Glasses and Metastable States

Last time

Kinetics of phase transitions

Today

Glasses and metastable states

Next time

New lecturer!

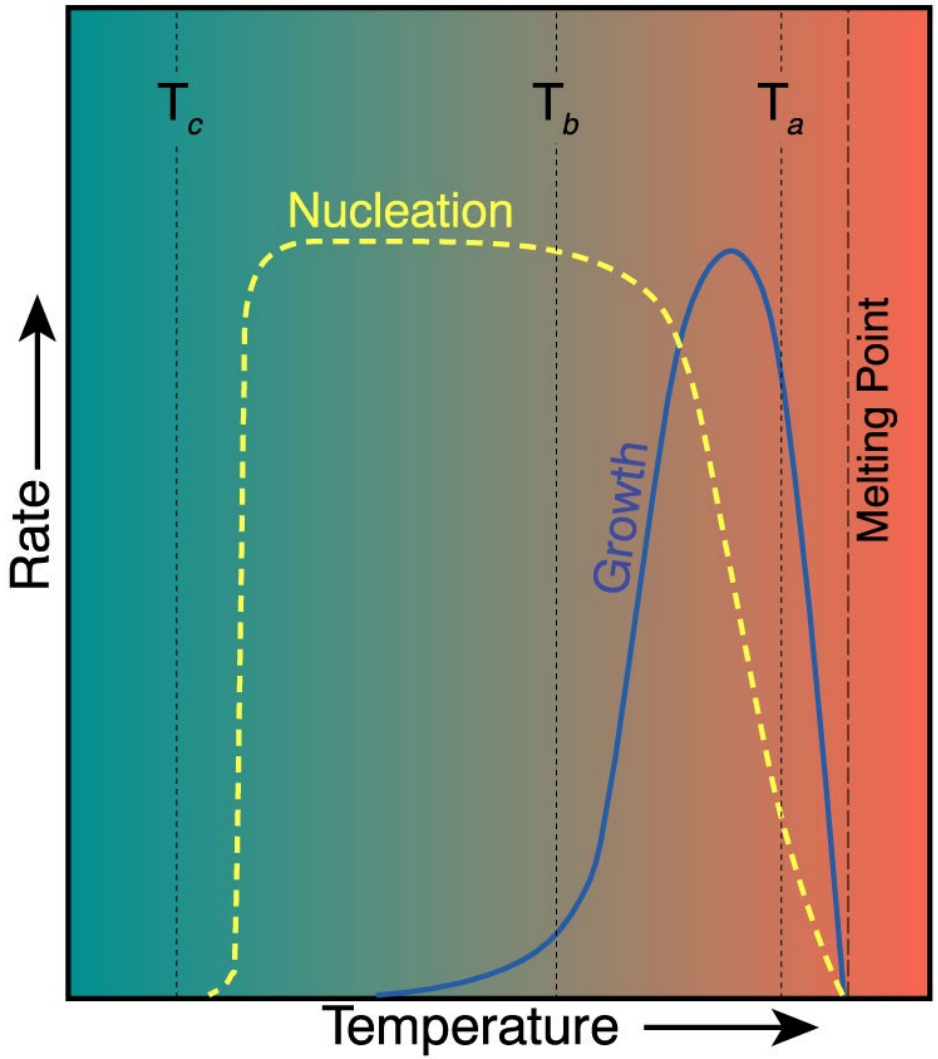
Soft matter

Last time: Nucleation and growth

Last time, we studied the kinetics of phase transitions, i.e., their mechanisms and the speed

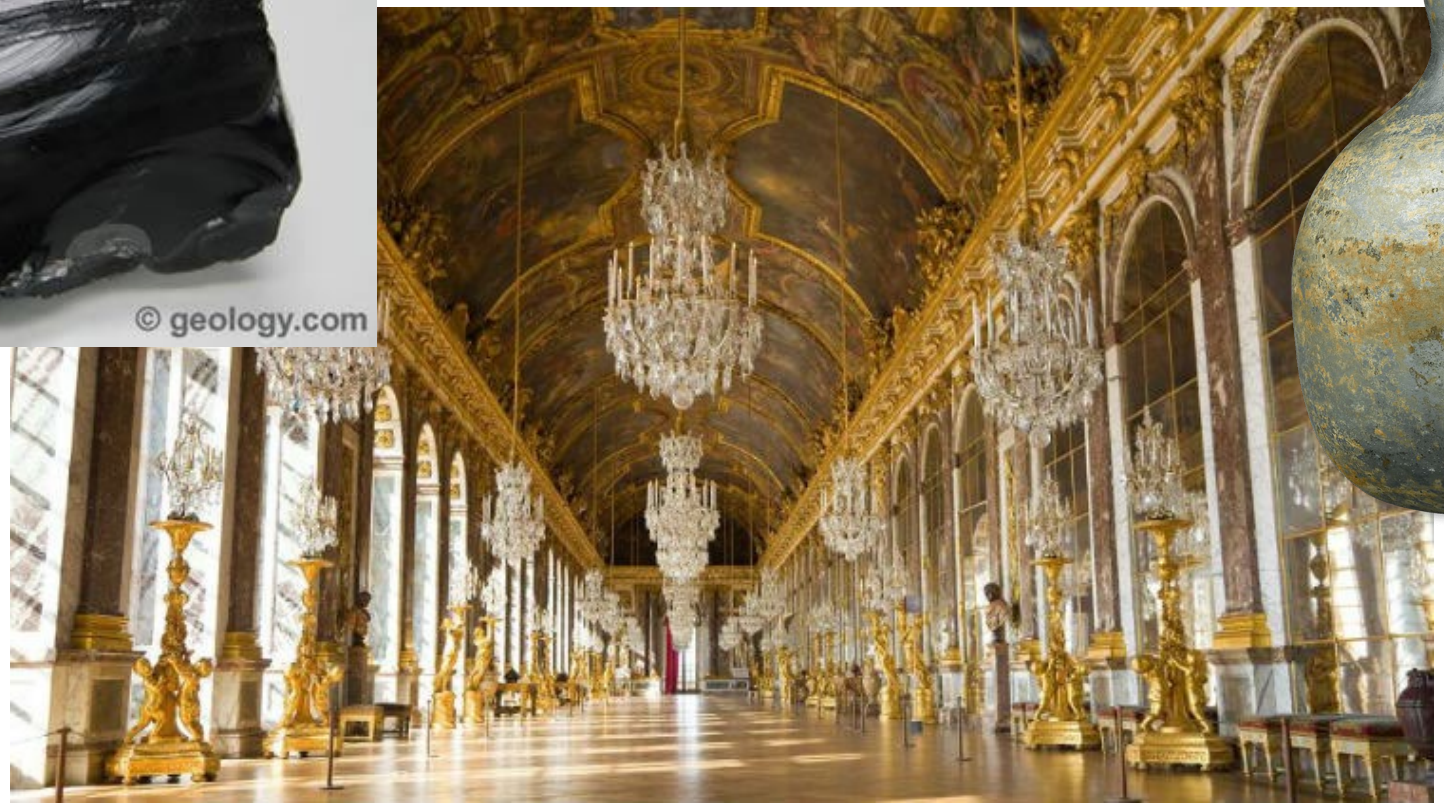
The most important mechanism—nucleation and growth—has a complicated temperature dependence

Today we'll look at what happens when deep undercooling prevents nucleation and growth altogether



Glass has been around for a long time

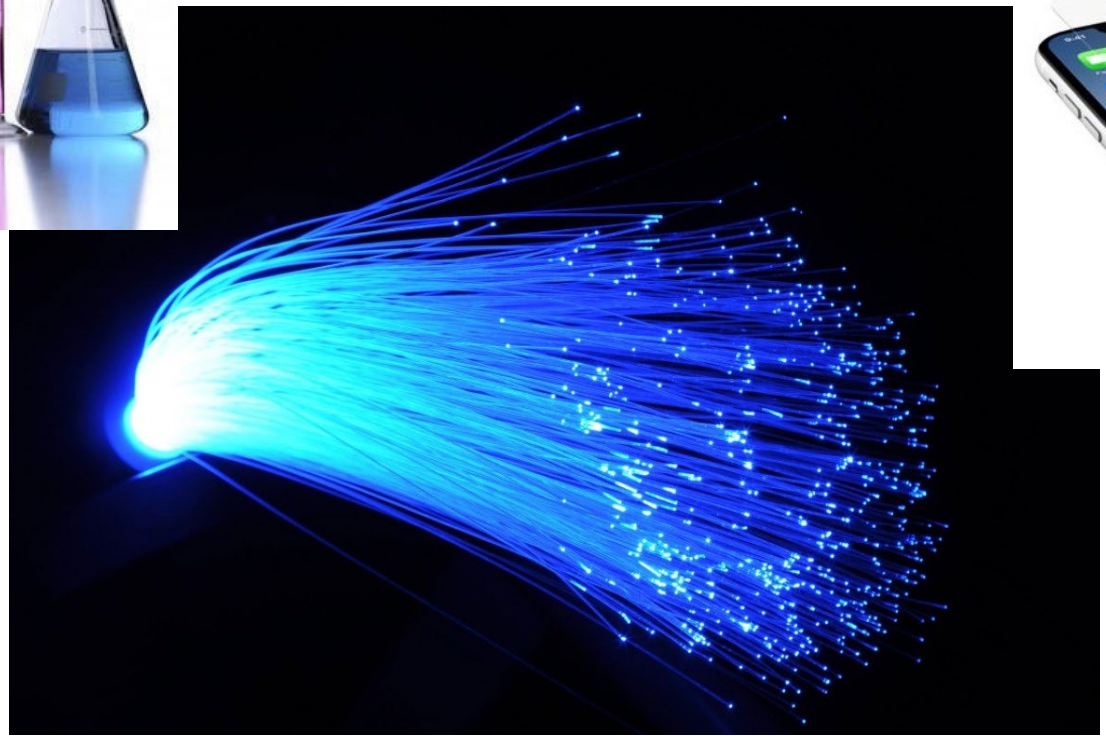






Glass is central to science and technology







The glass problem

"The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition."

P.W. Anderson, *Science* (1995)

Mentimeter

Does glass flow in windowpanes?

Once solidified, window glass does not flow on the scale of millions of years.

- In some cathedrals, there are panes with the thicker end on top, due to worker mistakes.
- Ancient Egyptian and Roman glass bowls are not found to be sagging.
- Flow of glass could be observed interferometrically. An old camera would get a distorted image after just a few decades, let alone LIGO.
- The viscosity of glass is a billion times more than the lead that holds the pieces in place.



So glasses are solids?

It's complicated…

Glasses are usually considered to be solids because they do not flow appreciably on very long time scales

But the line is not clear cut, and it is possible to measure the viscosity of glasses

Pitch

The world's longest-running experiment is the Pitch Drop Experiment at the University of Queensland

Pitch was melted and placed in a funnel in 1927; there have been 9 drops since

This works out to a viscosity of ~10^{8} Pa·s
Compare: Water: 10^{-4} Pa·s, Ketchup: 10 Pa·s





Fused silica glass

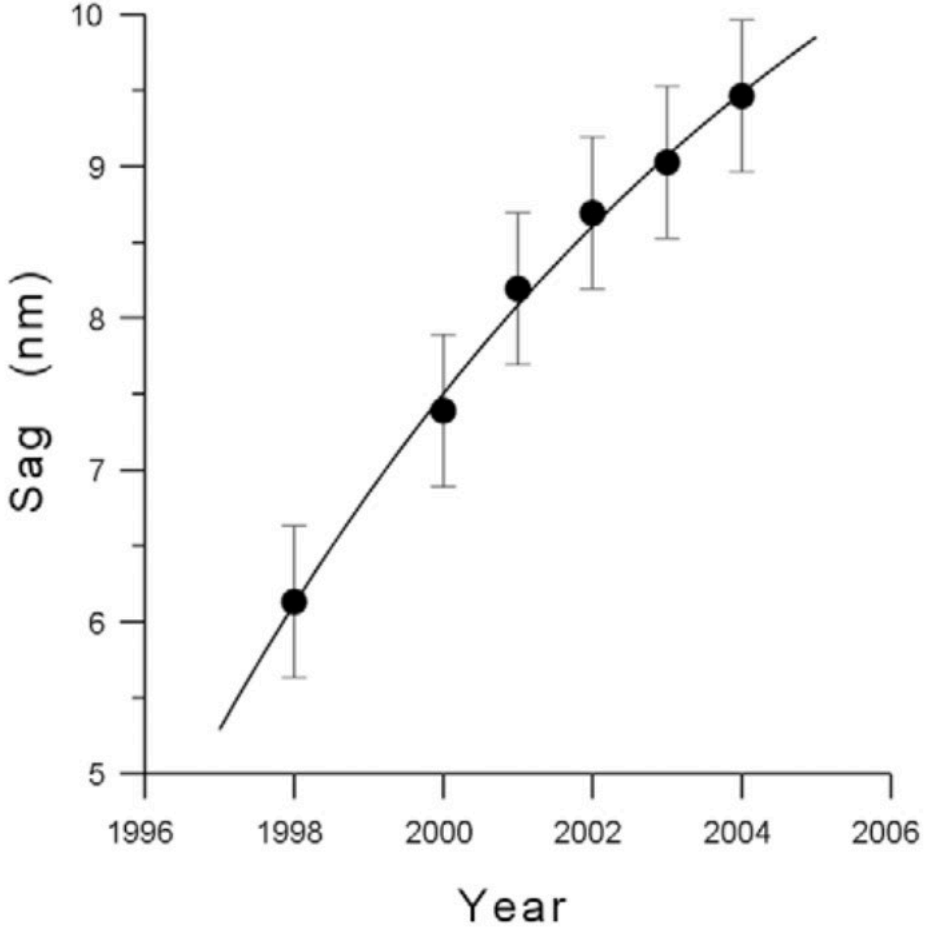
The viscosity of fused silica glass has been reported at around ~10^{18} Pa·s

(Vannoni et al., *Eur. Phys. J. E* (2011) 34: 92)

This corresponds to a sag of less than 1 nm per year in a glass plate 15 cm across

Compare: glacier ice (a polycrystalline solid) flows with viscosity of ~10^{12} Pa·s

Whether this makes glass a liquid depends on where you draw the line



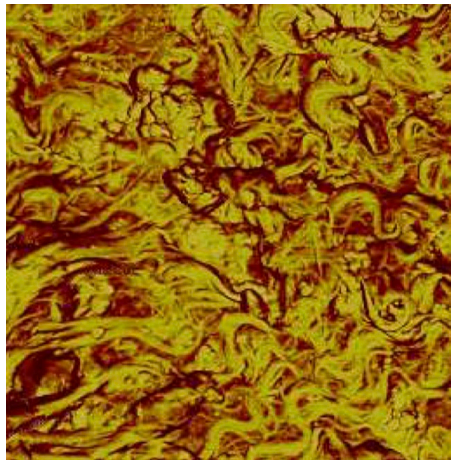
What is glass?

Old books tend to define glass as any amorphous/disordered material, i.e., any material without the long-range translational order of crystals.

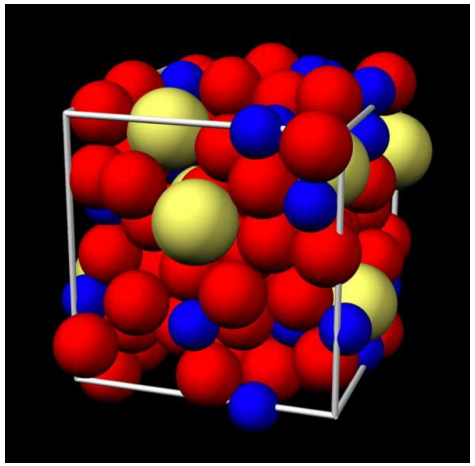
Ionic/covalent glasses
(e.g. SiO_2)



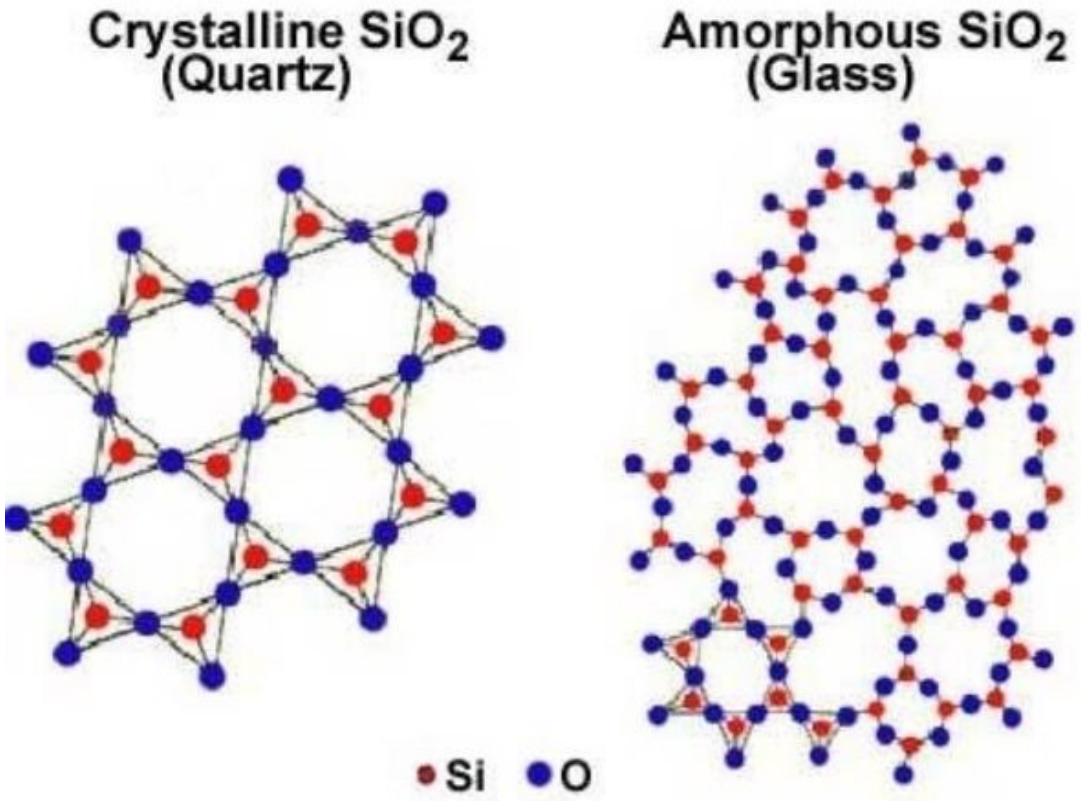
Polymeric glasses
(e.g. PMMA)

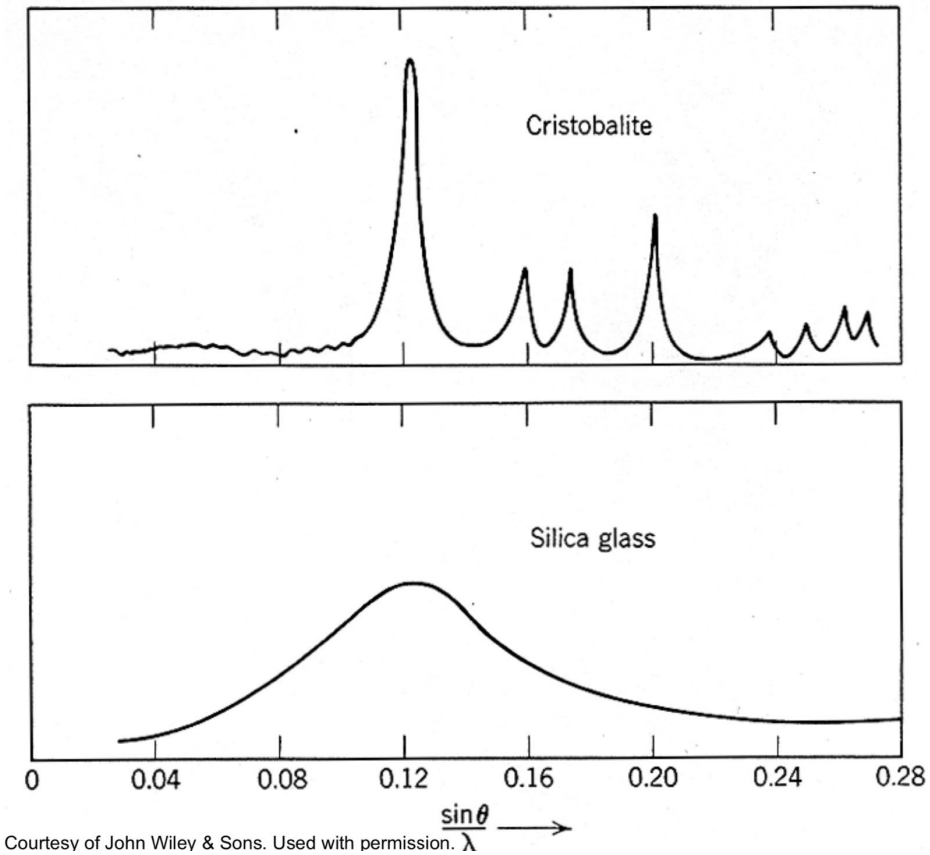


Metalic glasses
(e.g. Zr-Ti-Cu-Ni-Be)



Example: silica glass





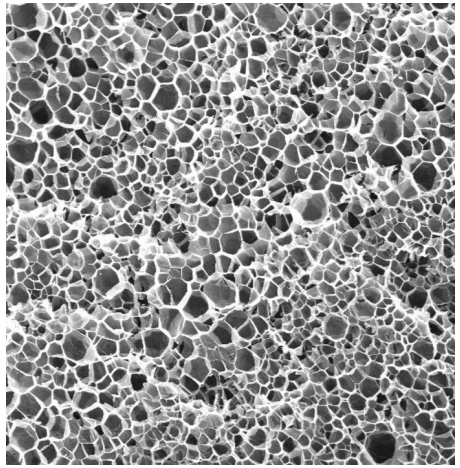
Courtesy of John Wiley & Sons. Used with permission.

What is glass?

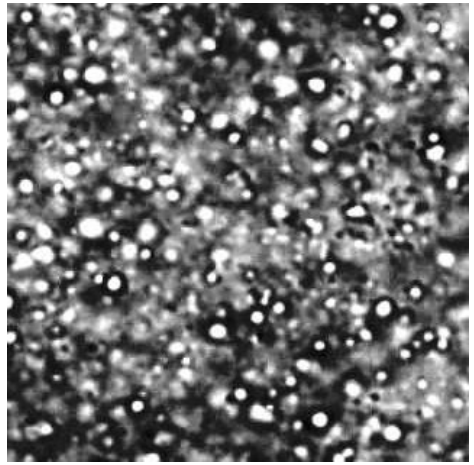
Old books tend to define glass as any amorphous/disordered material

This definition is too broad.

Also includes wood, foams, granular materials, and colloids







What is glass?

Modern definition:

Glass is an amorphous solid that exhibits a glass transition.

The glass transition is the gradual and reversible transition between the brittle glassy state and the liquid state as the temperature is increased.

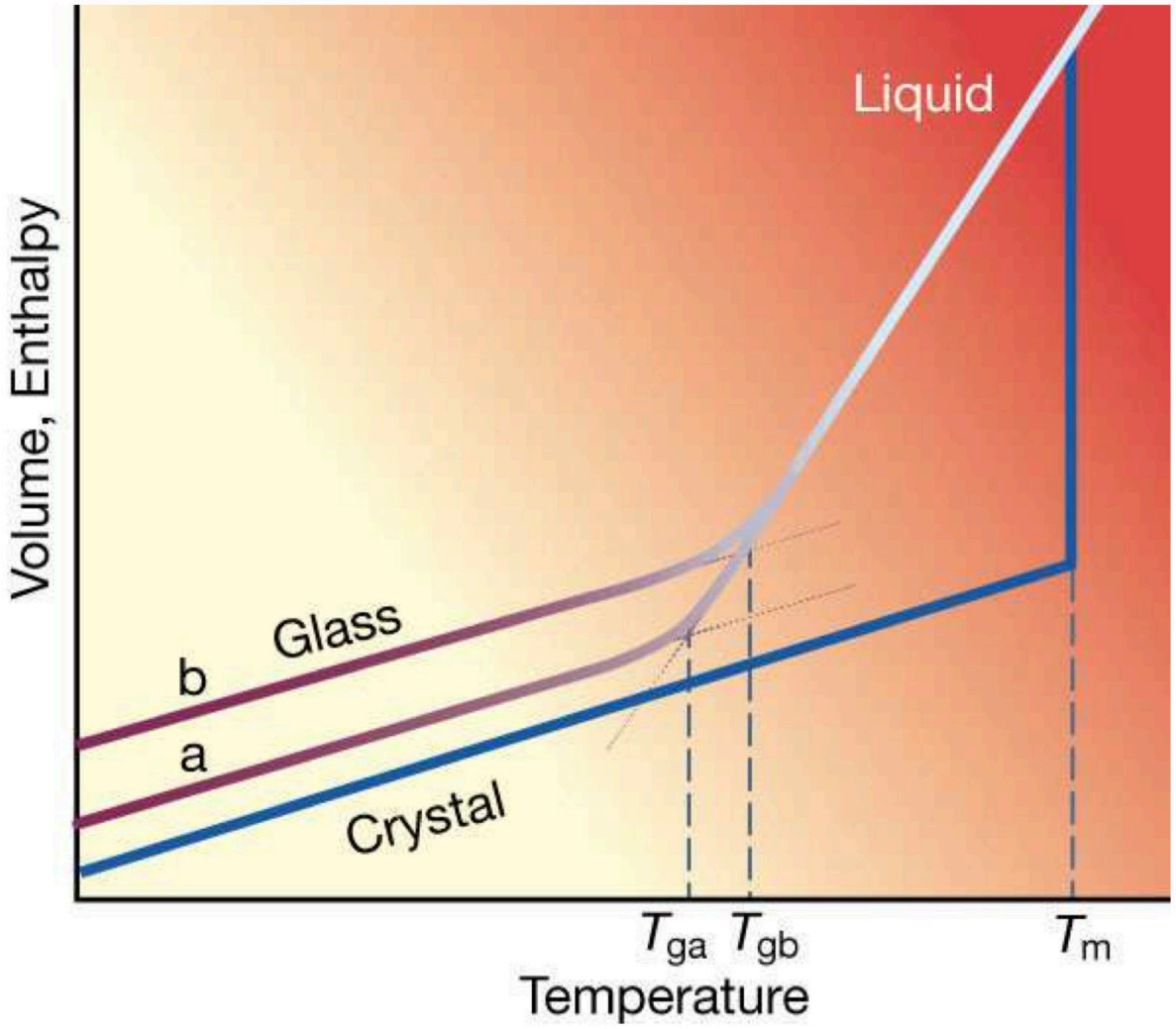


Glass transition temperature

The glass transition temperature is not precisely defined

It is a range, depending on whether the glass is cooled slowly (a) or quickly (b).

T_g is always less than the melting point T_m of the crystal.



Mentimeter

Glass transition temperature examples

Material	T_g (°C)
Tyre rubber	-70
Polypropylene (PP)	-10
Polyvinyl chloride (PVC)	80
Polystyrene	95
Polycarbonate	145
Chalcogenide GeSbTe	150
Cotton	230
Soda-lime glass	500
Fused quartz	1200





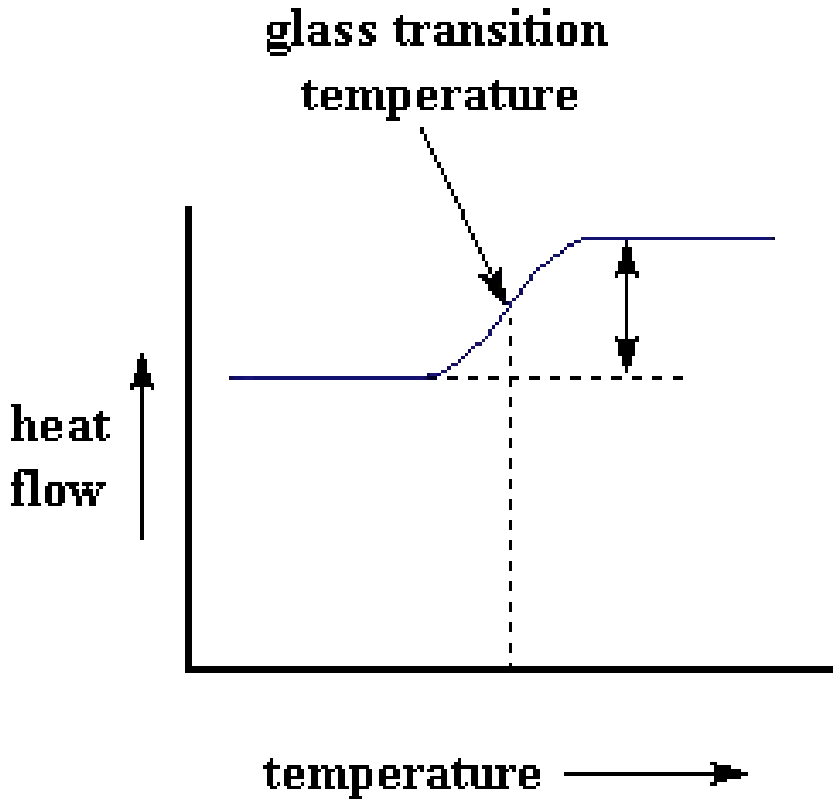




Calorimetry of the glass transition

Differential scanning calorimetry reveals several features of the glass transition:

- Different heat capacities in the liquid and the glass
- A *gradual* transition between the two states



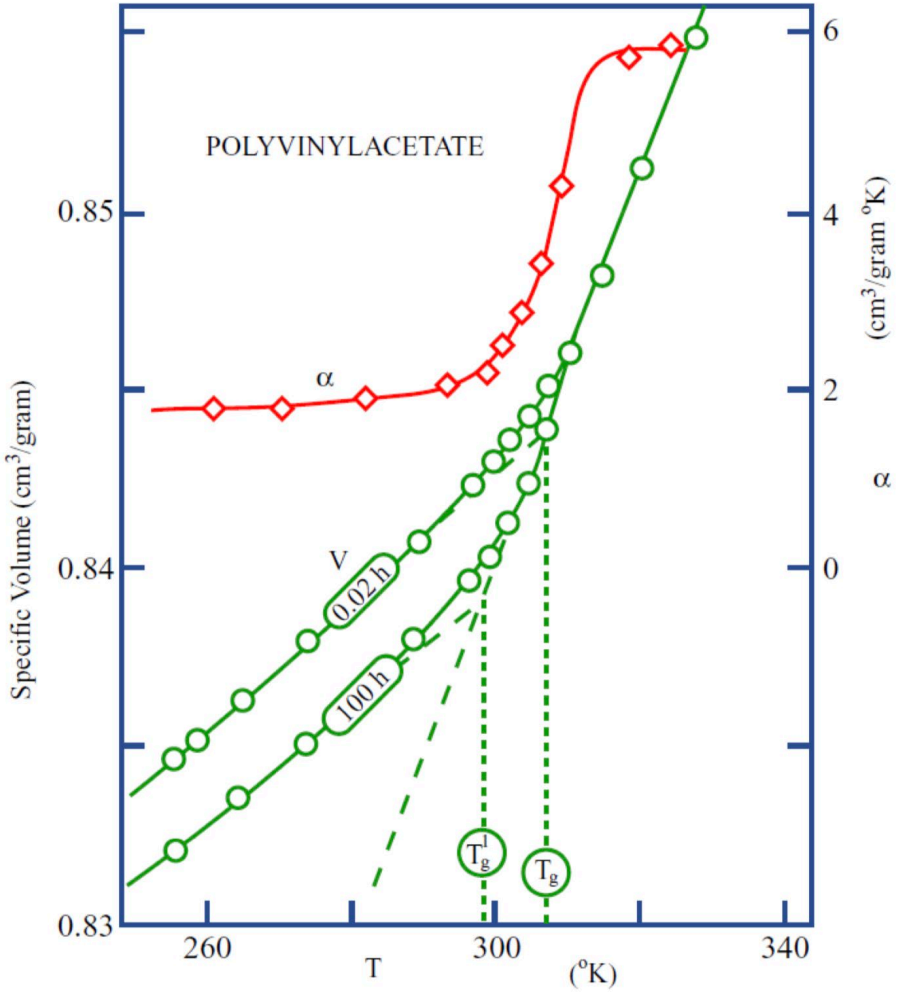
Mentimeter

Glass transition is not a phase transition

The glass transition is **not** a transition between two equilibrium states

As the liquid cools, the viscosity increases. In viscous liquids, diffusion is slow, making it difficult for the atoms to rearrange into the crystalline equilibrium state

T_g depends on the cooling rate, i.e., the glass depends on its past and thus cannot be the equilibrium state

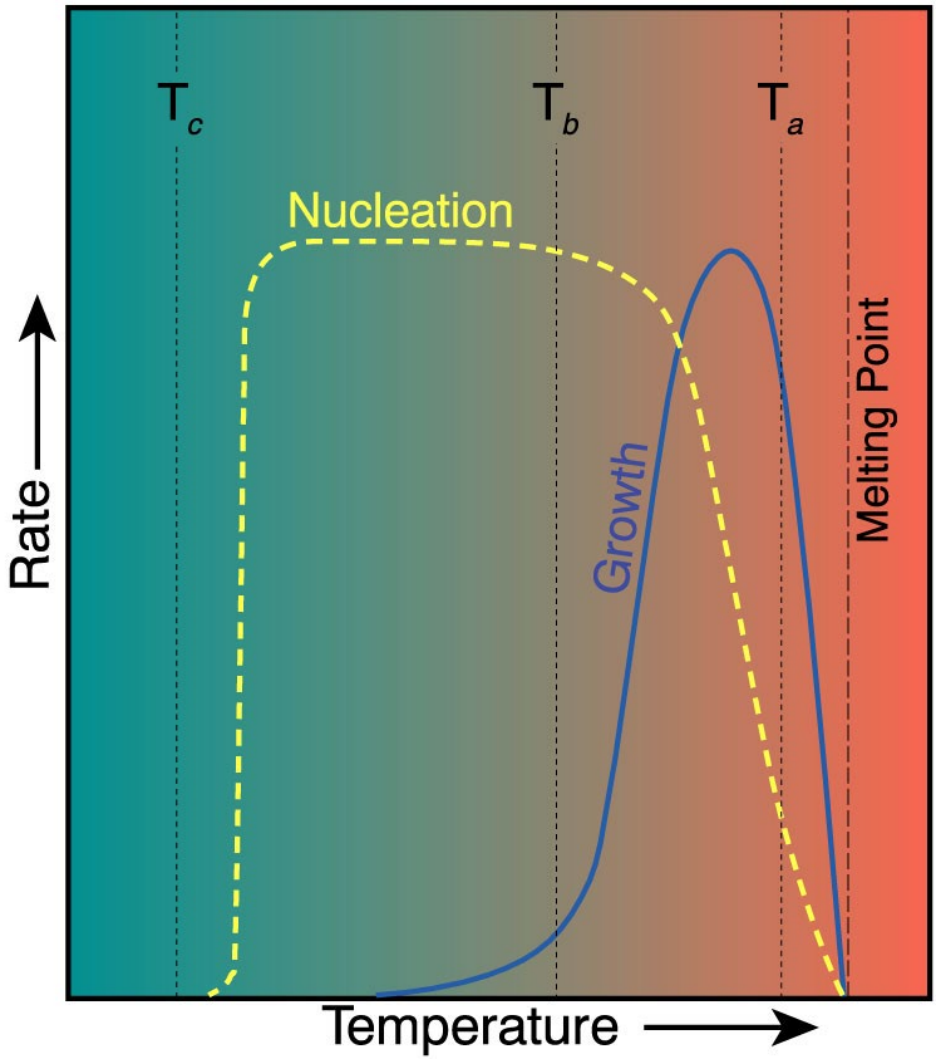


From last time: it's all about the kinetics

Very rapid cooling involves little if any nucleation or growth (T_c on the diagram), producing a glass

Glass can therefore also be described as a deeply supercooled liquid

Glass-forming substances are those where nucleation and growth are slow because high viscosity inhibits atomic/molecular diffusion (e.g., in polymers where the chains can't move past each other easily)

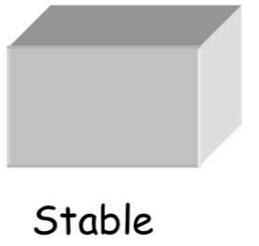


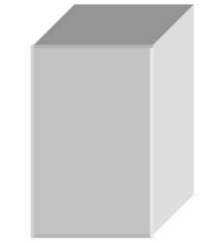
Glasses are metastable materials

Glass is a metastable material out of equilibrium, and can be thought of as frozen-in liquid-like structure

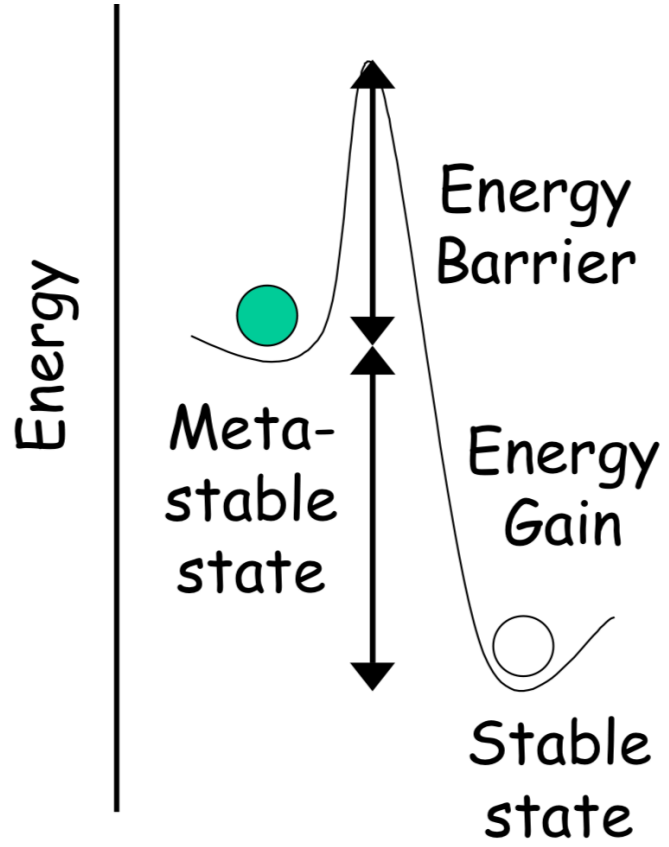
The glass transition is therefore a *kinetic* phenomenon, not a thermodynamic one

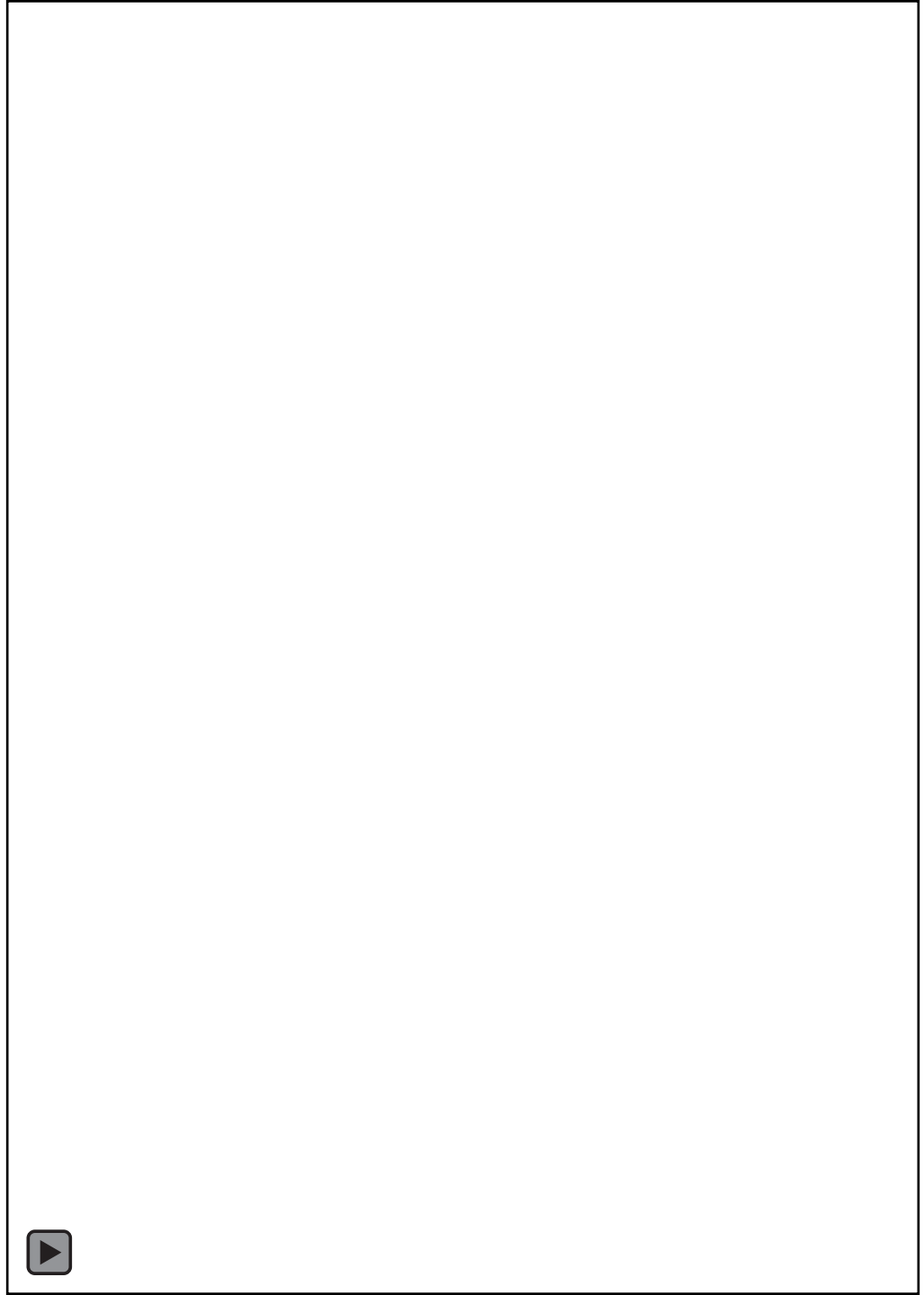
It is the temperature at which the thermal energy becomes so small that the energy barrier to crystallisation is insurmountable on any practical timescale



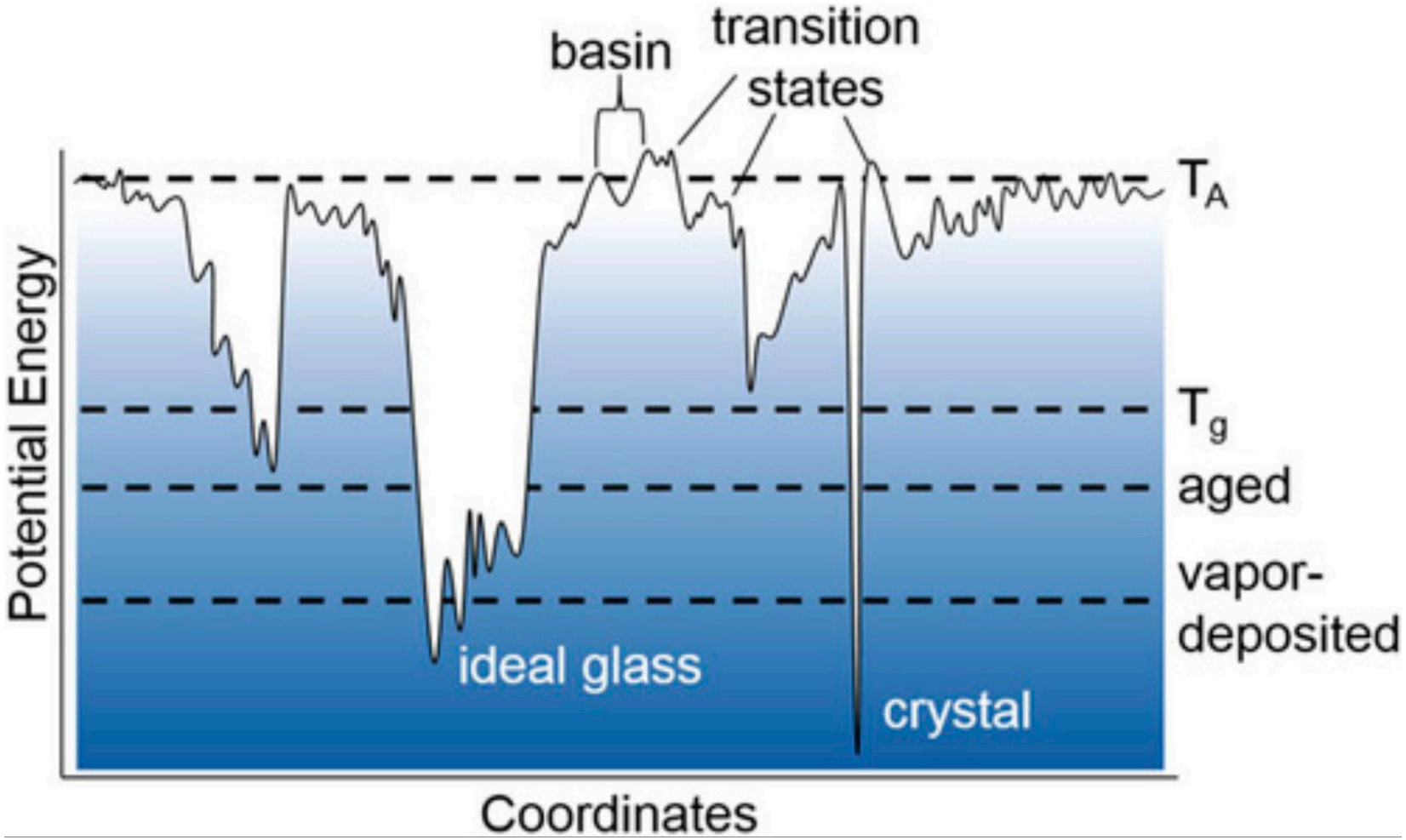




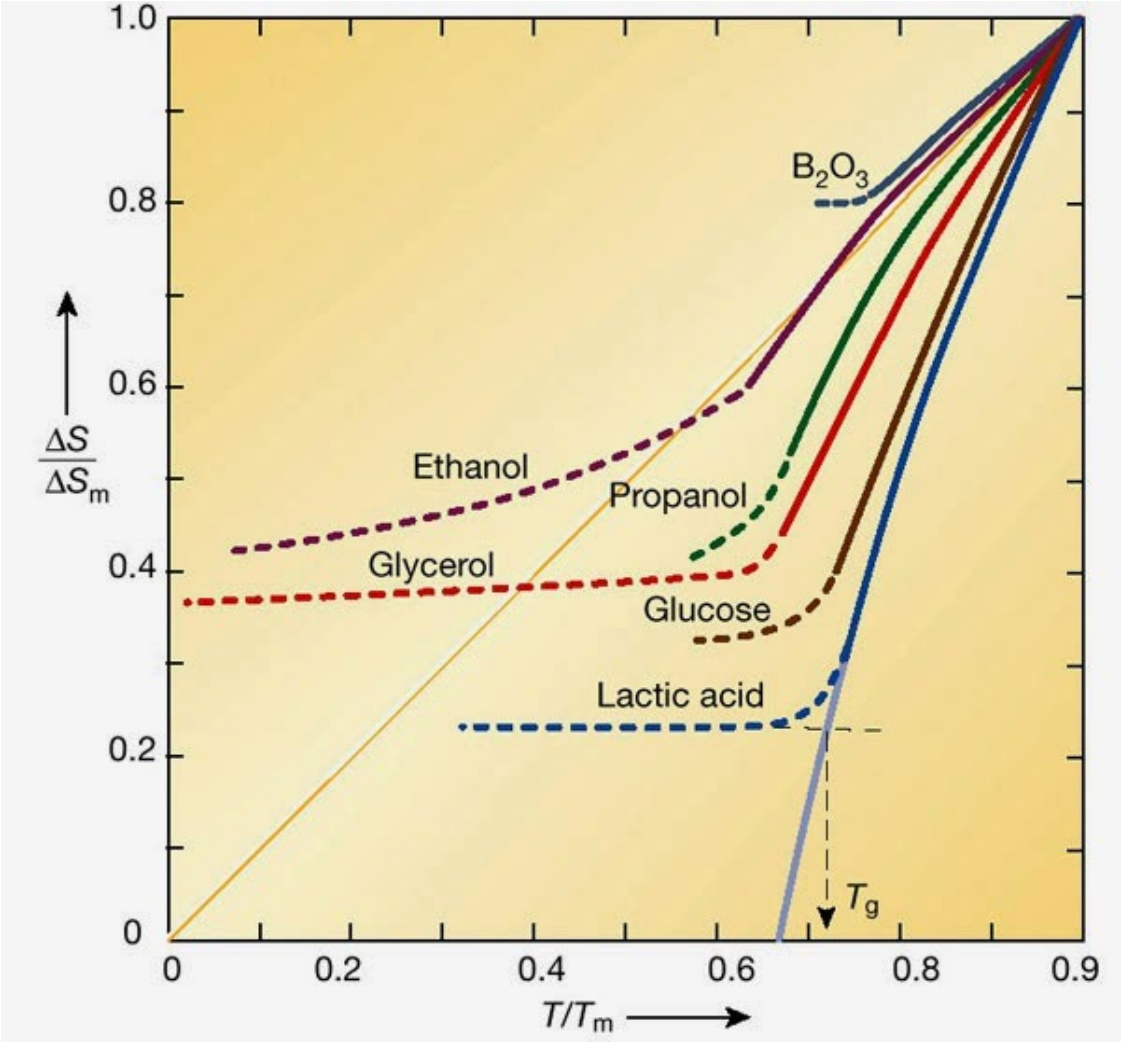




Glasses are metastable materials



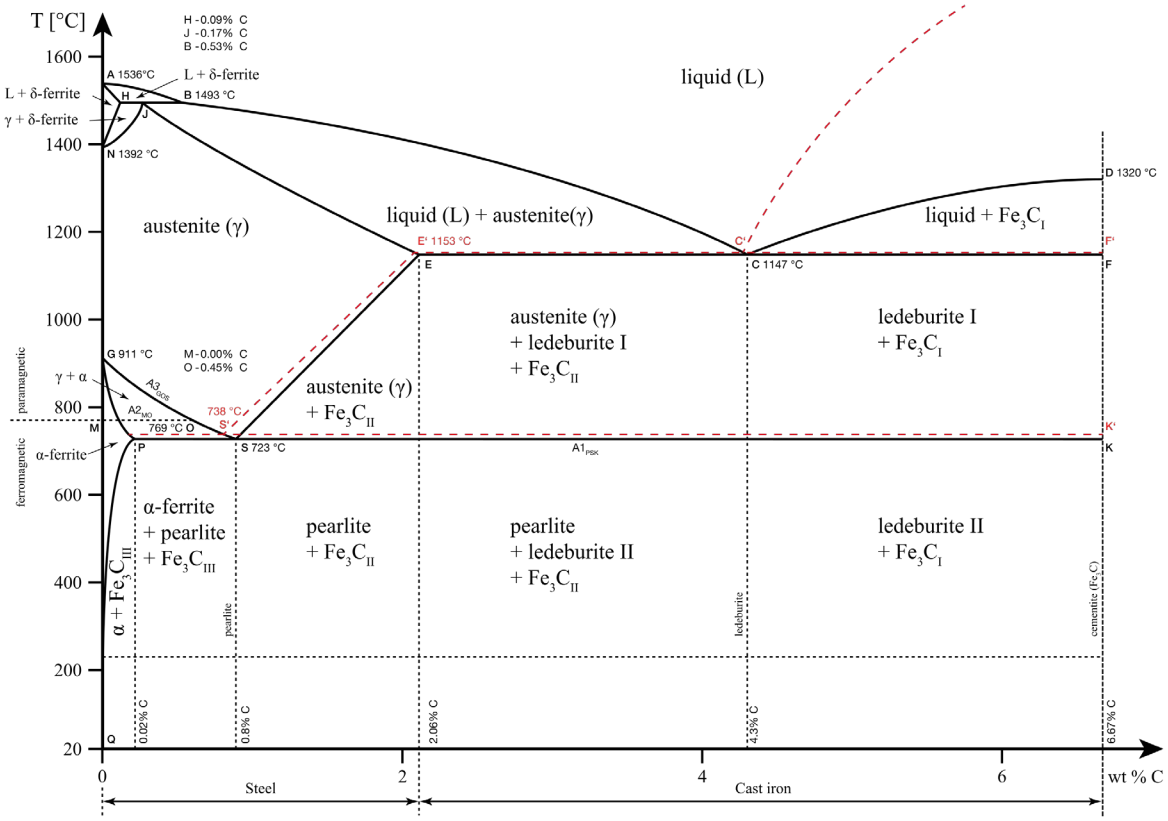
Residual entropy



Other metastable materials

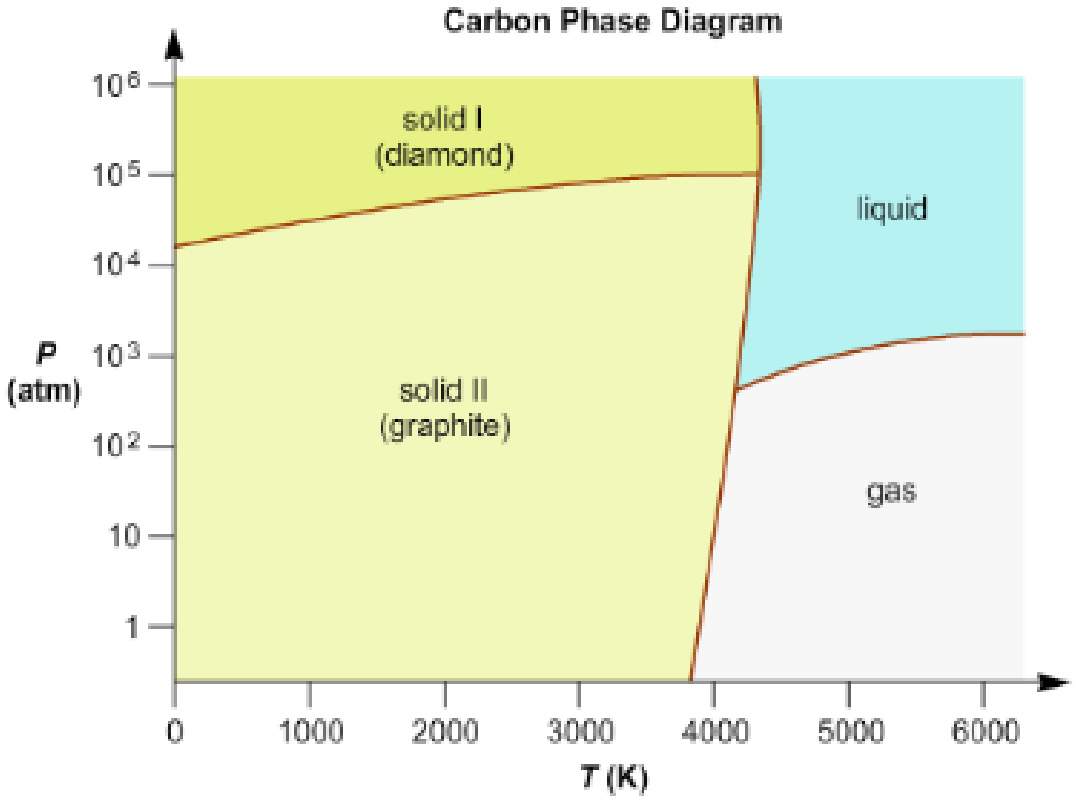
- Martensite (austenite-rich steel) with respect to normal steel (martensite is very hard, which is why steel is quench hardened)





Other metastable materials

- Diamond with respect to graphite at RTP (diamonds are *not* forever)



Other metastable materials

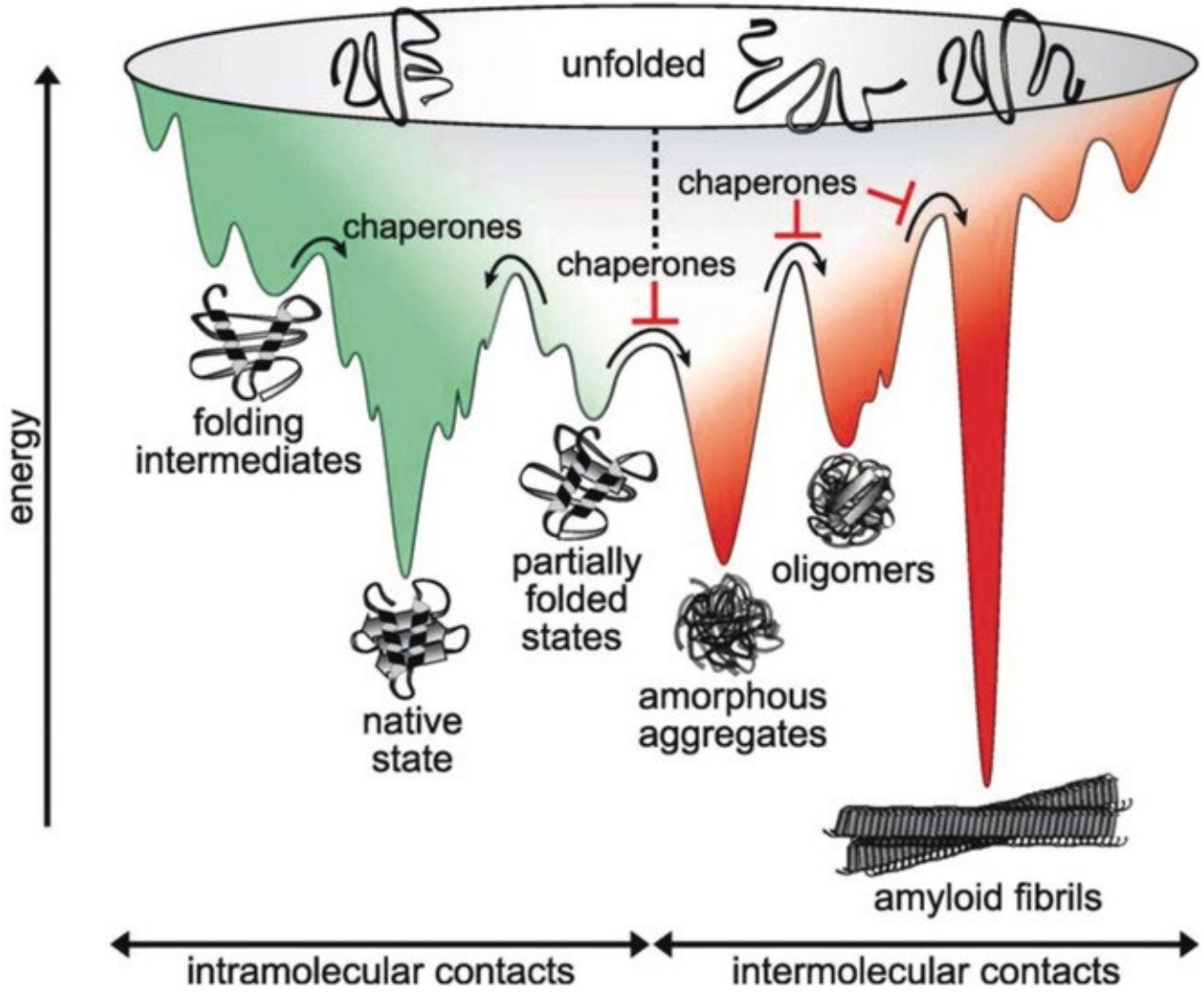
- Emulsions and colloids with respect to separated phases (including milk, mayonnaise, and espresso crema)





Other metastable materials

- Many native protein structures with respect to to amyloid fibrils
- Misfolded proteins are implicated in dozens of diseases, including Alzheimer's, Parkinson's, and prion diseases



Summary

Key points:

- Glasses are amorphous solids with a glass transition, i.e., they gradually soften to the melt
- The glass transition is *not* a phase transition
- Glasses are governed by kinetics: they are metastable non-equilibrium states, and their properties depend on their history



Next time

New lecturer!

Soft matter, liquids, surfaces…

It was great to meet you all, and if you have any questions for me, you can use Ed or email me. I will continue to be available for consultations by appointment.



A/Prof. Asaph Widmer-Cooper