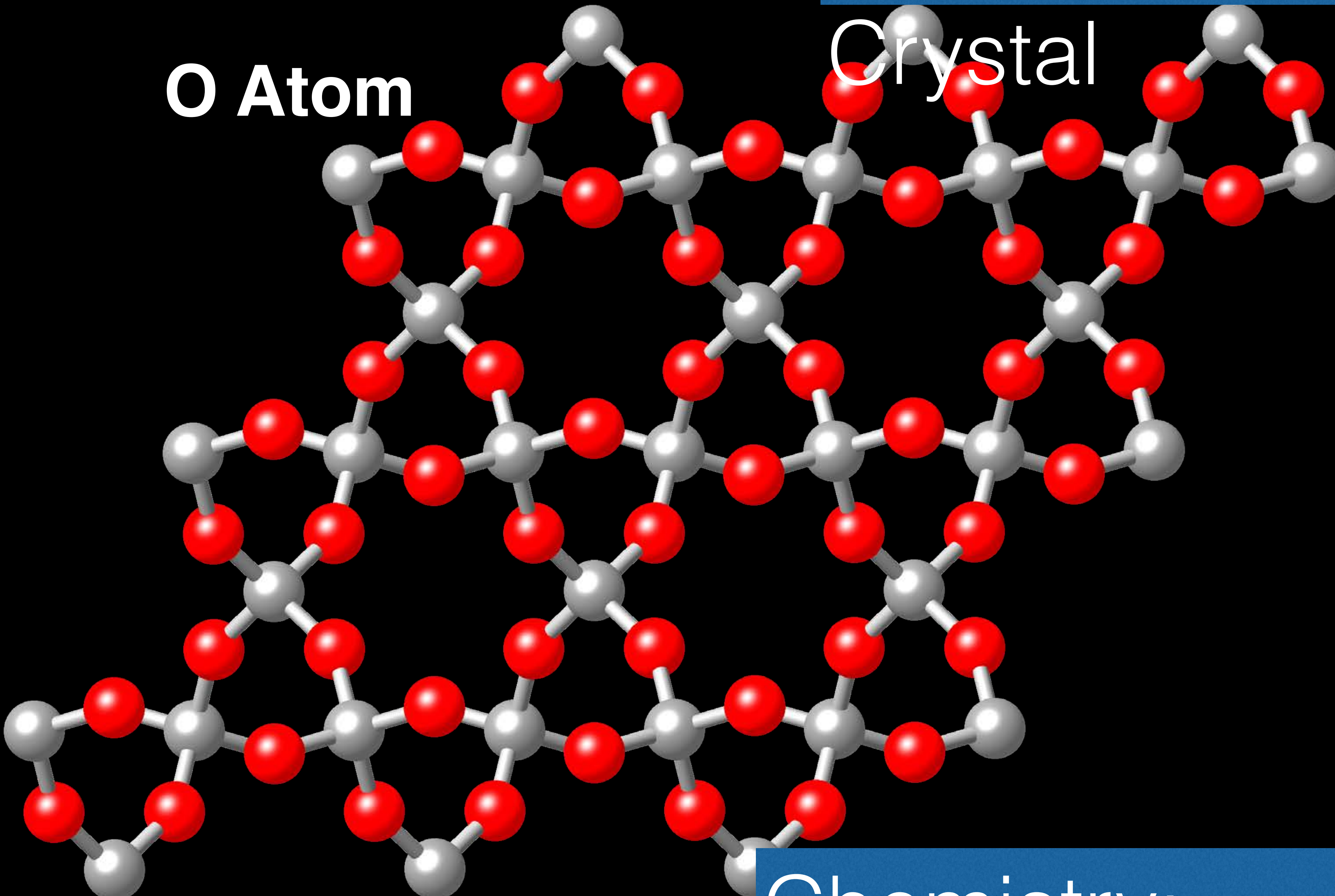
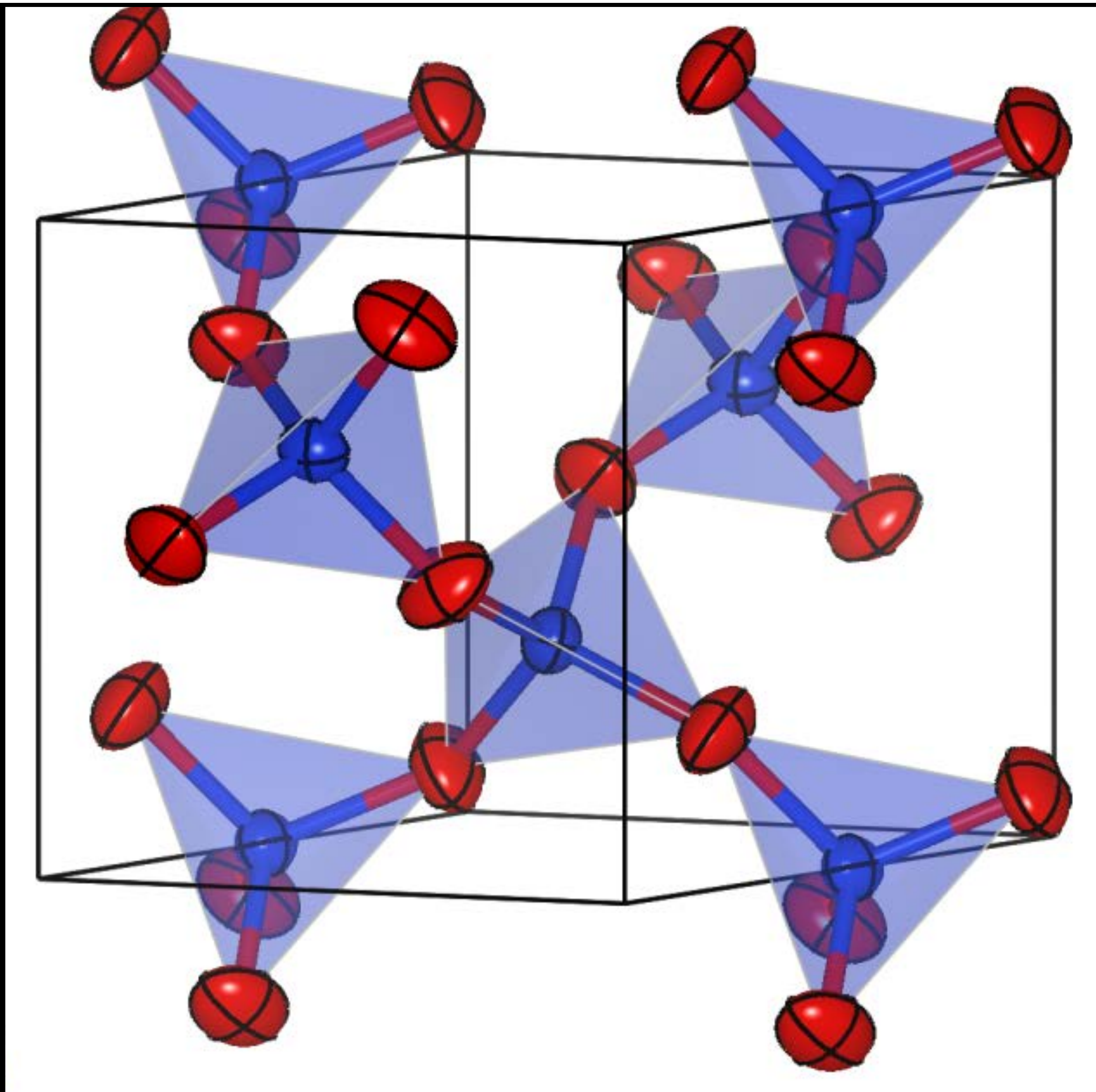
Extra Notes on Glass

Quartz Crystal

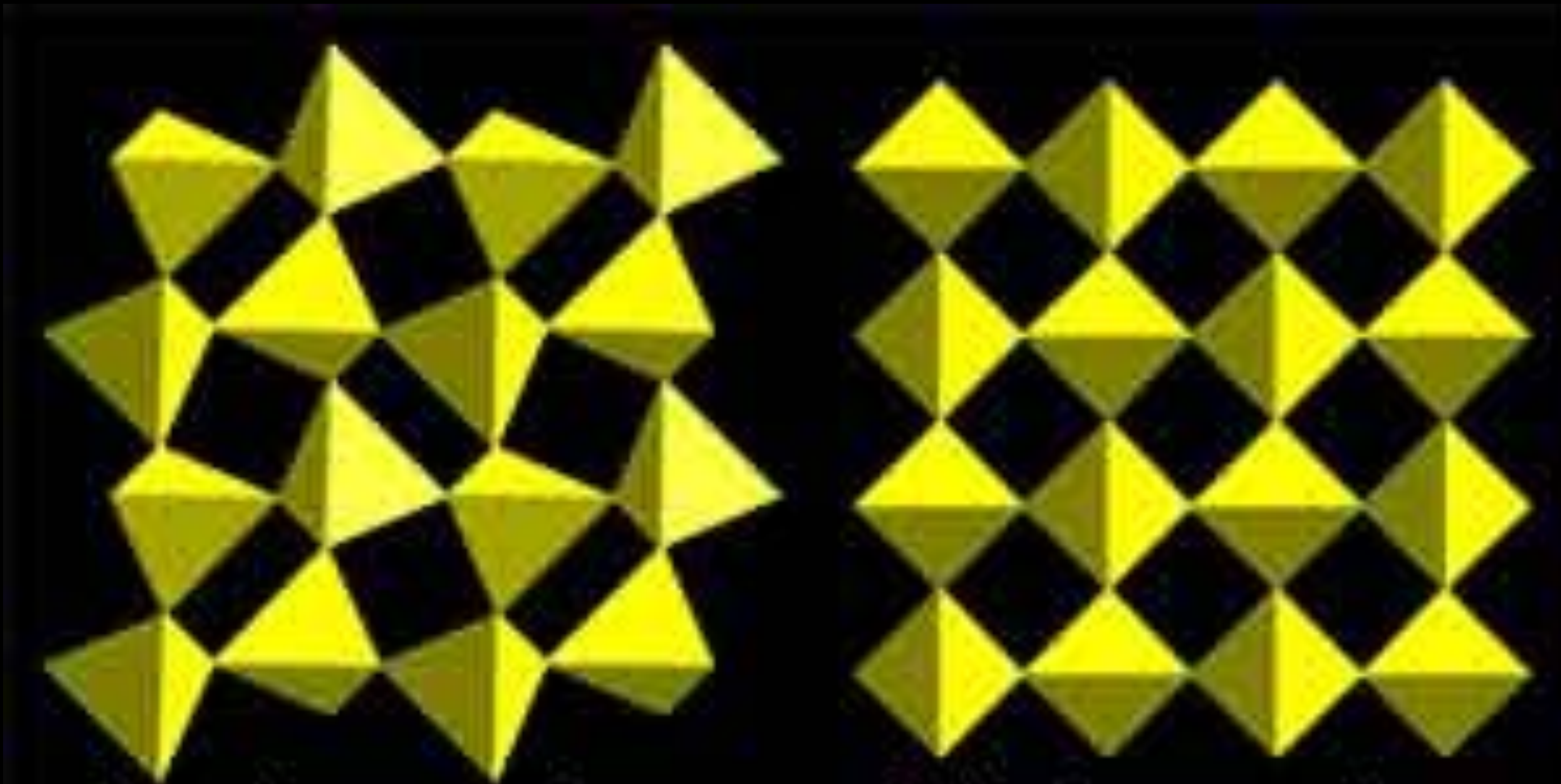


Chemistry:

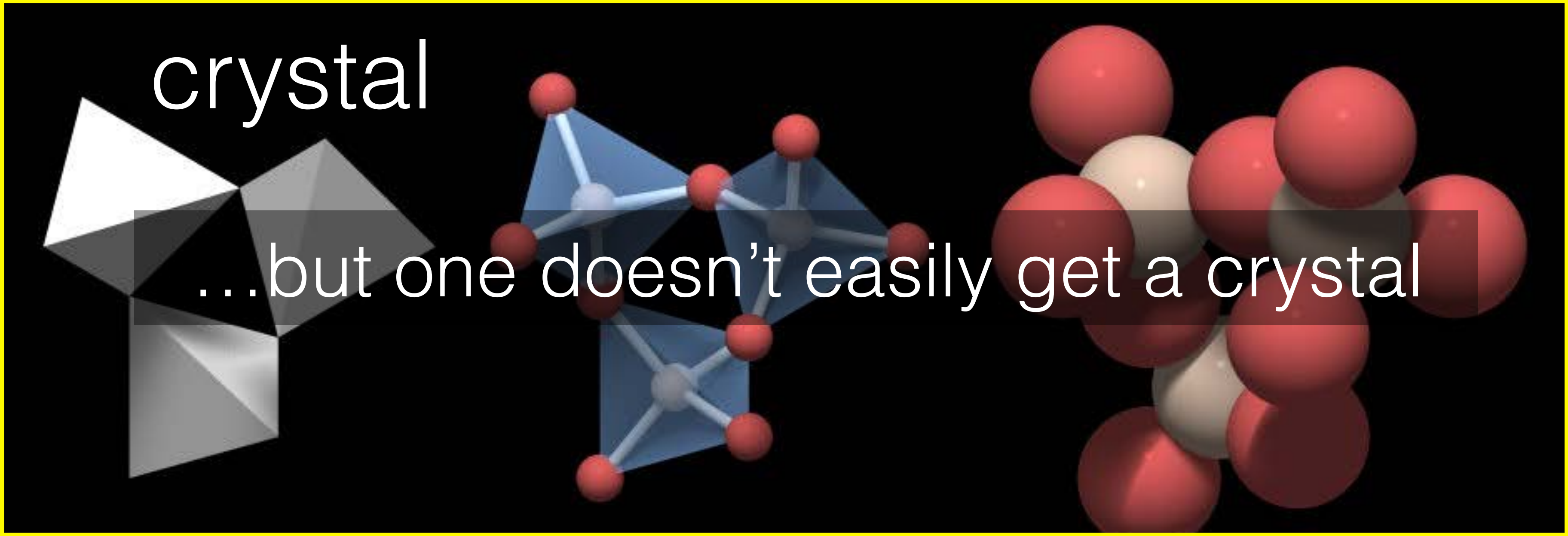


The silicate units stay intact but can rotate/distort relative to one another.

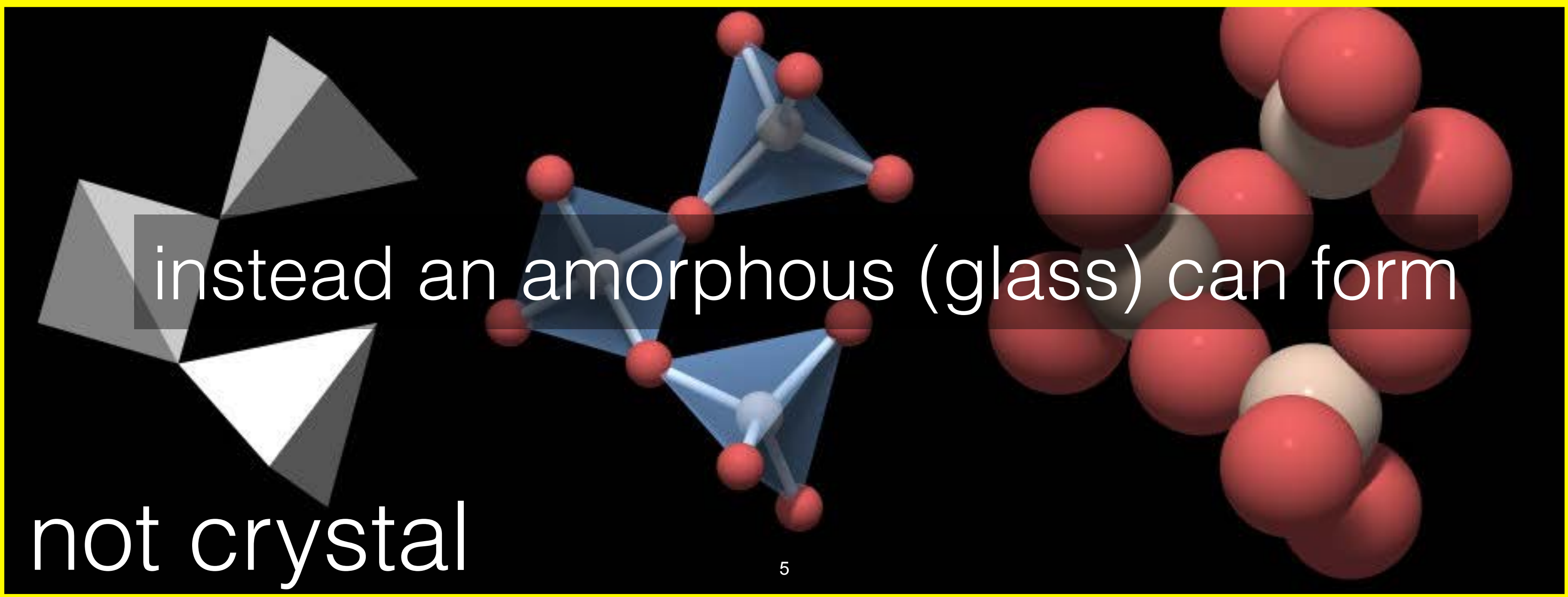
There are different crystal phases of SiO_2 that depend on temperature…



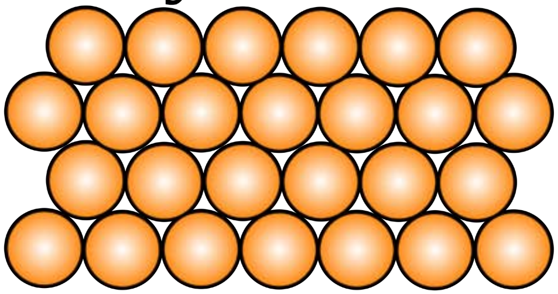
low temperature high temperature



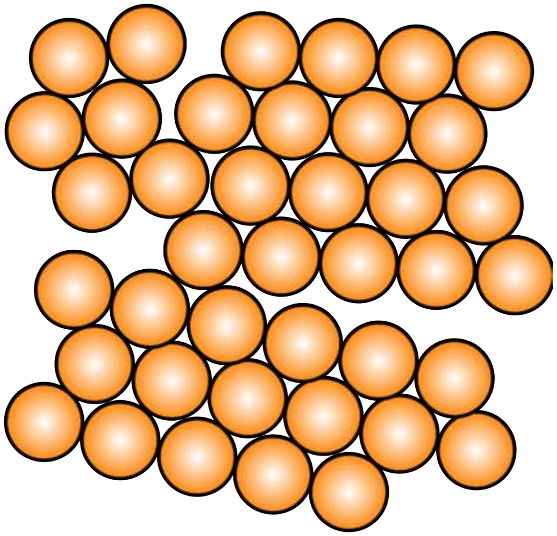
Depends on: 1) T and 2) cooling



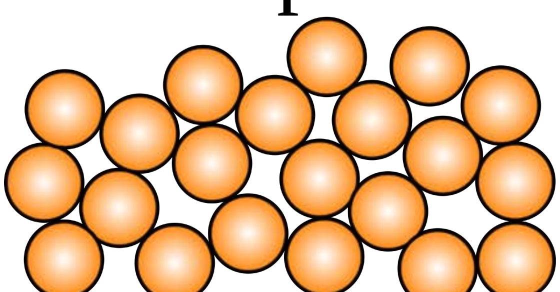
Crystalline



Polycrystalline



Amorphous

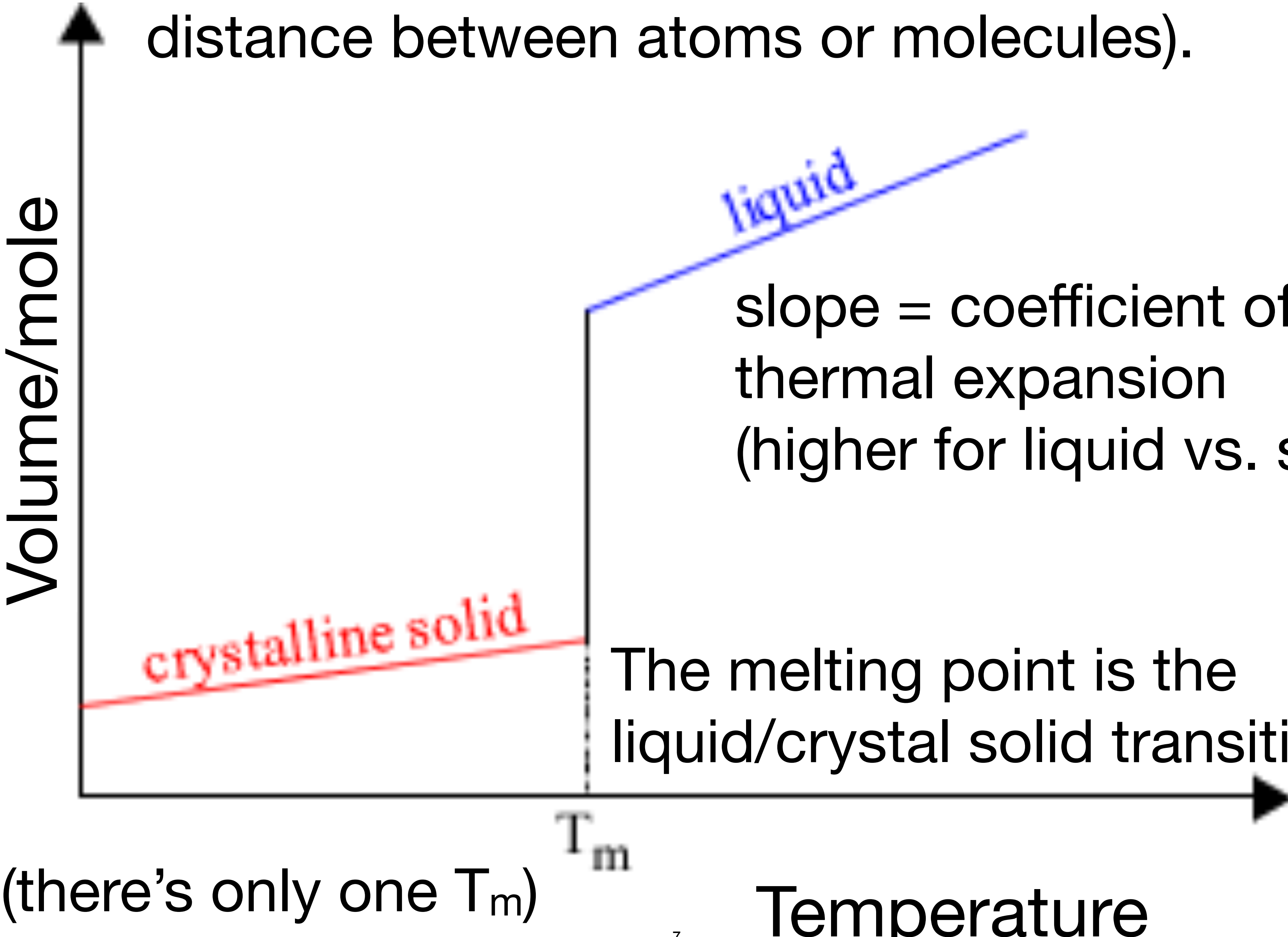


In class I made the analogy to musical chairs: silicates = people, chairs = xtal lattice sites

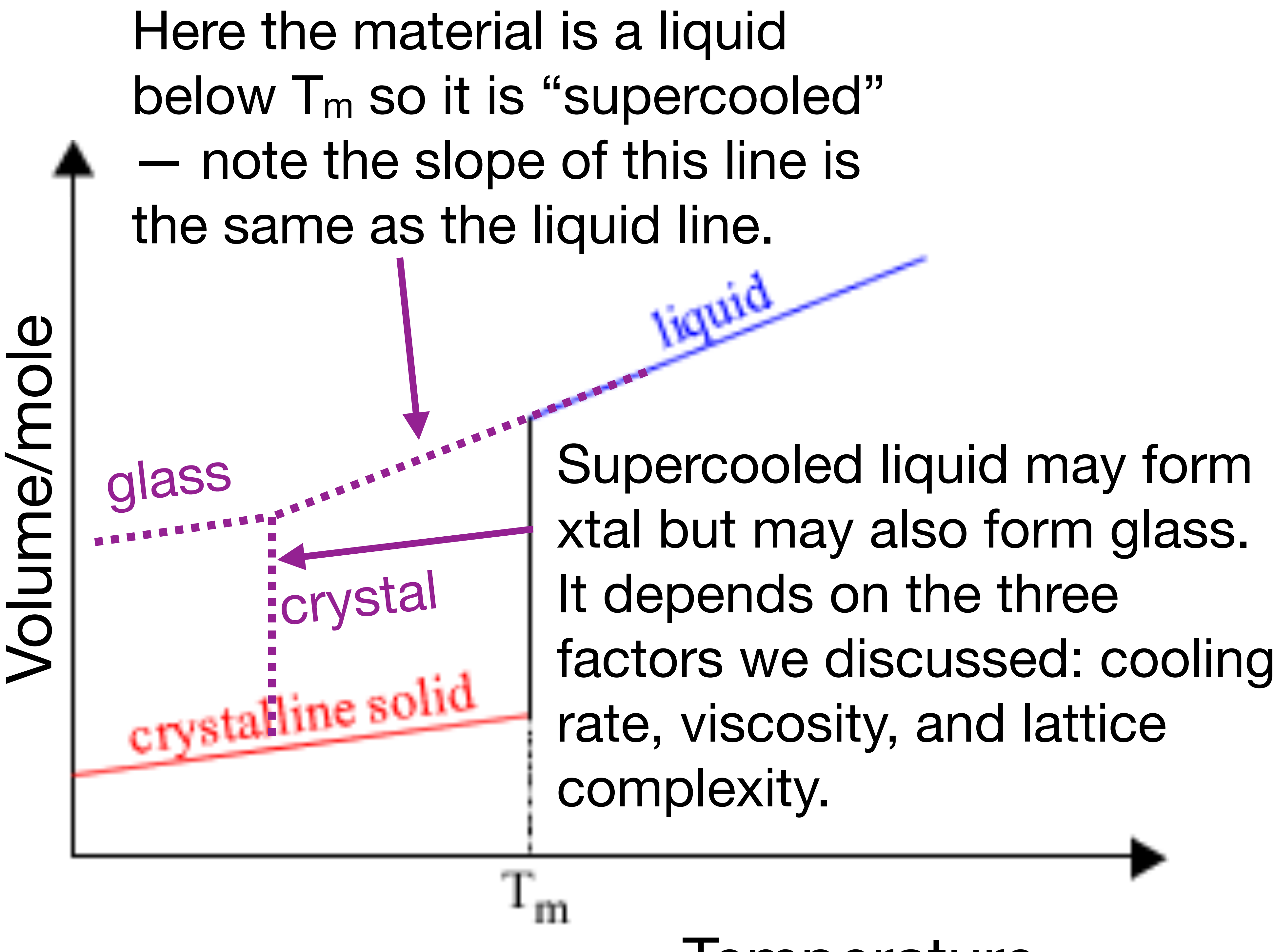
1) **Speed** around chairs: high mobility gets to lattice site faster, high 1/mobility (viscosity), gets there slower —> leads to glass
2) arrangement of chairs: **xtal complexity** : more complex —> leads to glass
3) how fast the music stops: **cooling rate** : faster rate —> less chance to find a chair —> leads to glass

When does glass form?

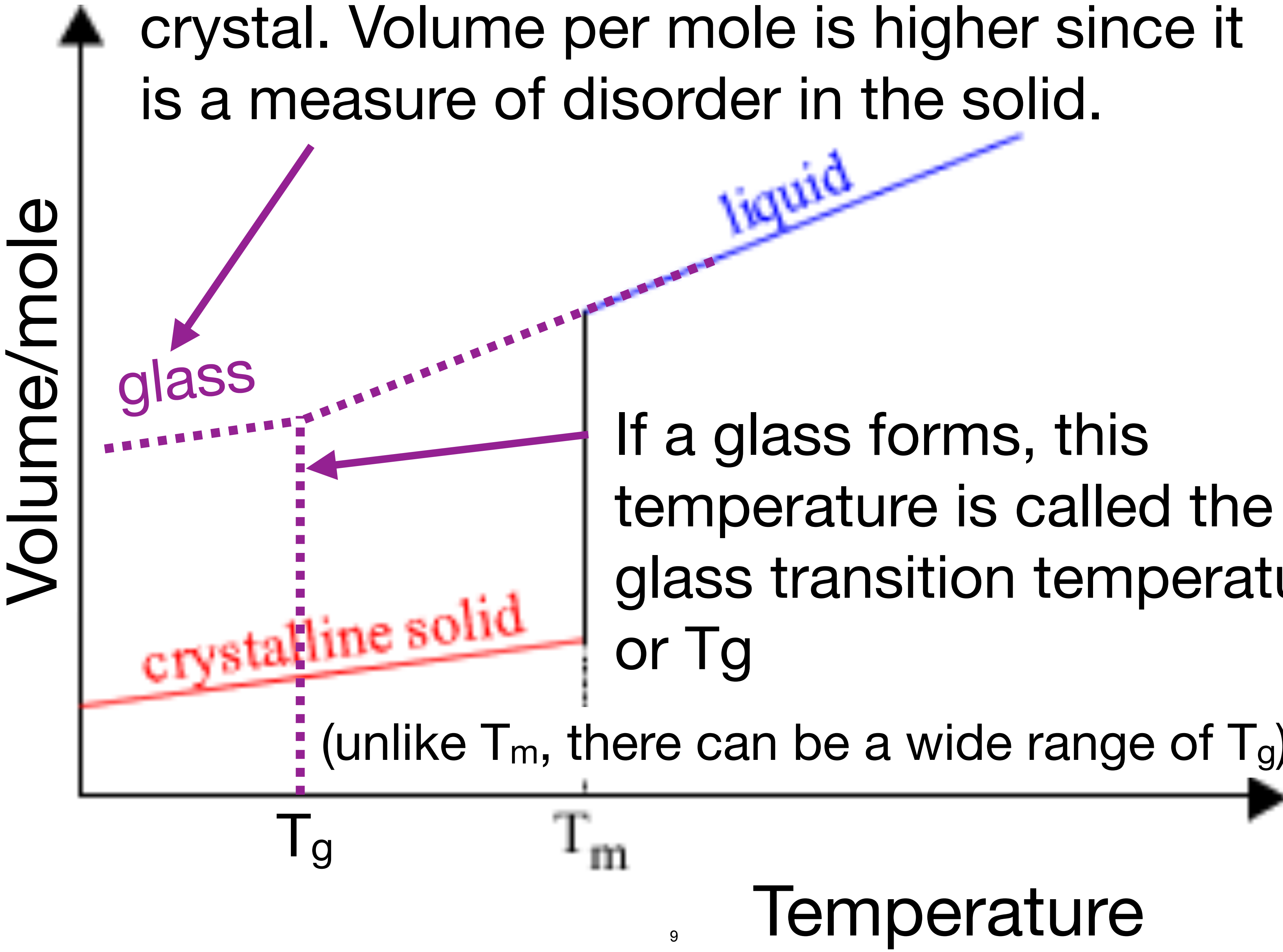
Volume per mole increases with temperature (more kinetic energy leads to greater average distance between atoms or molecules).



(there's only one T_m)


Here the material is a liquid below T_m so it is "supercooled" — note the slope of this line is the same as the liquid line.
liquid
glass
crystal
crystalline solid
Supercooled liquid may form xtal but may also form glass. It depends on the three factors we discussed: cooling rate, viscosity, and lattice complexity.
Volume/mole
T_m
Temperature

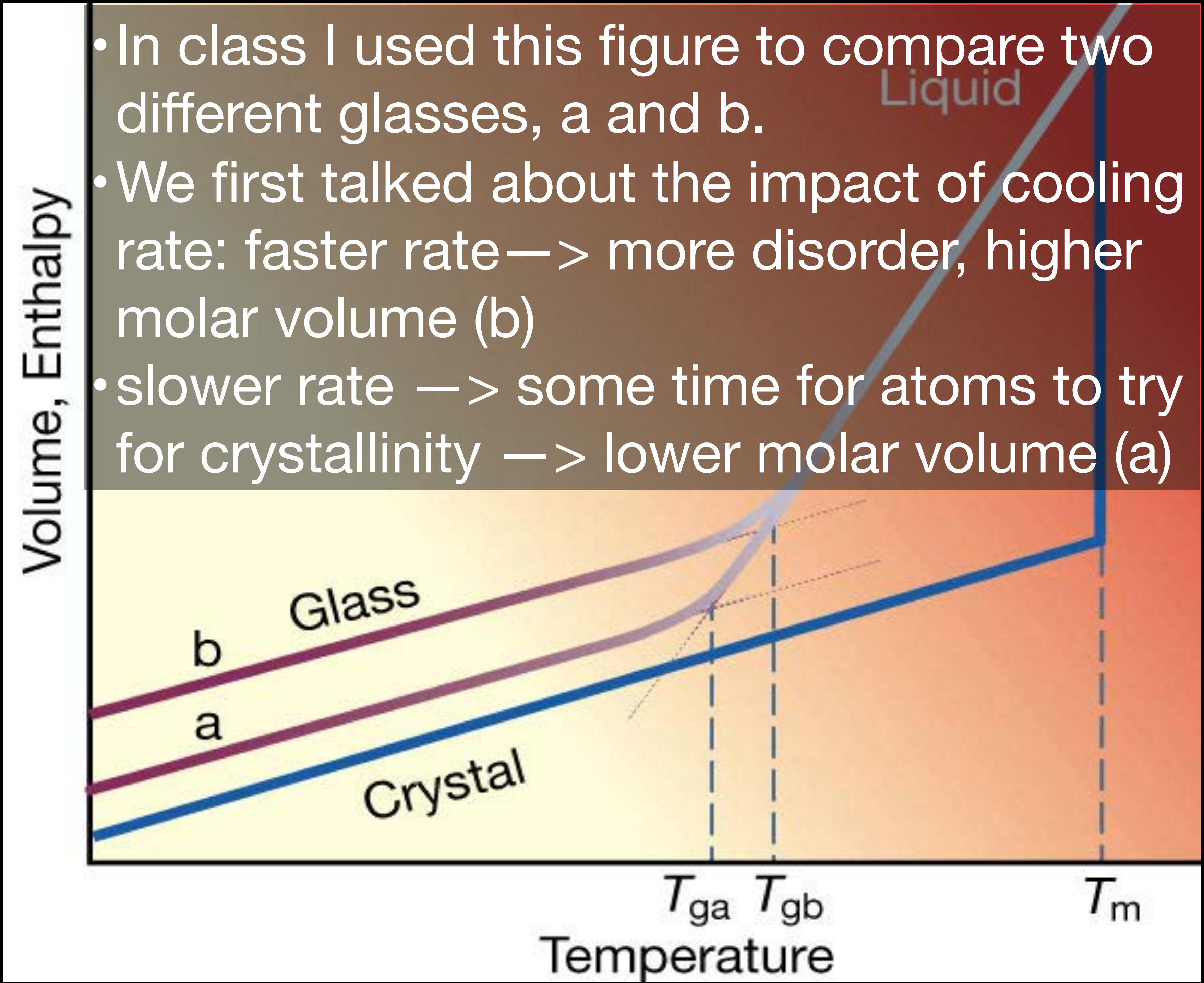
If the material forms a glass, it will be a solid and have the same slope as the crystal. Volume per mole is higher since it is a measure of disorder in the solid.



If a glass forms, this temperature is called the glass transition temperature, or Tg

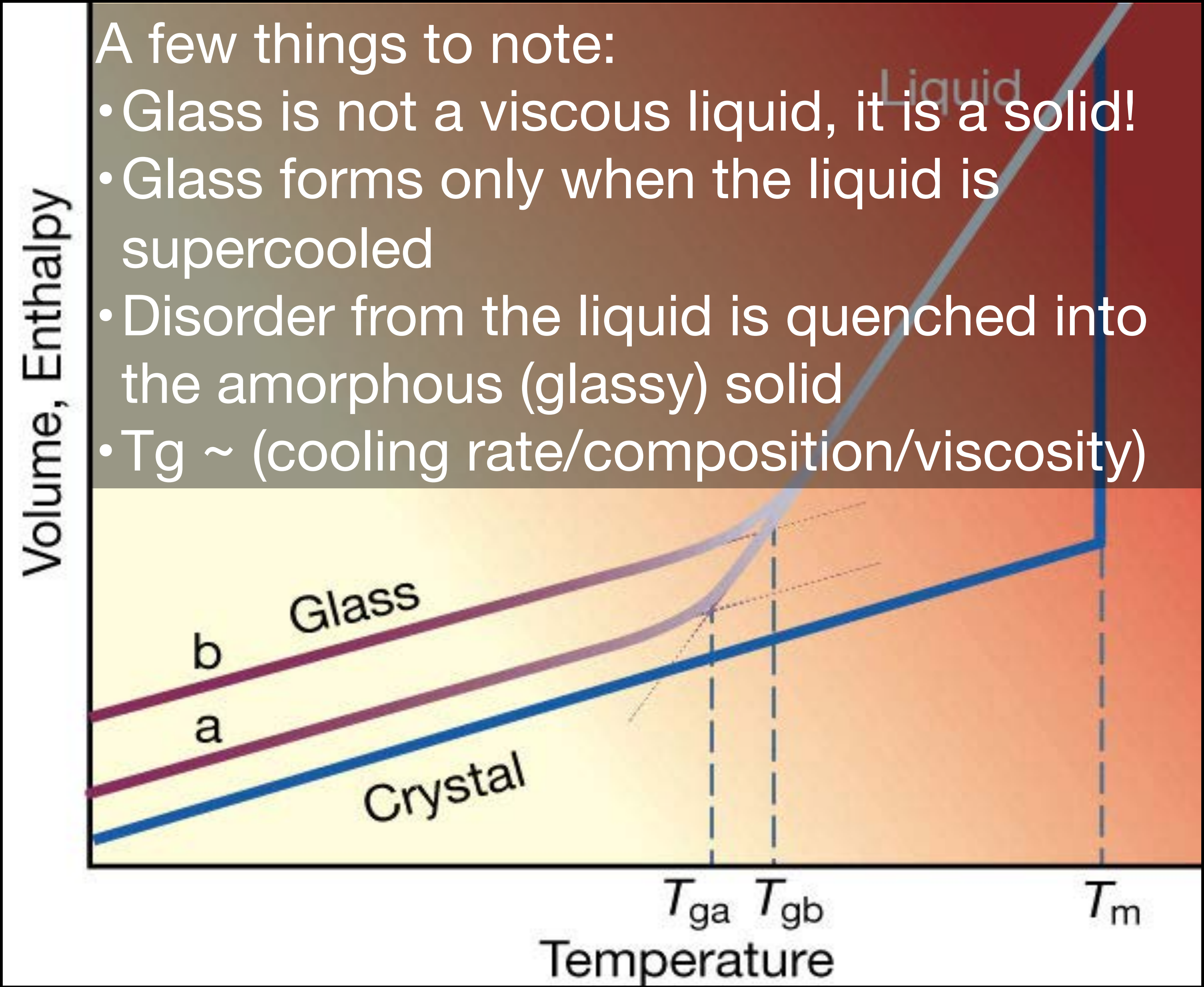
(unlike T_m, there can be a wide range of T_g)

- In class I used this figure to compare two different glasses, a and b.
- We first talked about the impact of cooling rate: faster rate —> more disorder, higher molar volume (b)
- slower rate —> some time for atoms to try for crystallinity —> lower molar volume (a)



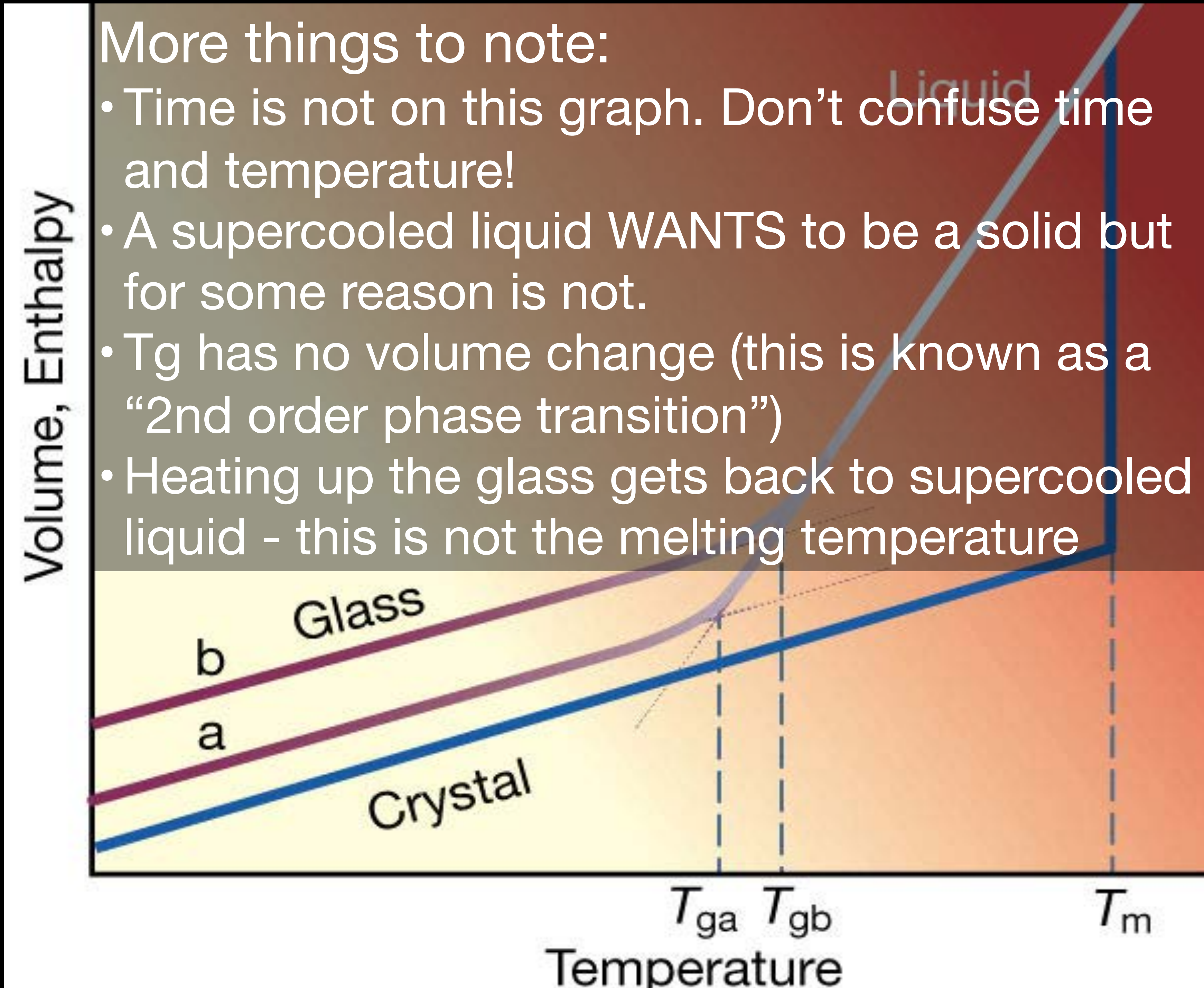
A few things to note:

- Glass is not a viscous liquid, it is a solid!
- Glass forms only when the liquid is supercooled
- Disorder from the liquid is quenched into the amorphous (glassy) solid
- Tg ~ (cooling rate/composition/viscosity)



More things to note:

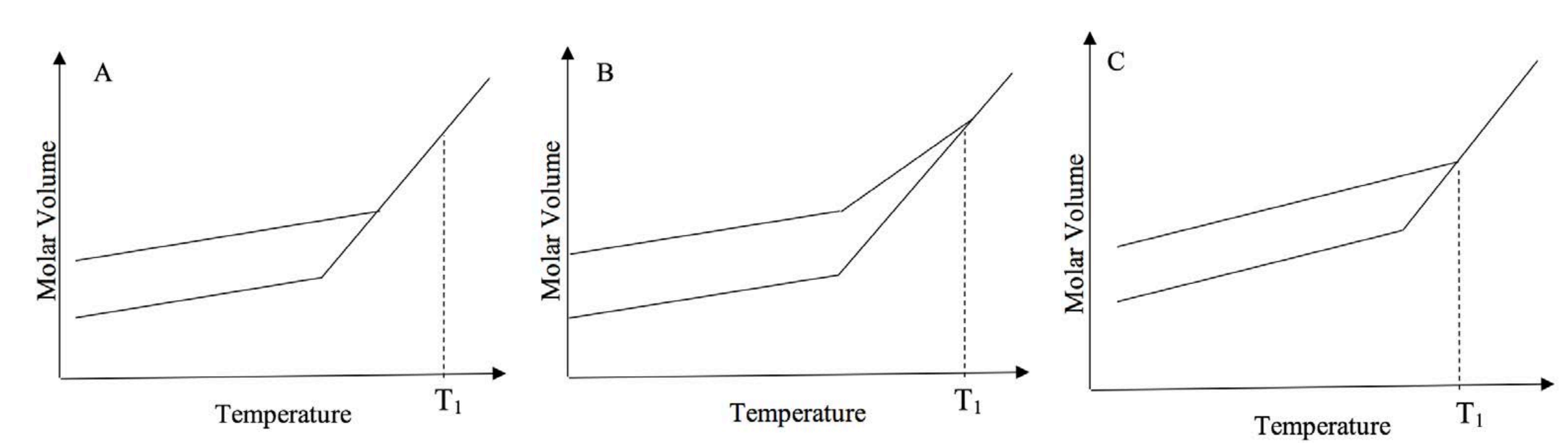
- Time is not on this graph. Don't confuse time and temperature!
- A supercooled liquid WANTS to be a solid but for some reason is not.
- Tg has no volume change (this is known as a "2nd order phase transition")
- Heating up the glass gets back to supercooled liquid - this is not the melting temperature



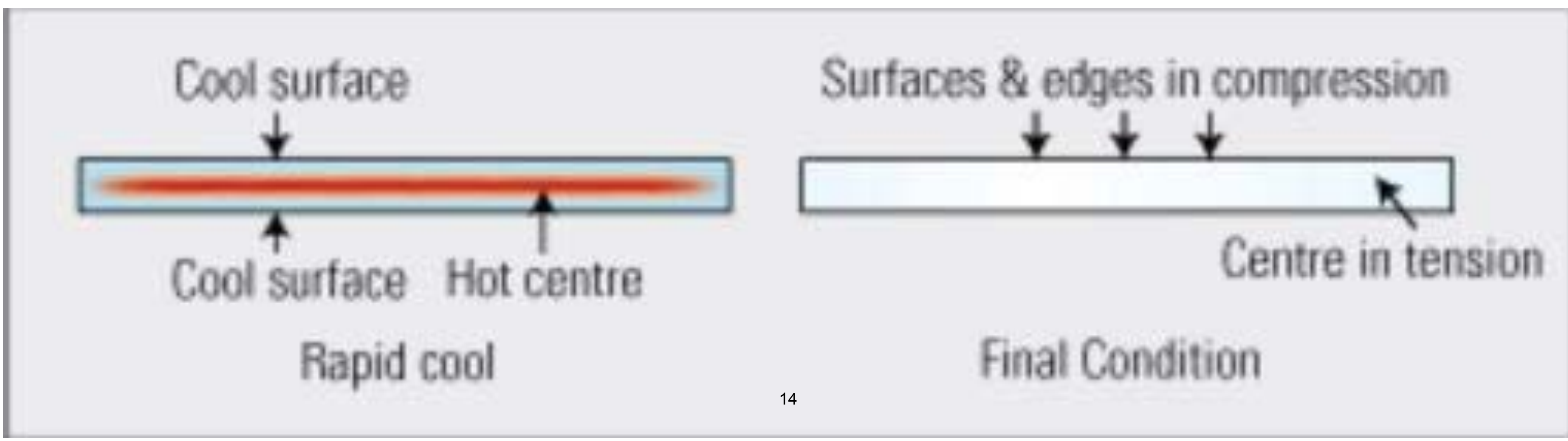
This is the example question I gave in class today (it's from an old Exam 3 question):

Two glass forming liquids of identical composition are cooled at the same rate to a temperature T_1, where $T_1 > T_m$. One glass is then cooled more quickly than the other. Which graph represents the molar volume vs. T curve of the two glasses?

The answer is (a) since it has T1 correctly greater than Tm (past Tg1 and Tg2), and it has the two slopes of the glasses the same.



- We used cooling rate as an example for how to engineer the mechanical properties of glass.
- In a process called tempering, the outside layer is cooled more rapidly than the inside, leading to a “desire” for the inside to have a smaller volume (slower cooling rate).
- This can be understood from the curves drawn on the previous slides, with for example glass (b) being the surface layer and (a) being the inside.
- The volume change between surface and core leads to (sometimes huge) compressive stress which makes the glass stronger.



		bottles/ windows	Bakeware/ lab glass	Optical	High Temp	Ancient Rome
Silica	SiO_2	73.6%	80.0%	35.0%	96.5%	67.0%
Soda	Na_2O	16.0	4	--	--	18.0
Lime	CaO	5.2	--	--	--	8.0
Potash	K_2O	0.6	0.4	7.2	--	1.0
Magnesia	MgO	3.6	--	--	--	1.0
Alumina	Al_2O_3	1.0	2.0	--	0.5	2.5
Iron Oxide	Fe_2O_3	--	--	--	--	0.5
Boric Oxide	B_2O_3	--	13.0	--	3.0	--
Lead Oxide	PbO	--	[illegible]	58.0	[illegible]	0.01

Glass can be widely engineered, by changing the cooling rate as discussed above or by adding chemistry (a "modifier"), that provides O^{2-}.

https://www.cmog.org/article/chemistry-glass

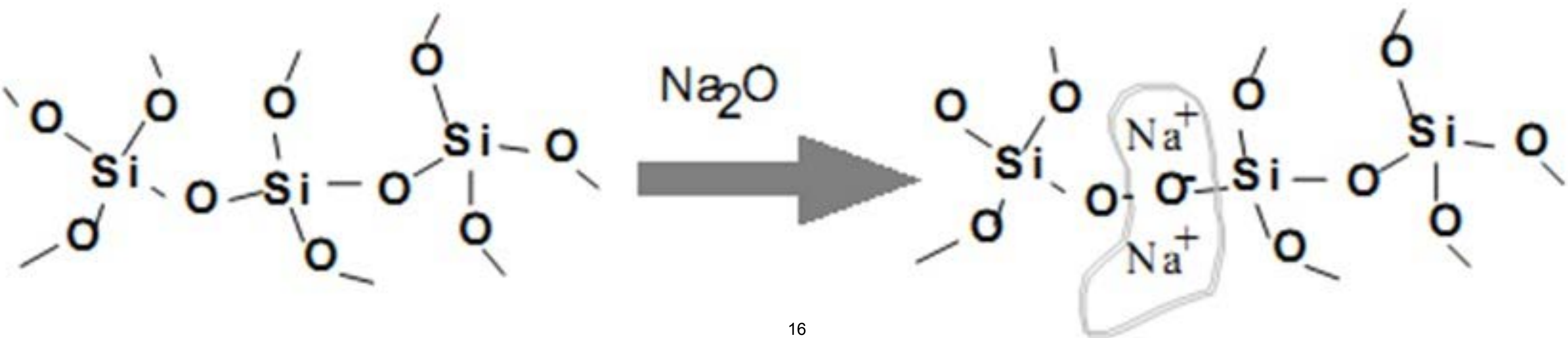
Note something in common with all glass modifiers: gives O^{2-} For example:

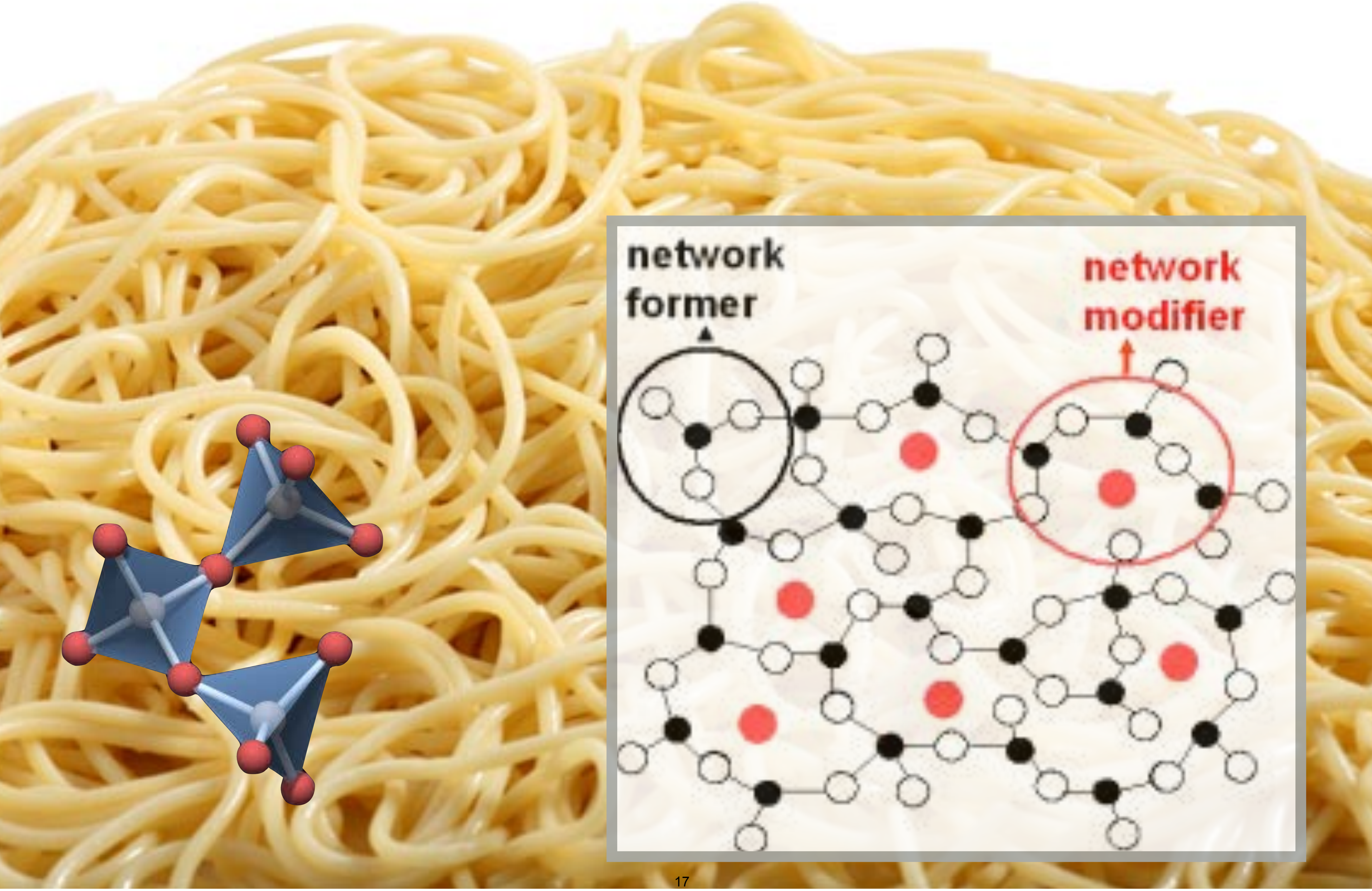
CaO —> Ca(2+) + O(2-)

Na2O —> 2Na(1+) + O(2-)

Al2O3 —> 2Al(3+) + 3O(2-)

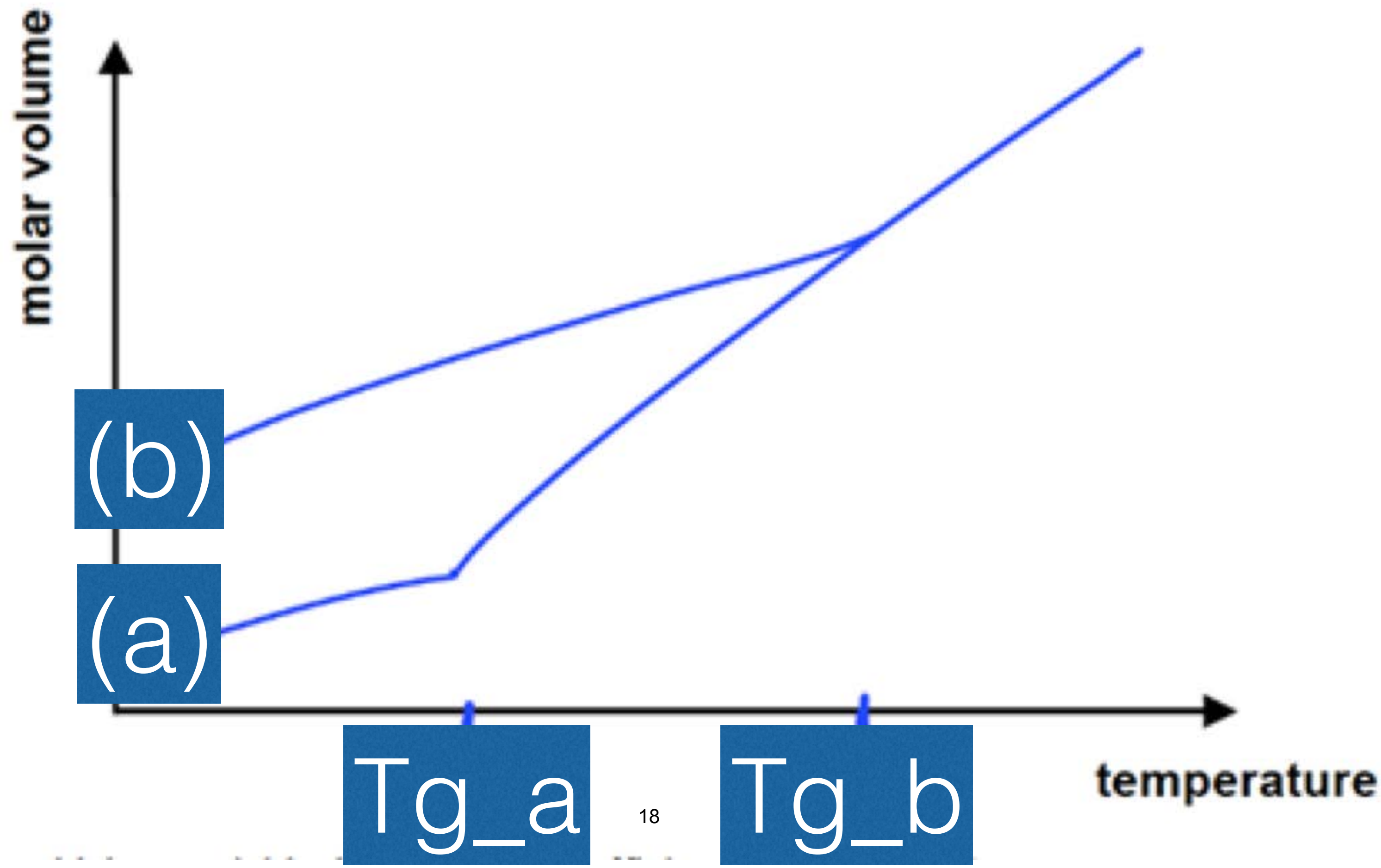
O^{2-} attacks the Si-O-Si bond and breaks it. This its called chain scission since the chain is broken (shorter pasta)

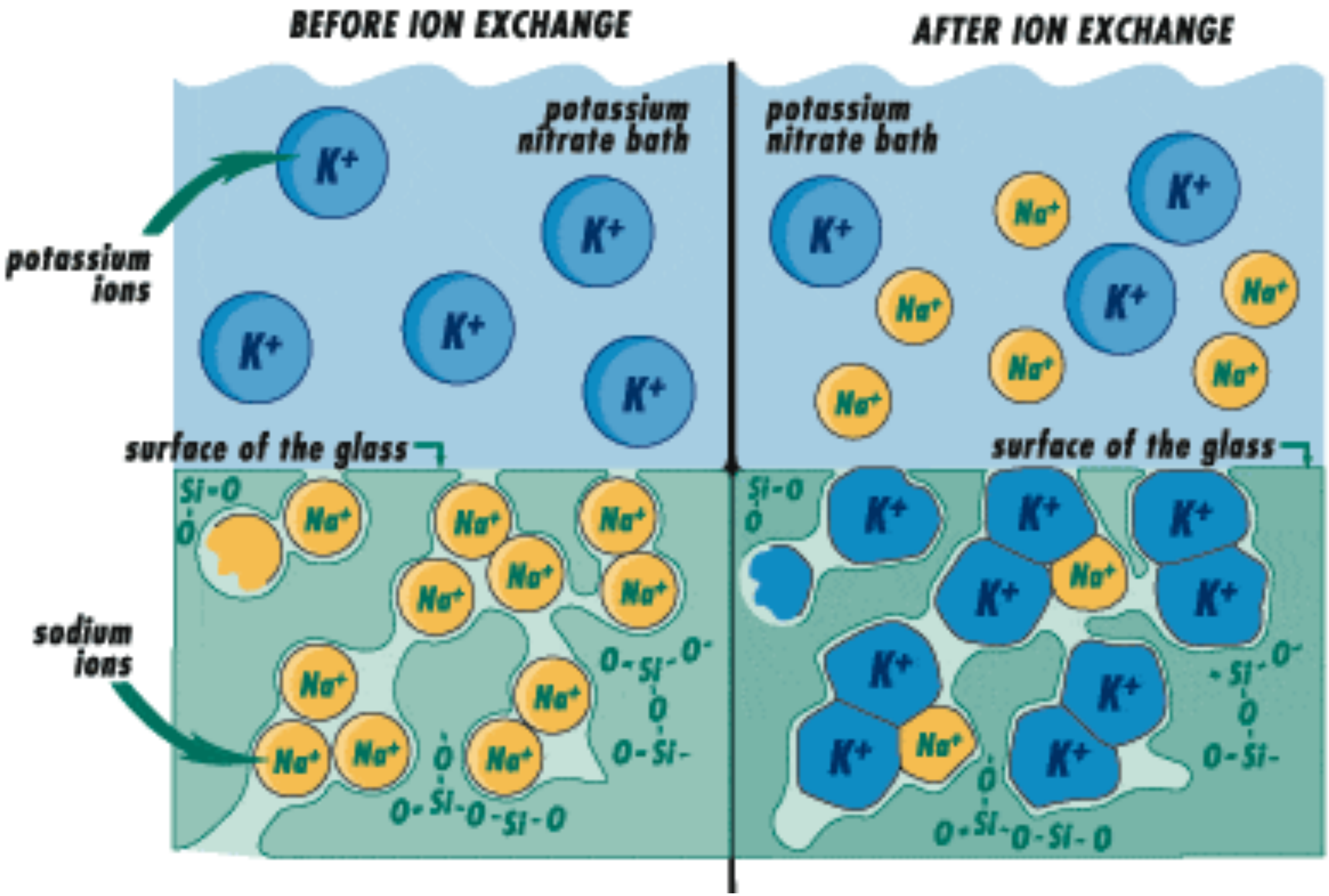



network former
network modifier

Chemical modification of the silicate network means that we can get the different glass curves in TWO DIFFERENT ways:

1) same material cooled at different rates. Faster cooling would give (b), slower (a) — this is what we've discussed
2) cooling at the same rate but different modifiers. e.g, (b) could be SiO2 with 5% PbO and (a) SiO2 with 10% PbO —> more cutting spaghetti = less viscous so can find better packing leading to lower volume/mole





Chemically strengthened glass: We also discussed ion exchange as a way to make glass stronger —> in this case bigger K+ ions substitute for Na+ that were there from a modifier, and push the glass network in between making it have the same compressive stress as tempering.