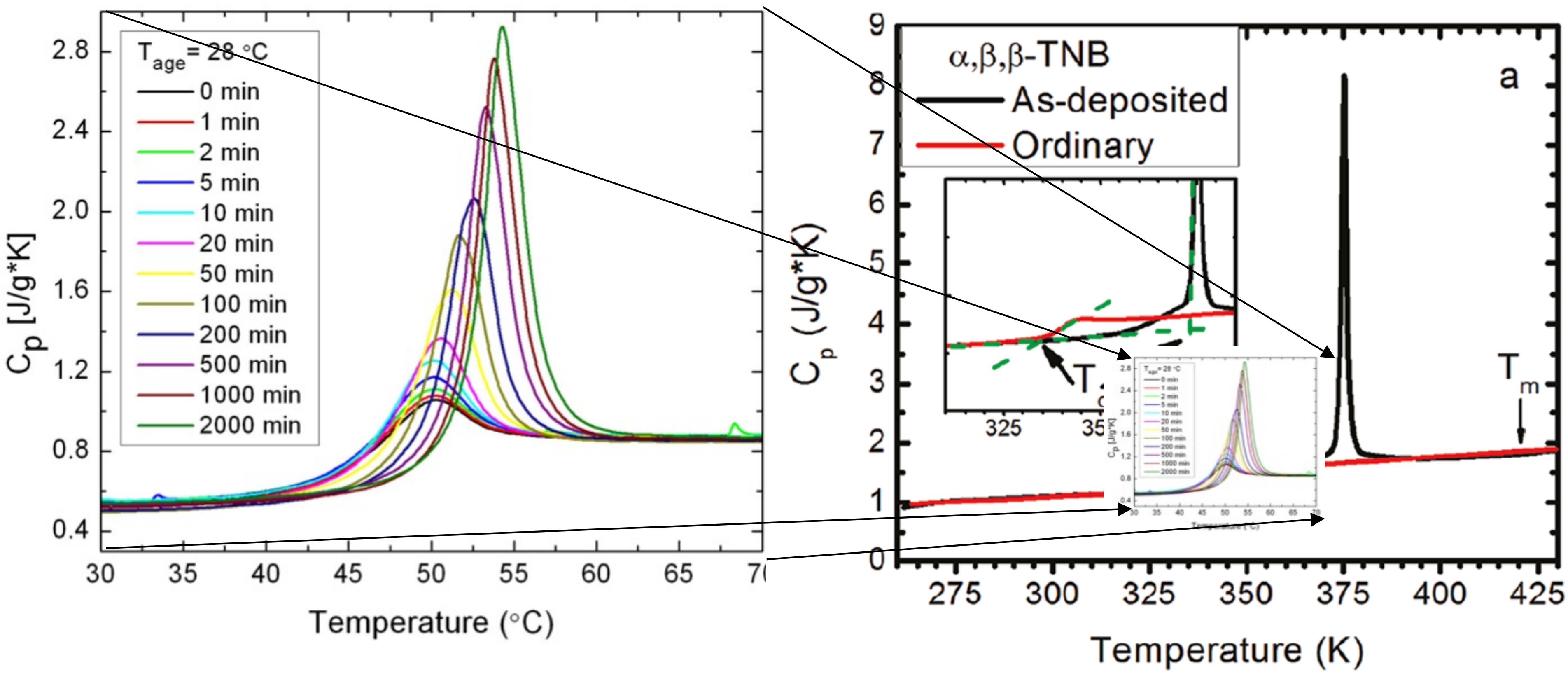
Liquid-cooled glasses are barely stable – PVD glasses can exhibit much higher kinetic stability (higher energy barriers)





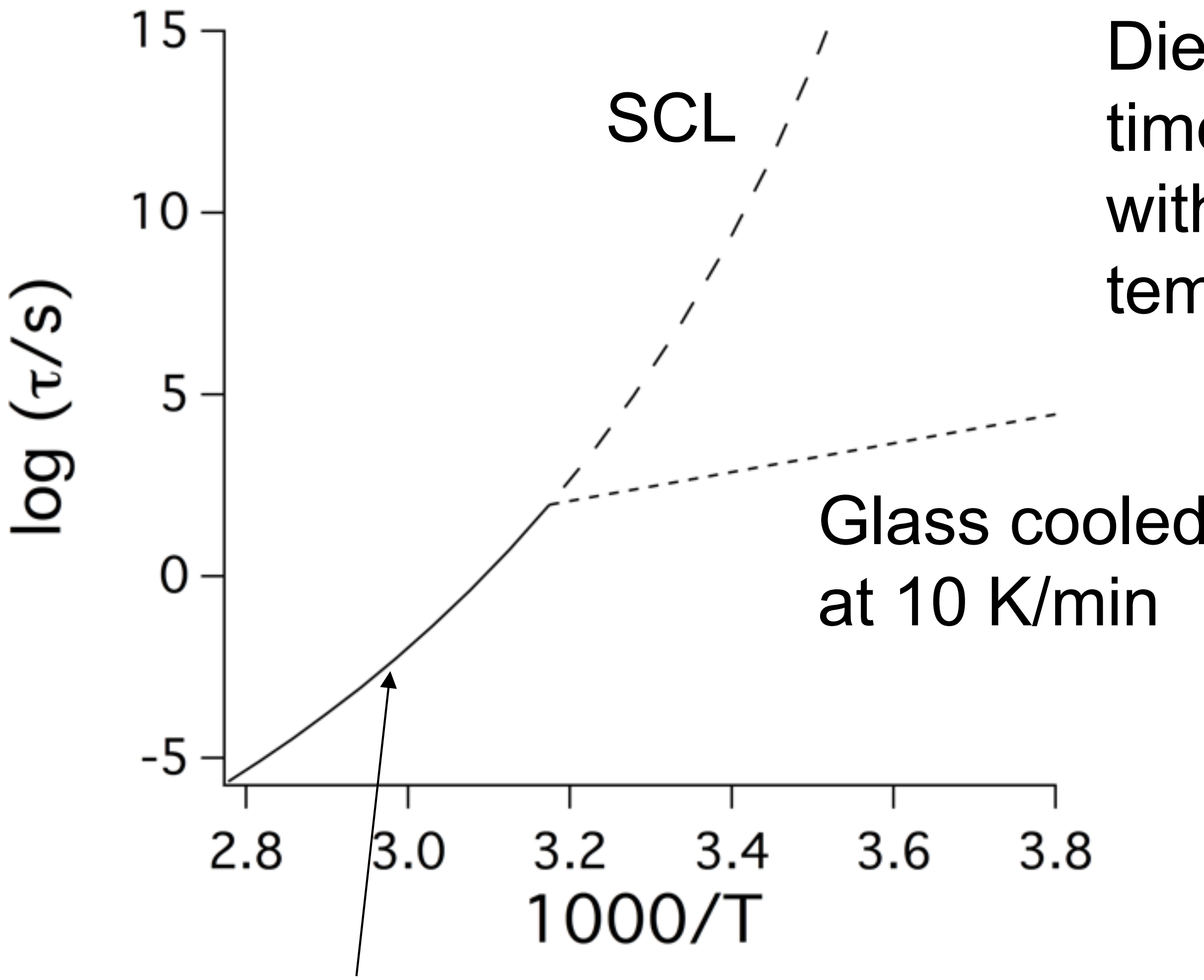
Dawson et al., JPC Lett (2011)

Liquid-cooled glasses are marginally stable – PVD glasses can exhibit much higher kinetic stability (higher energy barriers)

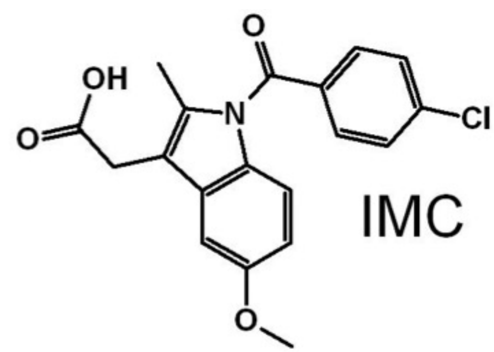


Dawson et al., JPC Lett (2011)

Estimate τ_α for PVD stable glass: evidence for/against divergence?



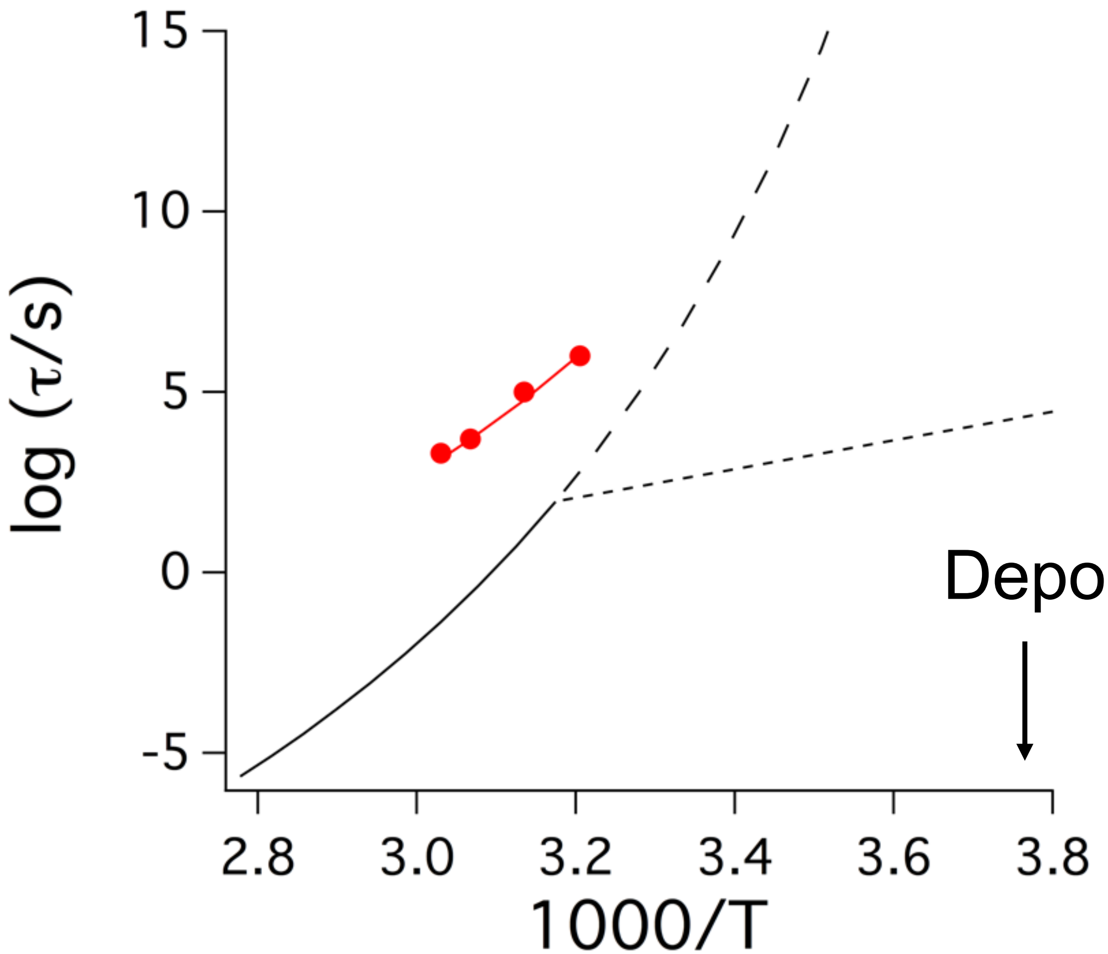
Dielectric relaxation times for indomethacin, with extrapolation to low temperature



IMC

Wojnarowska, et al., J. Phys. Chem. B 2009, 113, 12536–12545

Estimate τ_α for PVD stable glass

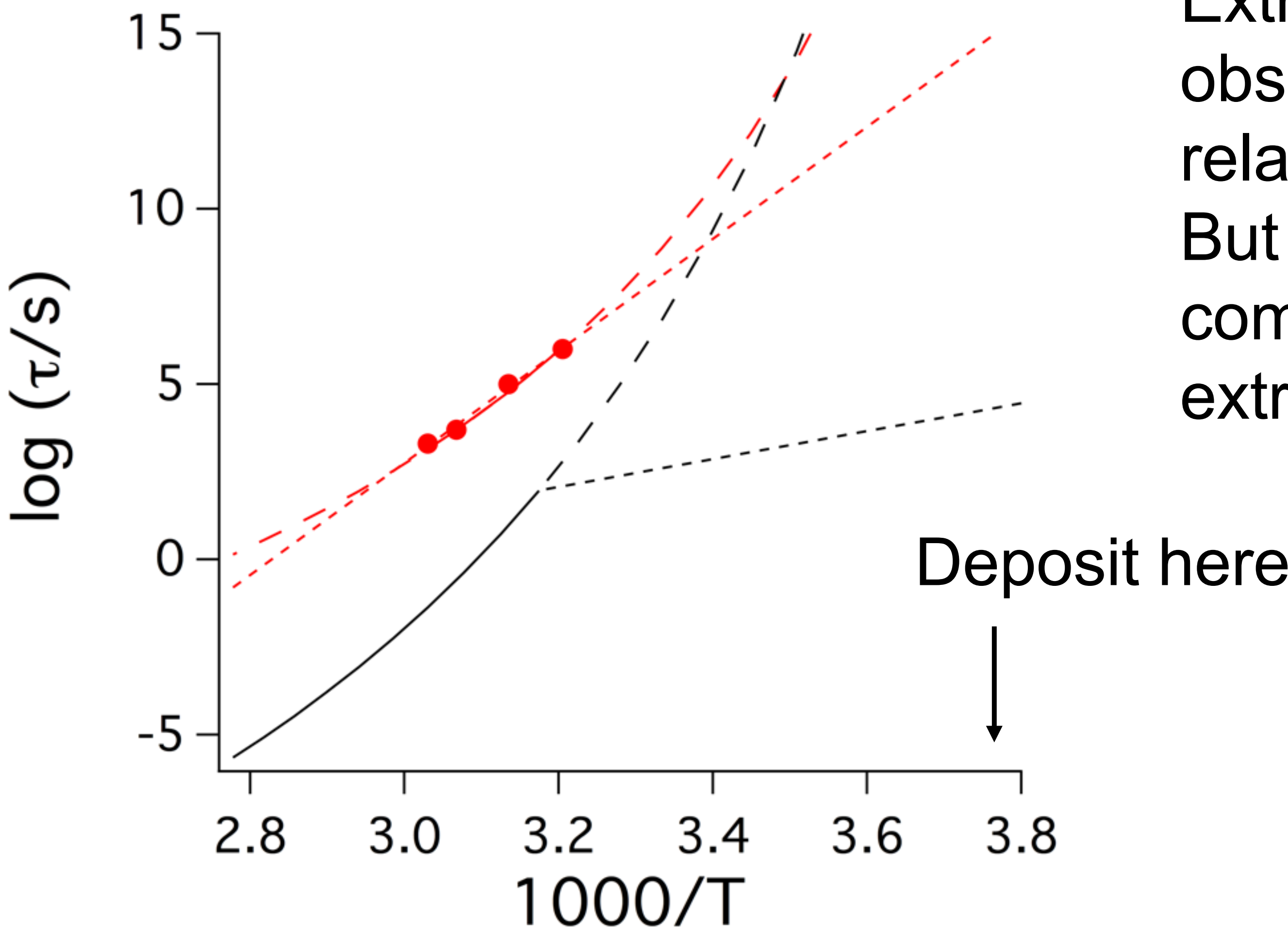


Deposit here

Relaxation is too slow to be observed at deposition T. Jump to much higher T and observe transformation to SCL

Dawson, et al. JCP 136, 094505 (2012)

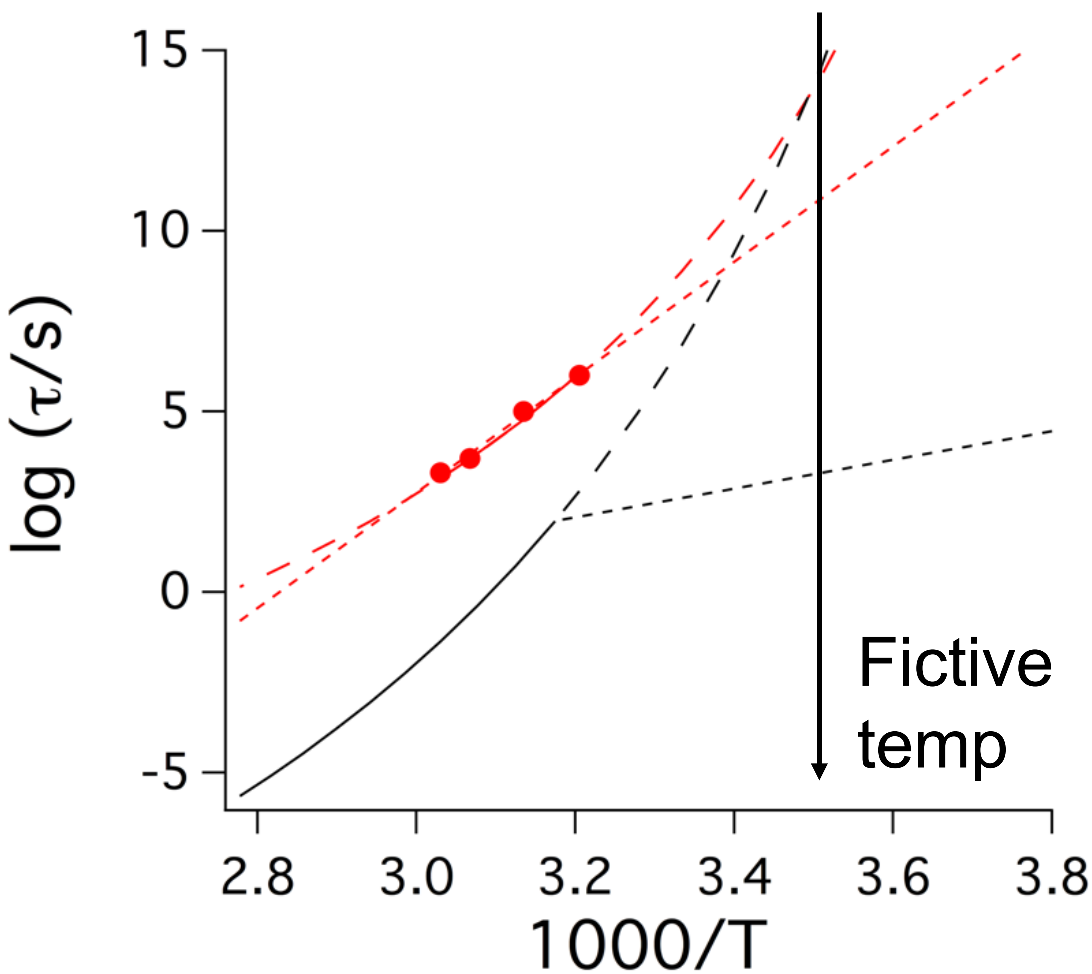
Estimate τ_α for PVD stable glass



Extrapolate observed glass relaxation to low T. But how to fairly compare with extrapolated SCL?

Dawson, et al. JCP 136, 094505 (2012)

Estimate τ_α for PVD stable glass



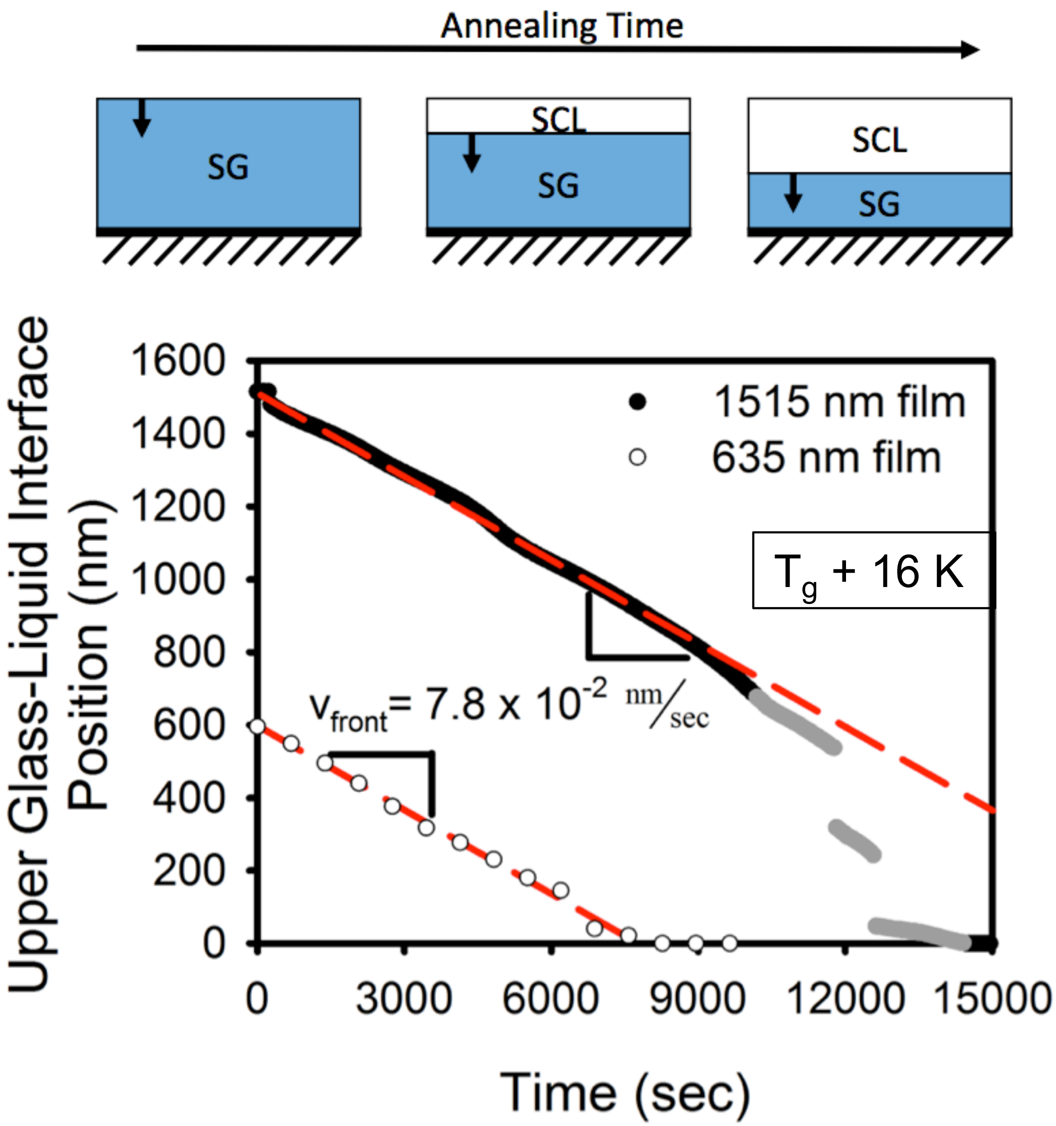
Compare to SCL with the same enthalpy (fictive temperature) =>
$\tau_\alpha = 10^{11} - 10^{15}$ s

> 8 decades slower than liquid-cooled glass

Consistent with both VTF and Arrhenius extrapolations

Dawson, et al. JCP 136, 094505 (2012)

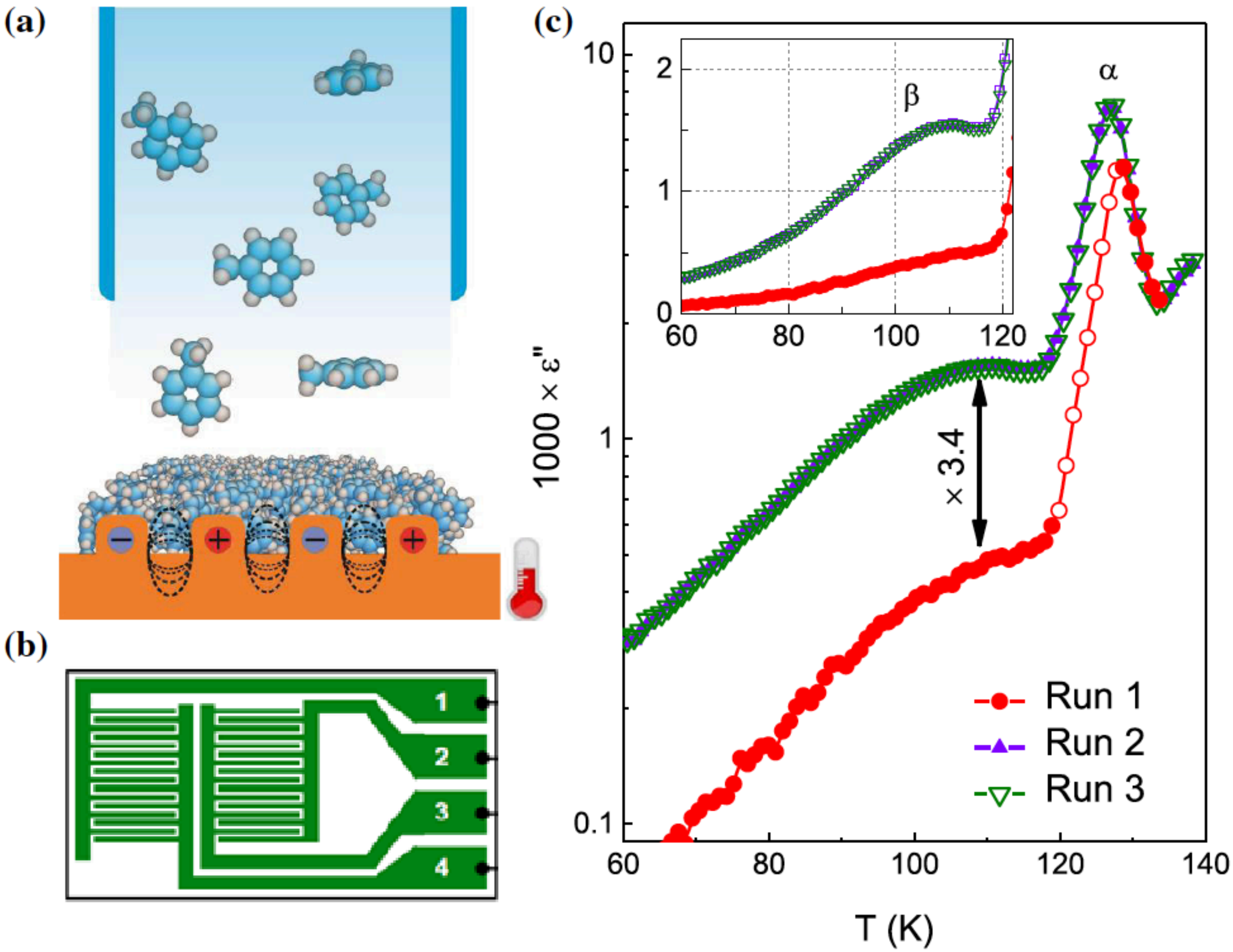
The best PVD glasses pack so tightly that they melt like crystals

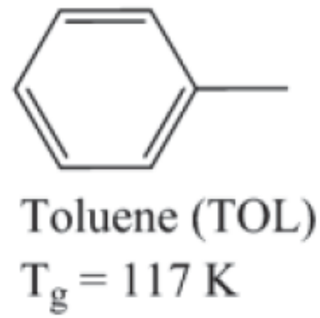


- Indomethacin
- Constant velocity "melting" front (also observed with SIMS)
- "Melting" front unprecedented for amorphous materials
- PVD glass requires 12000 s to "melt"
- Liquid-cooled glass requires less than 1 s to "melt"
- Expect an ideal glass to also have this property

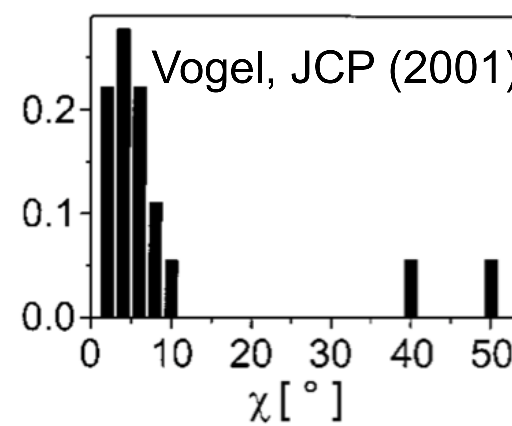
Dalal et al., J. Phys. Chem B. 2015

β relaxation is suppressed in stable PVD glasses



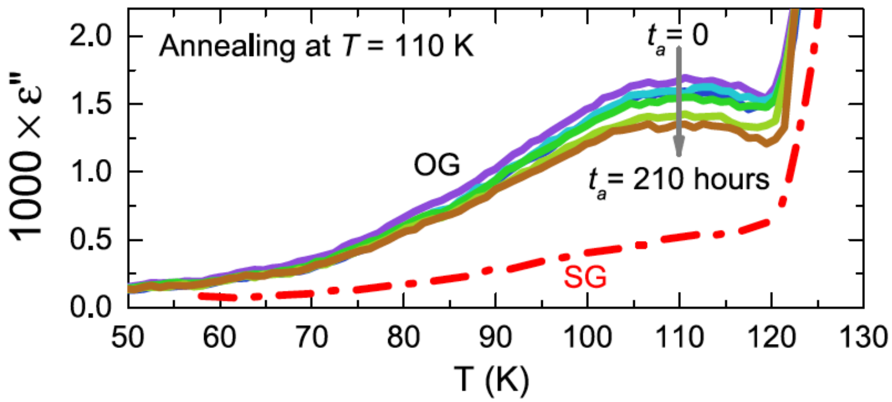


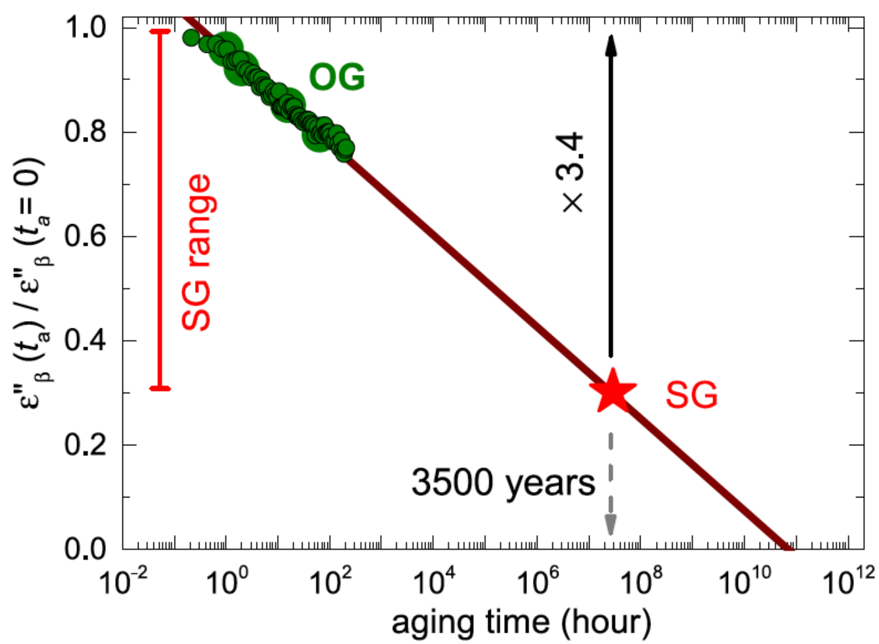
Possible physical picture: Orientation exploration in a cone of ~ 3° (vapor deposited glass) instead of ~ 7 ° (liquid-cooled glass)



Yu, Richert et al., PRL 115, 185501 (2015)

β relaxation can also be suppressed by aging a liquid-cooled glass, but it takes a long time

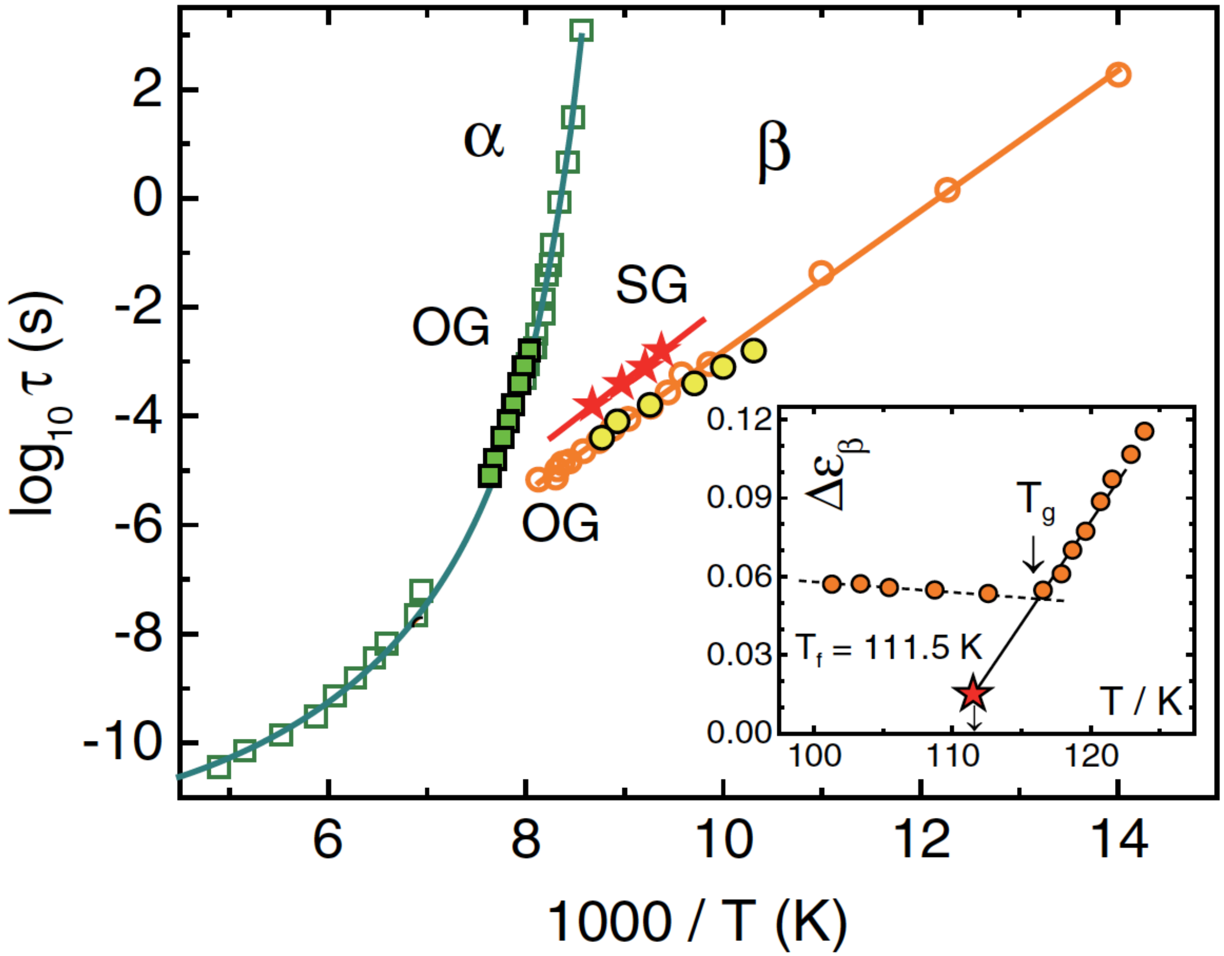




Is the strength of the β relaxation an indication of approach to ideal glass state?

Yu, Richert et al., PRL 115, 185501 (2015)

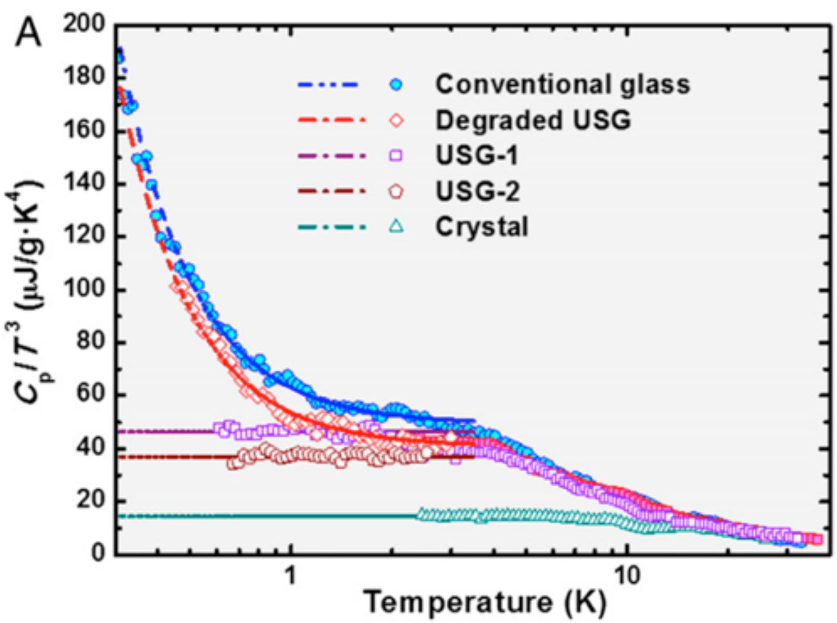
Is the β relaxation eliminated in the ideal glass state?

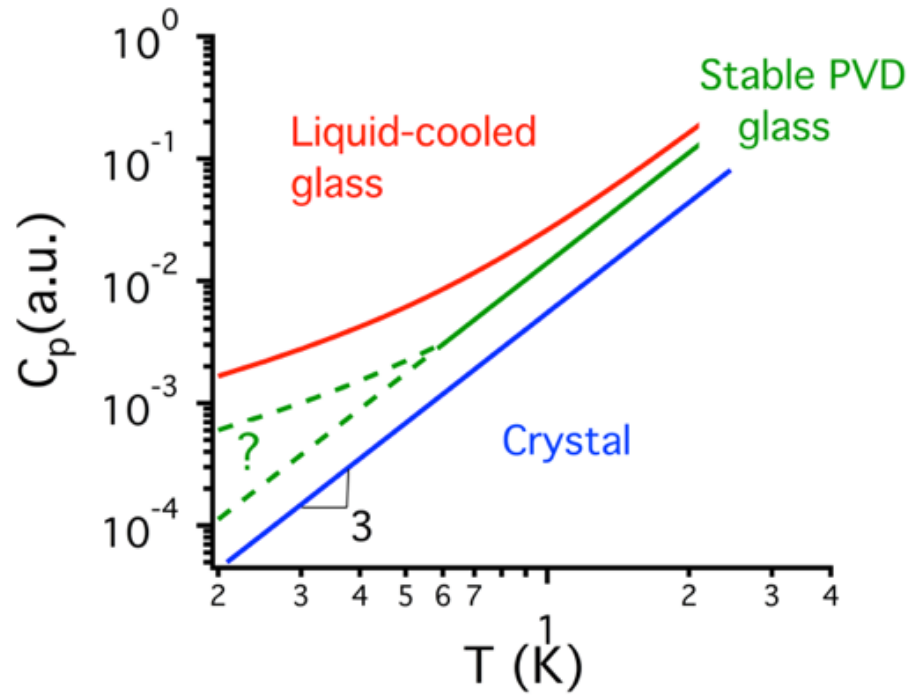


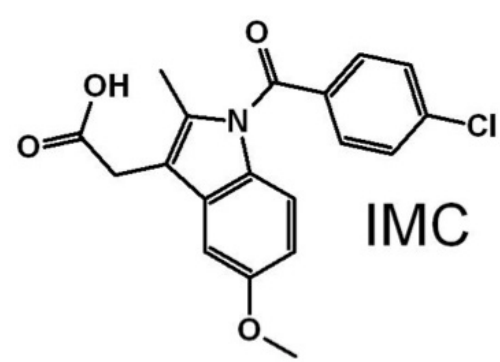
Amplitude of β relaxation in SCL extrapolates to zero near T_K = 108 K.
PVD glass lies on extrapolated line, using $T_{fictive}$.
This suggests that the ideal glass has no β relaxation.

Yu, Richert et al., PRL 115, 185501 (2015)

Heat capacity below 2 K is strongly suppressed in stable PVD glasses: Where are the two-level systems?

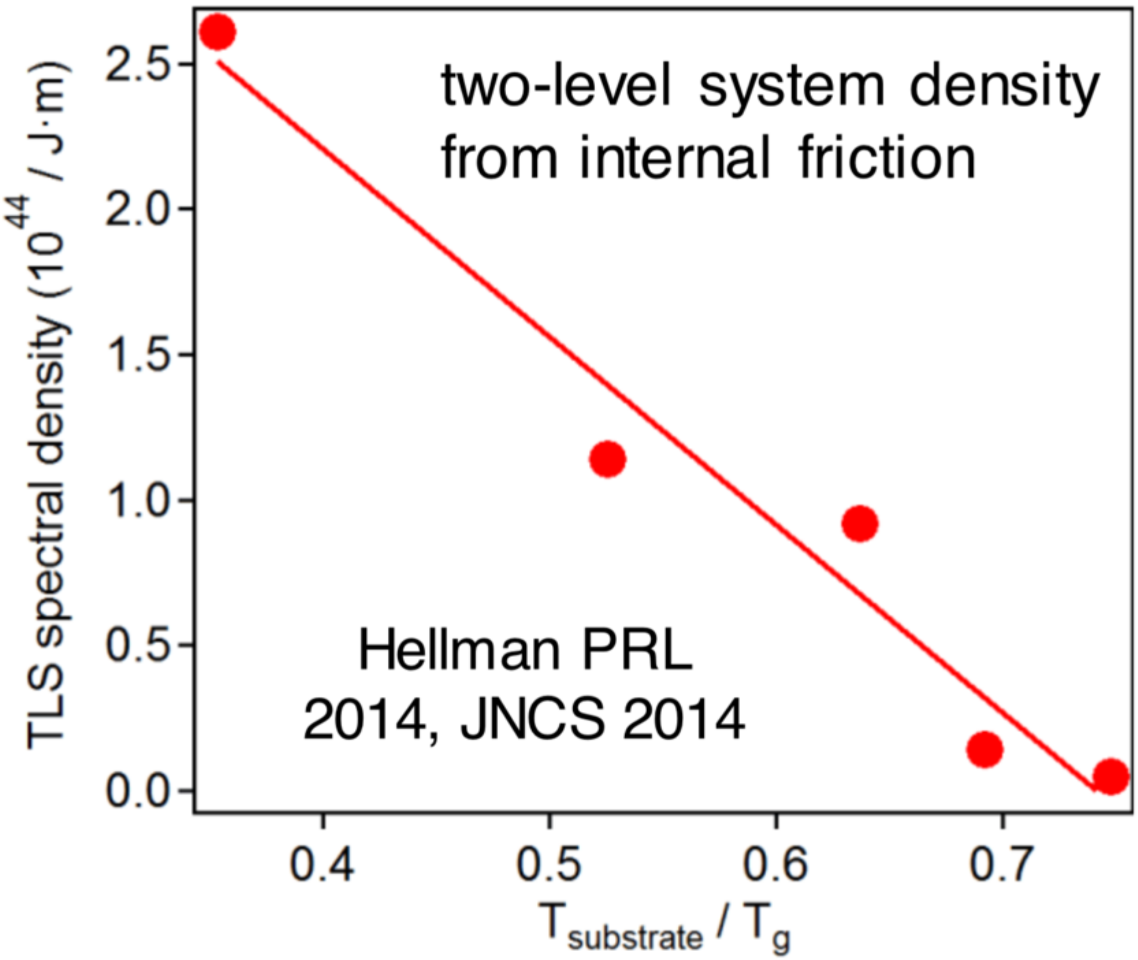






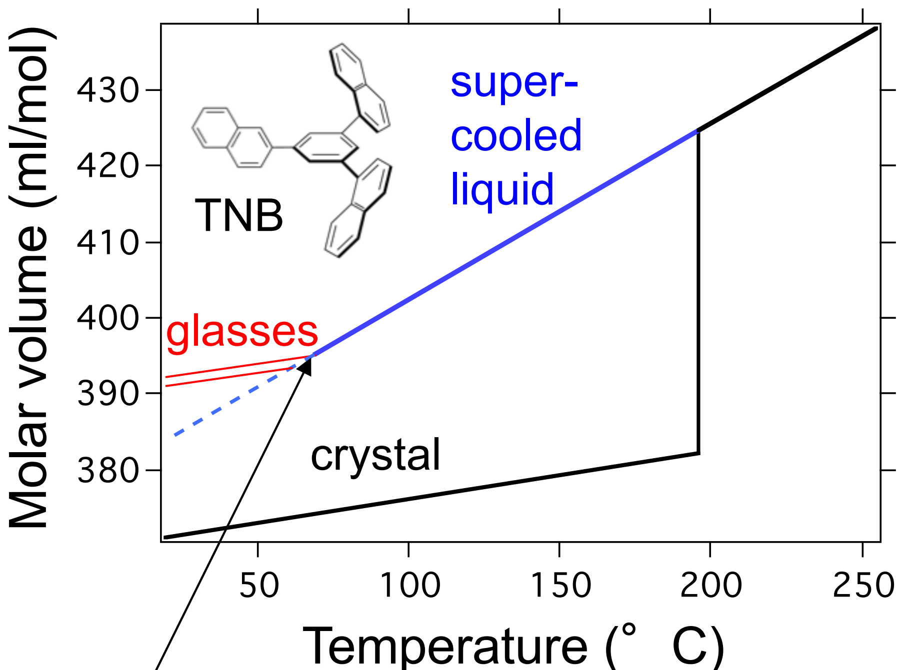
Perez-Castenada, PNAS 111, 11275 (2014)

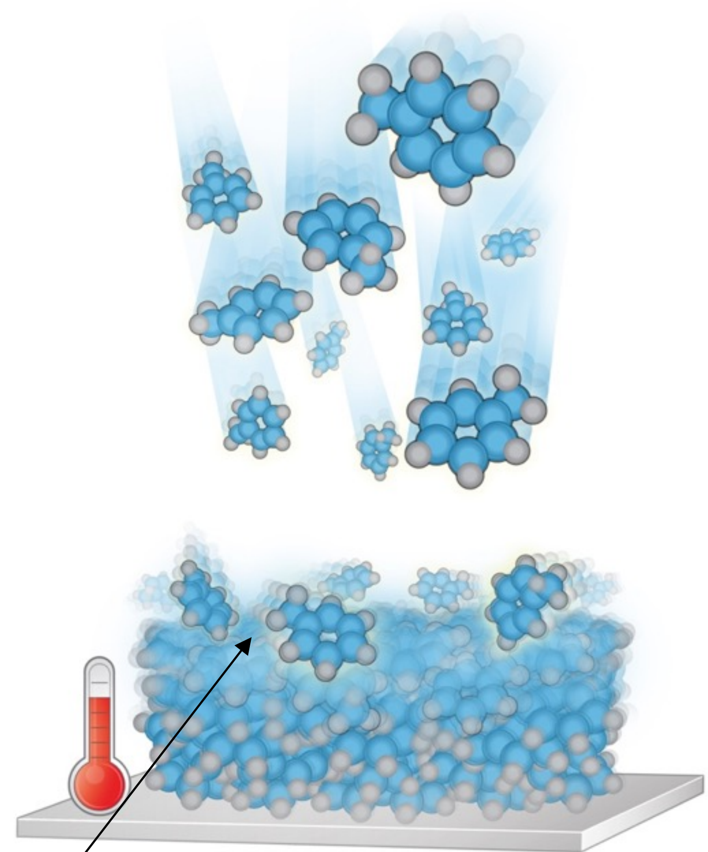
PVD silicon shows an even more dramatic reduction in two-level systems (Hellman)



Also see Queen et al., PRL 110, 135901 (2013)

Where does PVD glass structure come from?

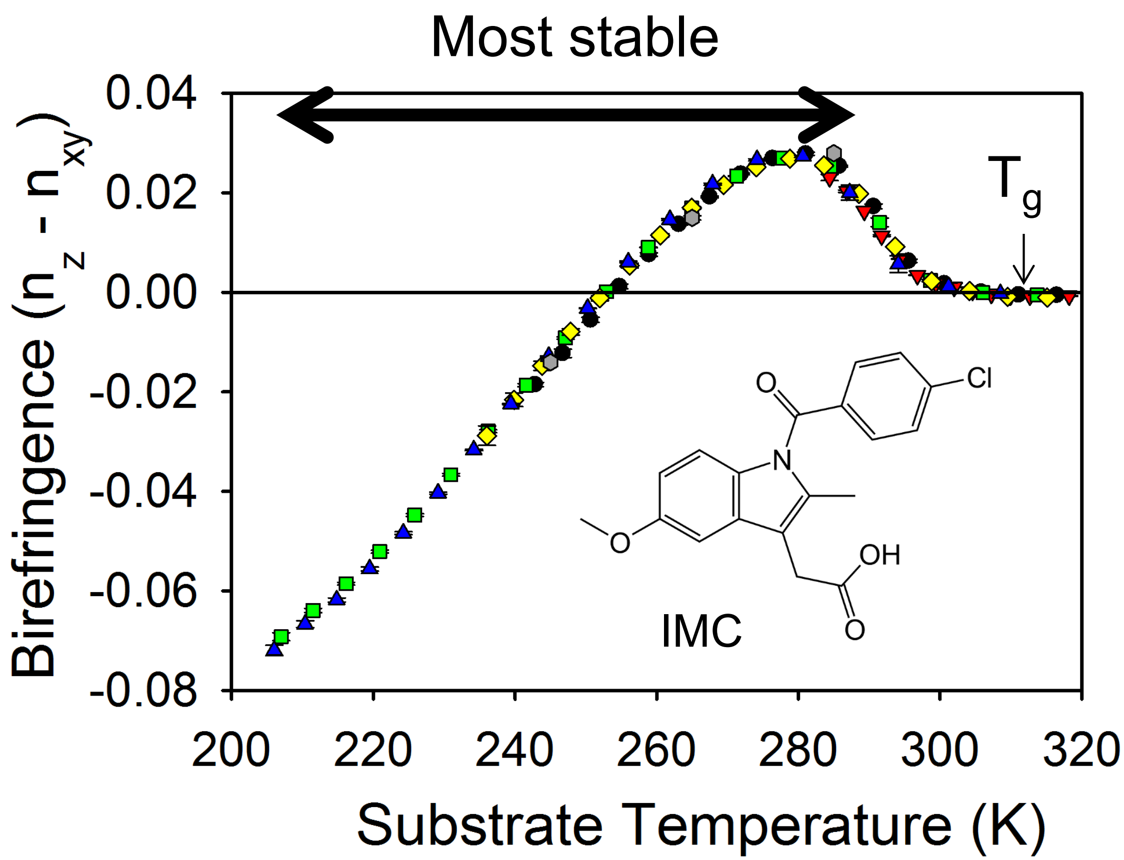


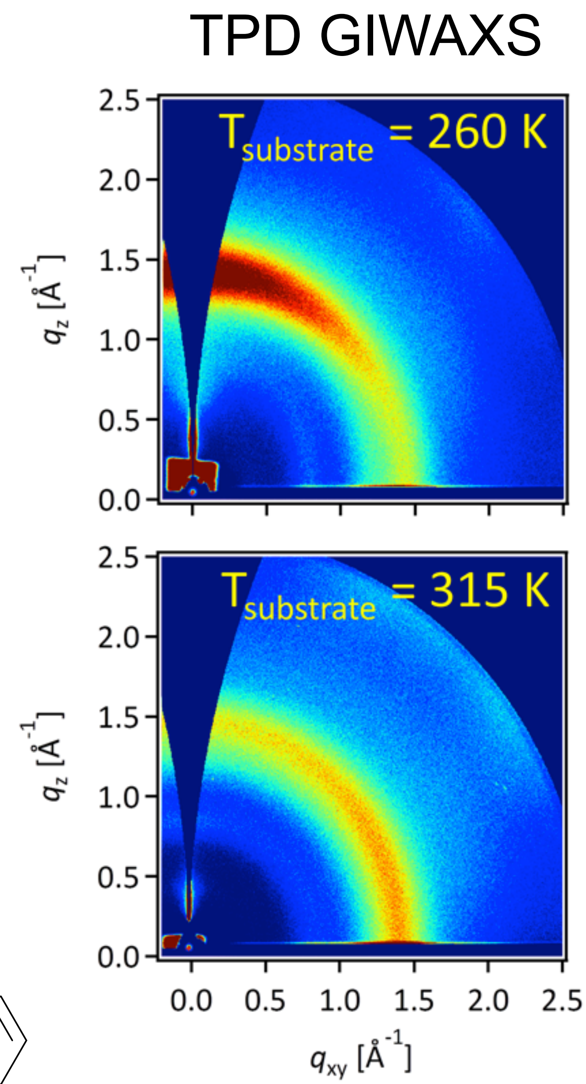


from the liquid

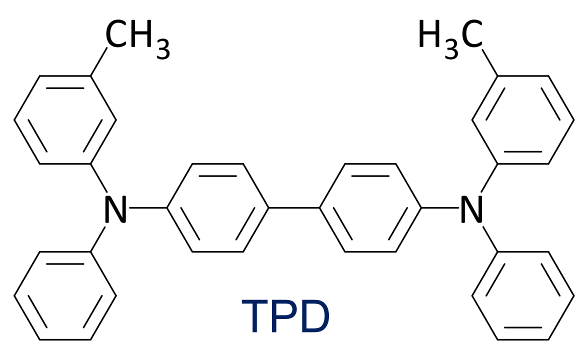
from the interface

Anisotropic interface => anisotropic glass



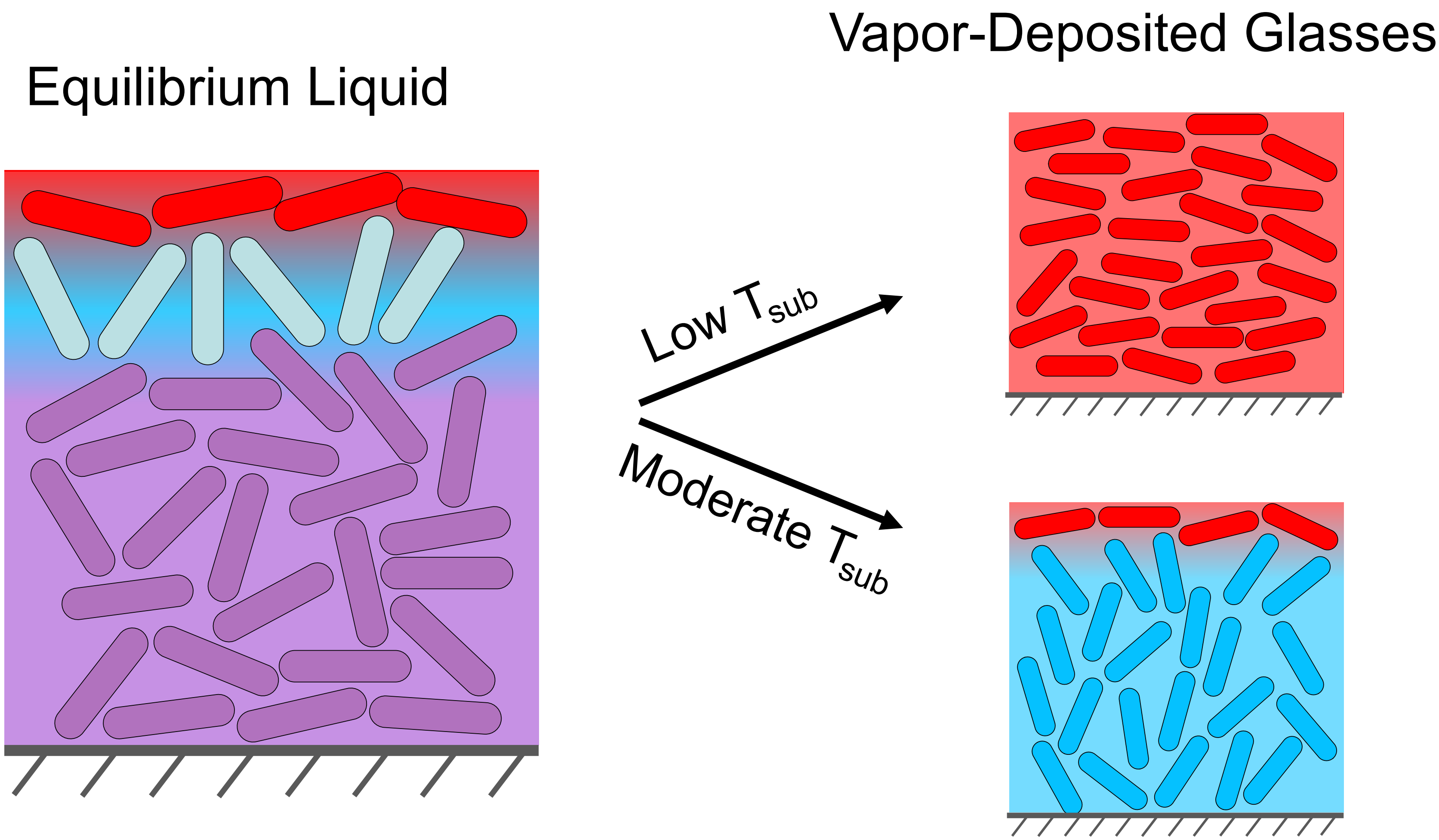


Dalal et al., JPCB (2013)



Gujral et al., Chem. Materials (2015)

Structure of PVD glasses is inherited from the structure of the surface of the equilibrium liquid



Dalal. et al., PNAS (2015)