Lecture 24

Materials and their structure- Part 2

Textbooks:

- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

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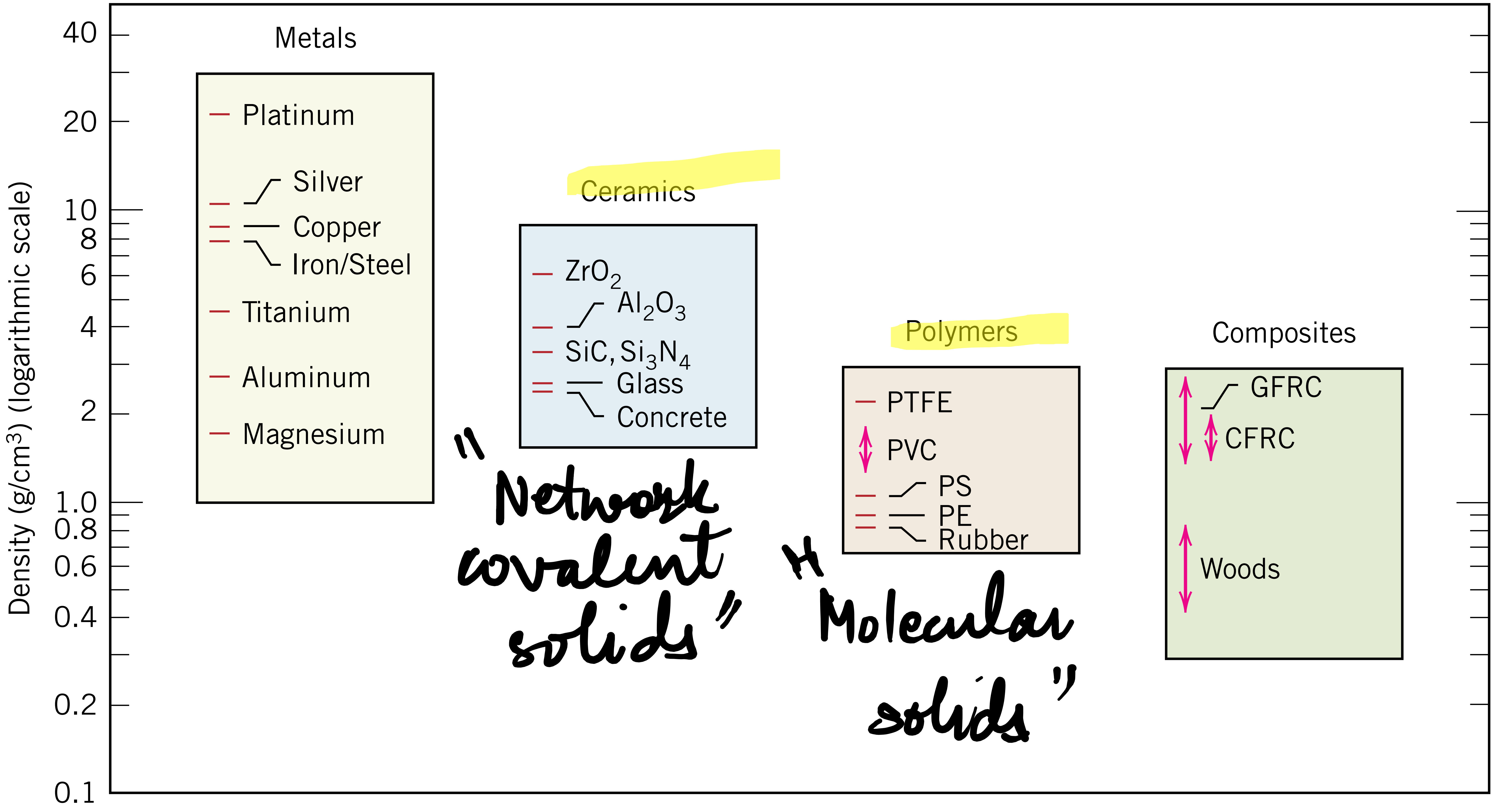
Recap…

1. Classification of materials
2. Different types of solids
3. Non-crystalline solids: amorphous solids (glass)
4. Structure of Silicates

Classification of materials



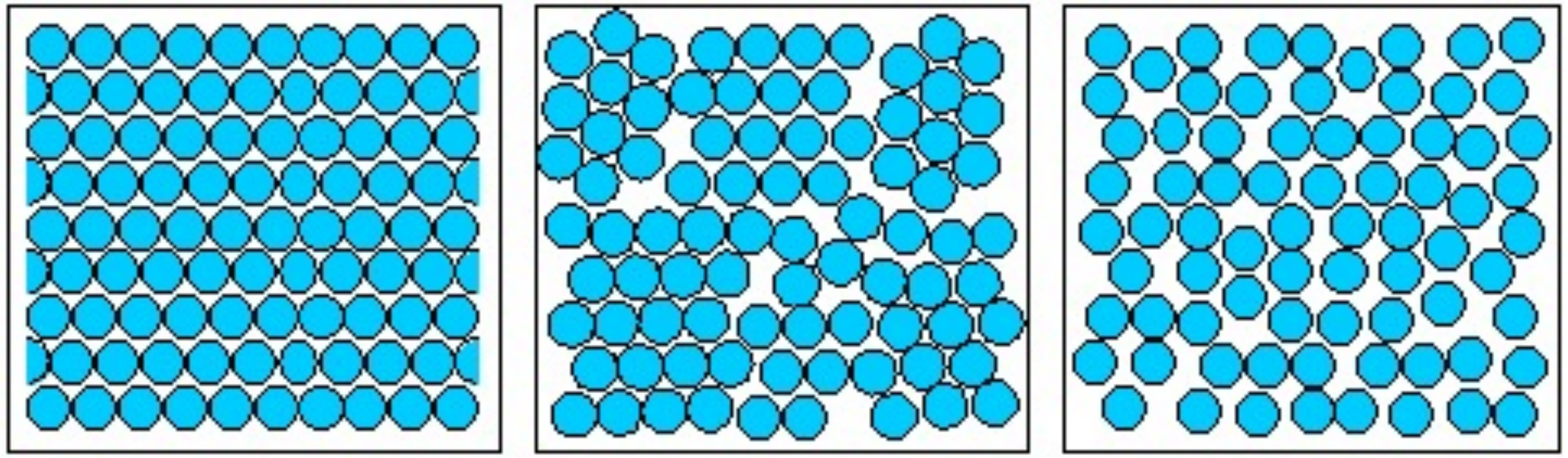
Crystalline and non-crystalline states

Crystalline solids

- Long-range order (translational periodicity)
- Defects (vacancy, dislocations etc)
- Atomic arrangement is ordered
- Sharp melting point
- Need slow cooling rates
- Free energy is lowest
- Grain boundaries
- Example: metallic Cu, NaCl

Amorphous solids

- No long-range translational order i.e. short-range order (not totally random)
- Disordered or random arrangements of atoms
- Gradually softens over a range of temperature.
- Fast cooling rates.
- Free energy is high
- No grain boundaries
- Example: glassy solids (silicates)



Single crystal	Polycrystal	Amorphous solid
Periodic across the whole volume.	Periodic across each grain.	Not periodic.

Amorphous solids (Ceramics: glass)

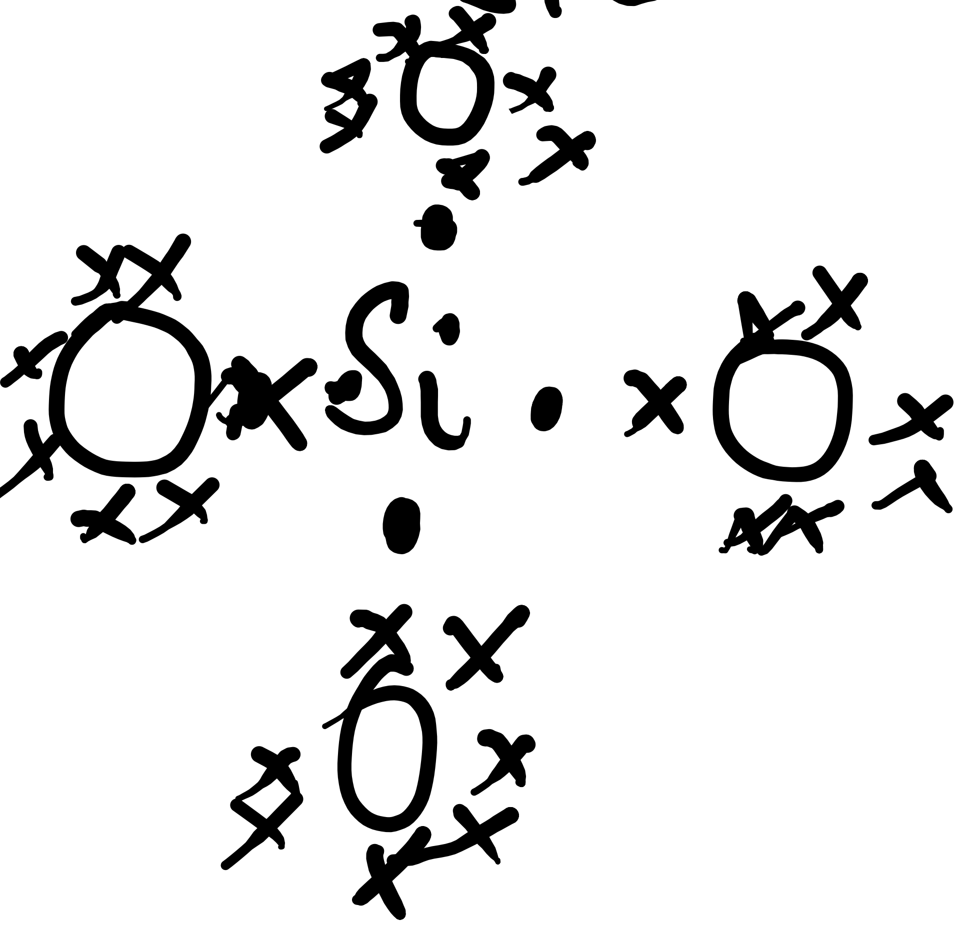
Silicates: Glassy solids

Ceramics: composed of clay minerals (i.e., porcelain), as well as cement, and glass e.g. aluminum oxide (or alumina, Al_2O_3),silicon dioxide (or *silica,* SiO_2), silicon carbide (SiC), silicon nitride (Si_3N_4)

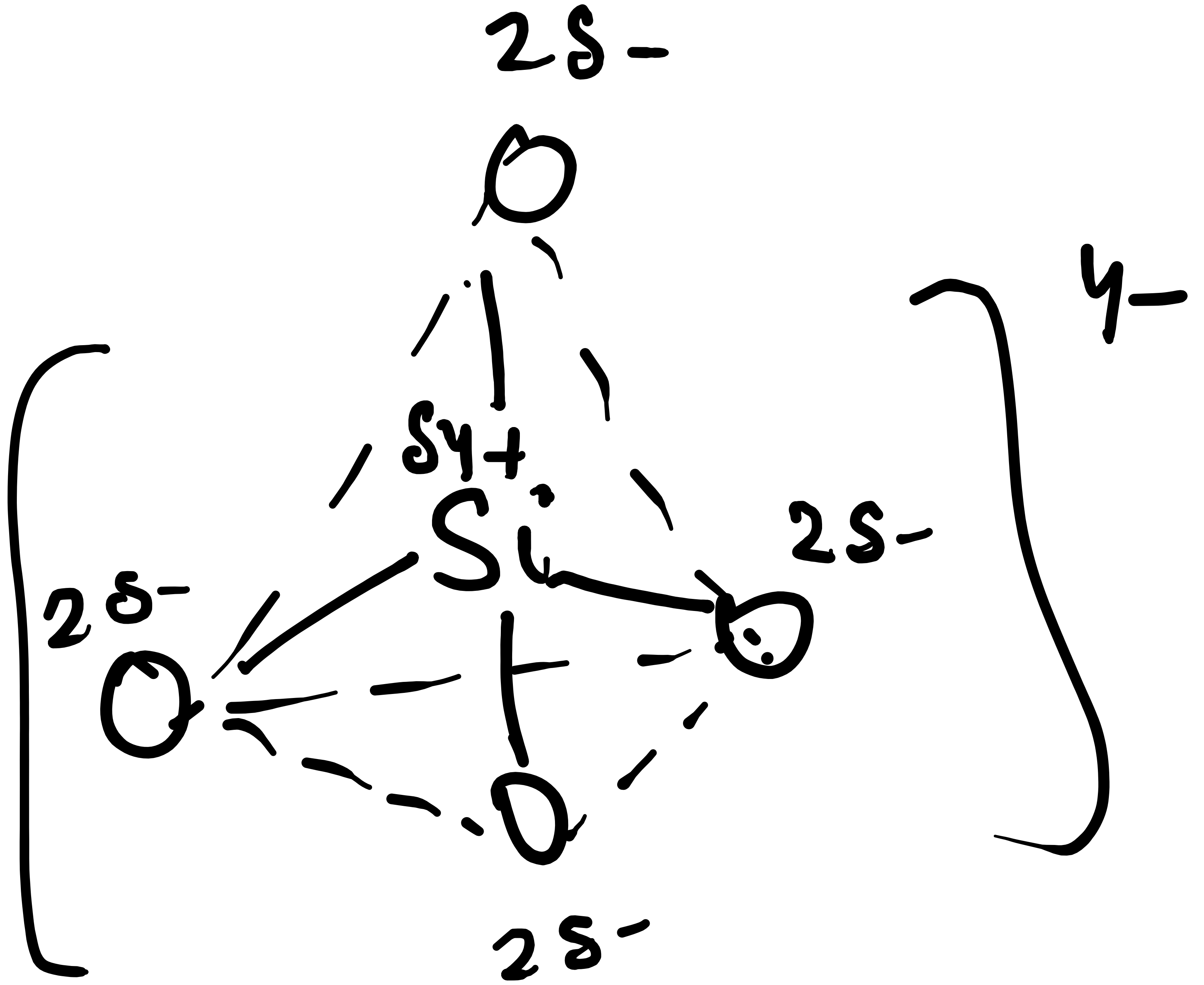
- stiff and strong
- Brittle (less ductile)
- Susceptible to fracture
- Low heat and electrical conductivities

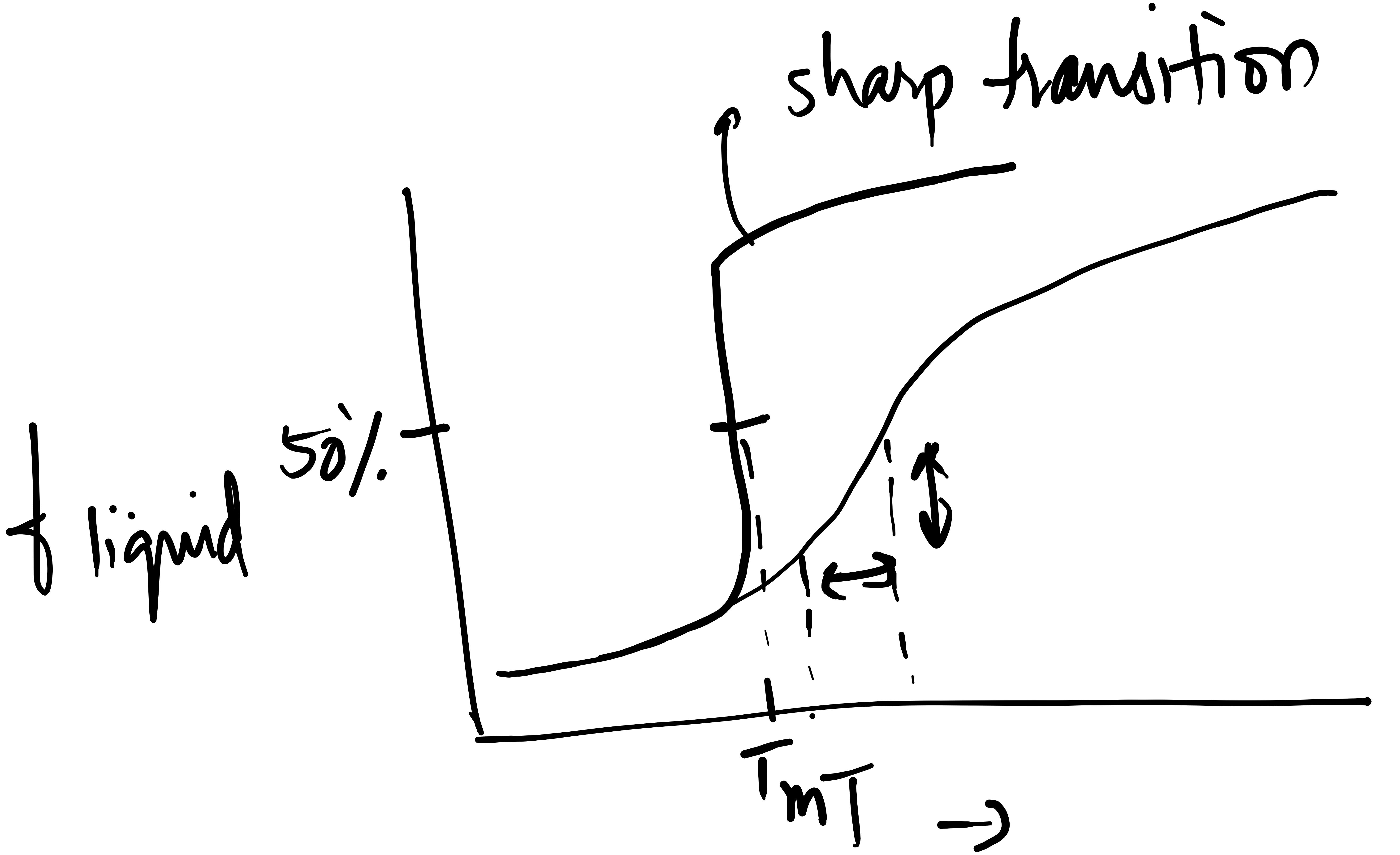
SiO_2 (silica): crystalline (quartz) and amorphous (glass)

Basic unit: $[SiO_4]^{4-}$

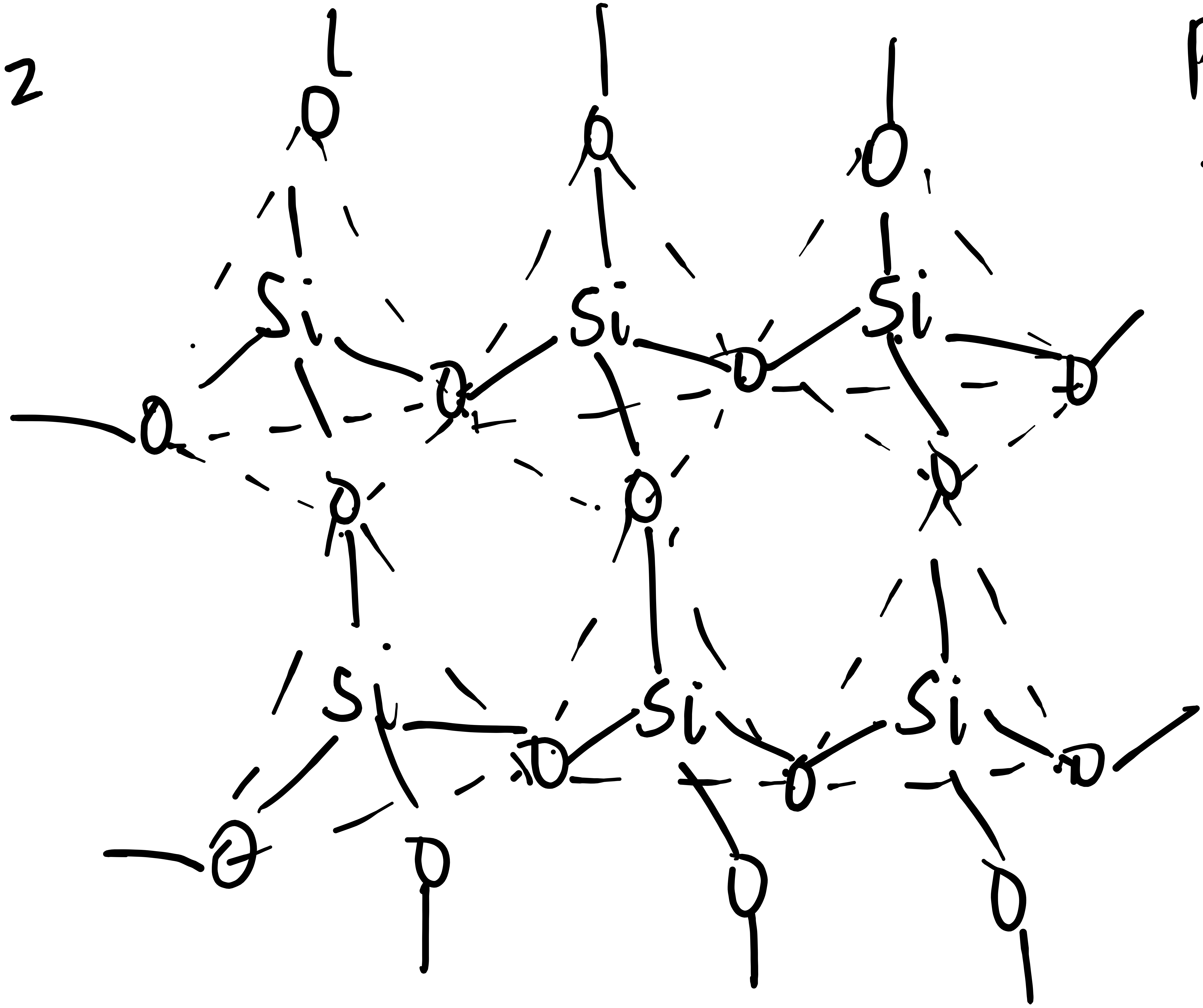


$\rightarrow [SiO_4]^{4-}$




sharp transition
f liquid
50%
T_m
T →

$\underline{SiO_2}$



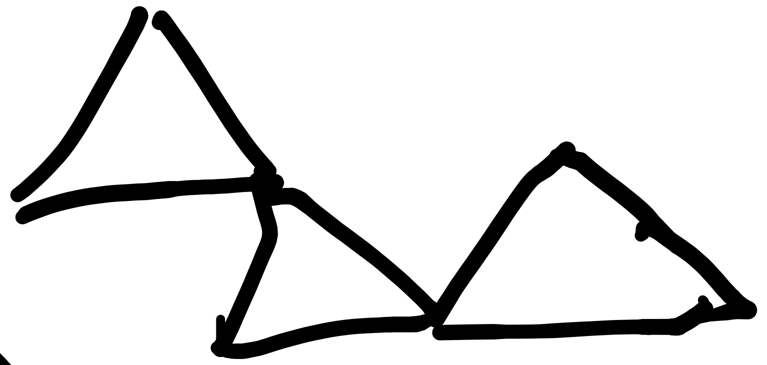
Per tetrahedron:

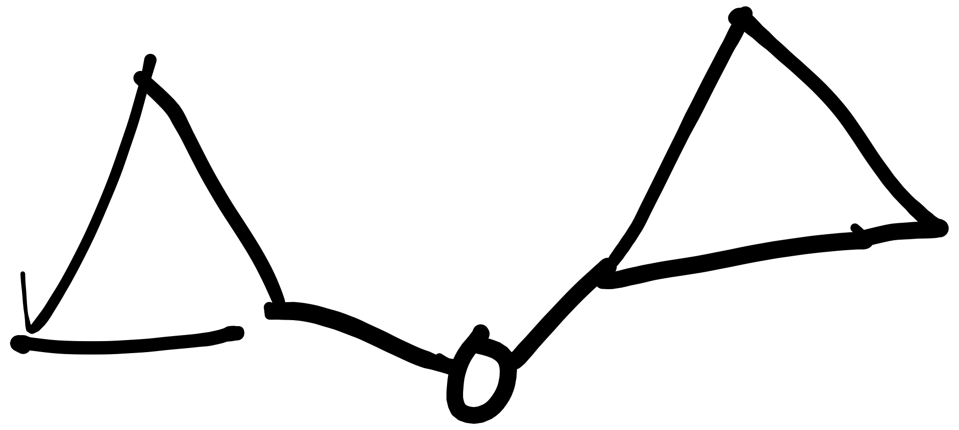
1 Si

$\frac{1}{2} \times 4$ O = 2 O atoms

- Composition is maintained

- Charge neutrality.



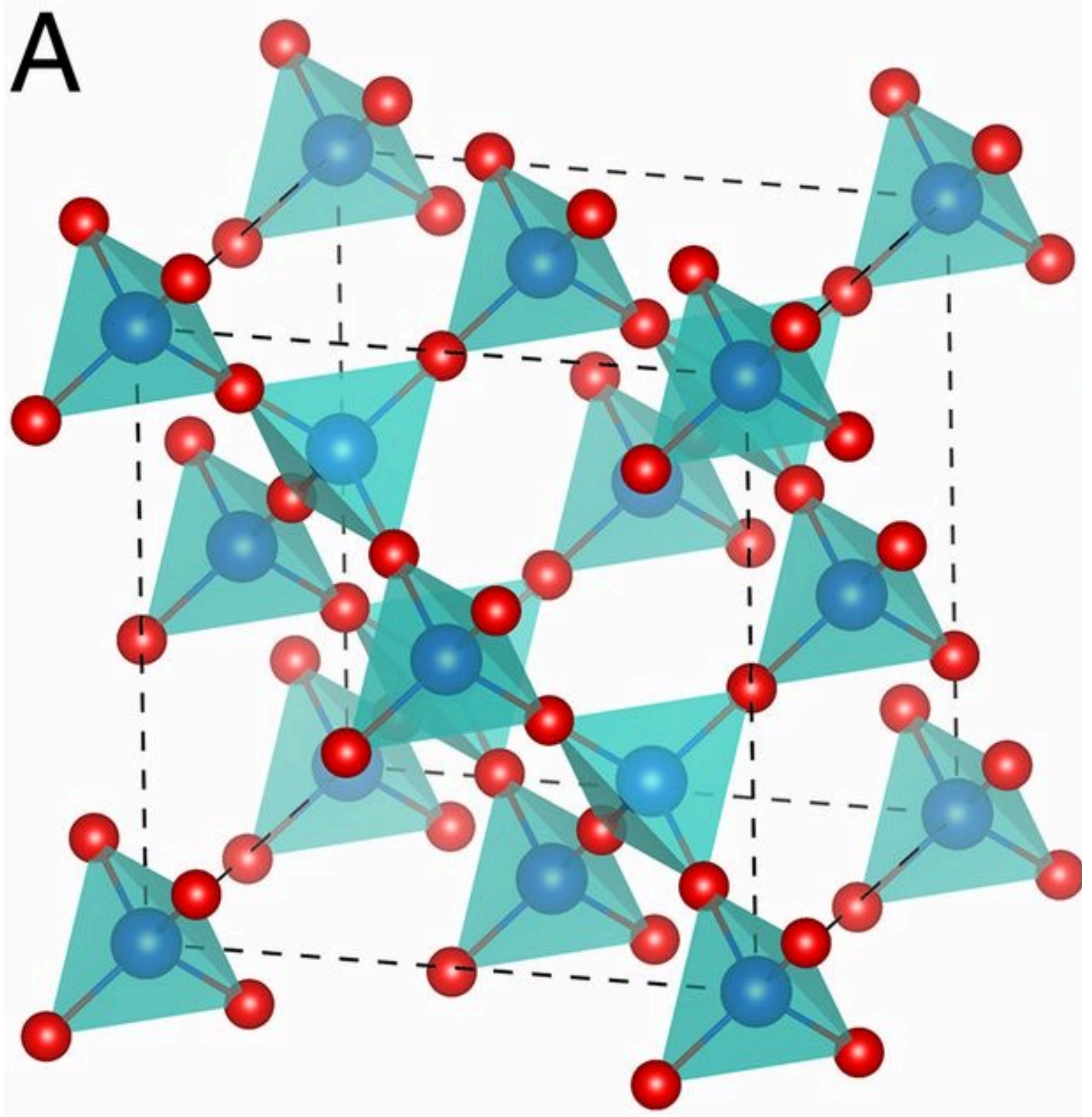


$[SiO_4]^{4-}$

$[Si_2O_5]^{x-}$

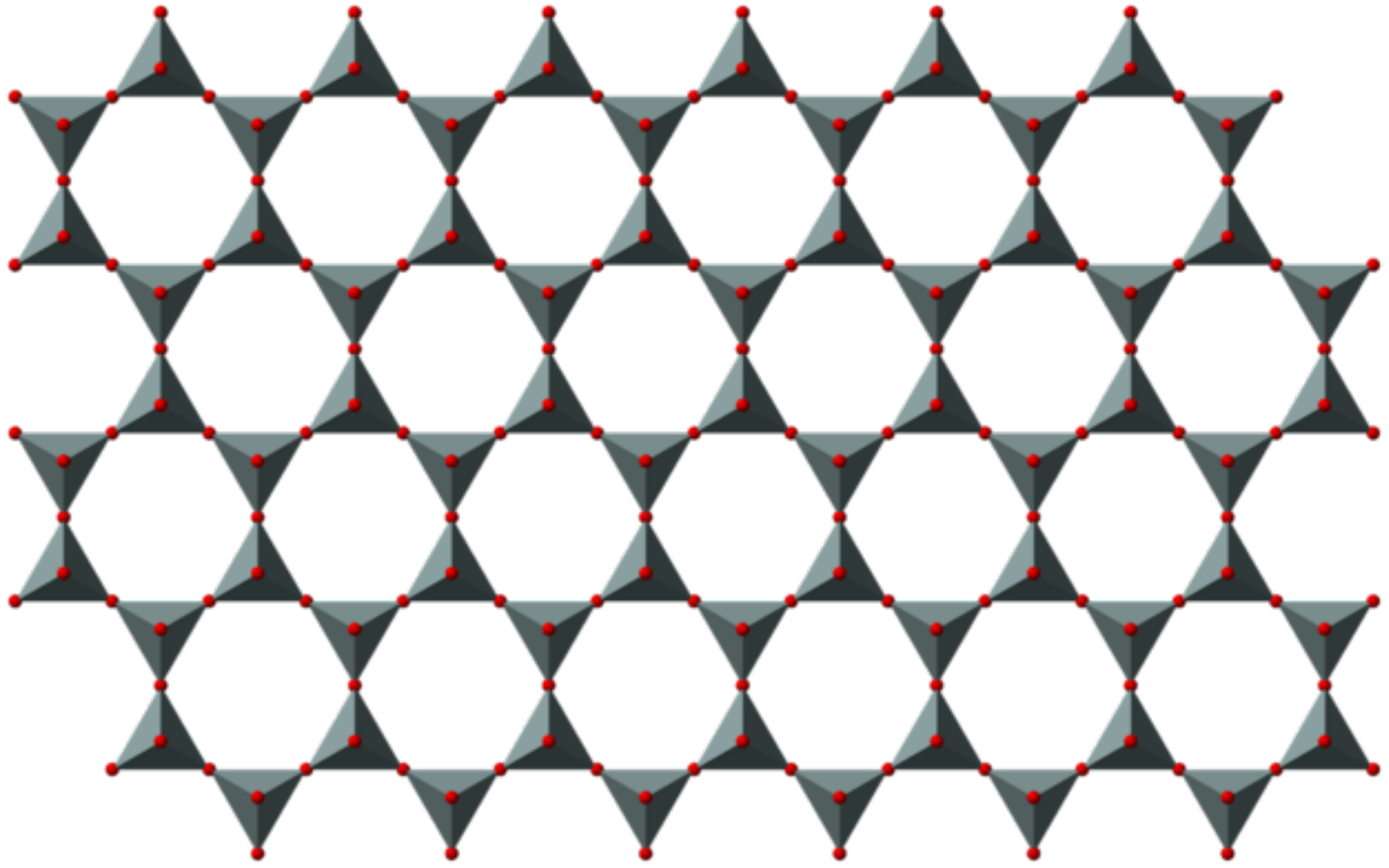
Three-dimensional network of silicate

Tetrahedra can rotate



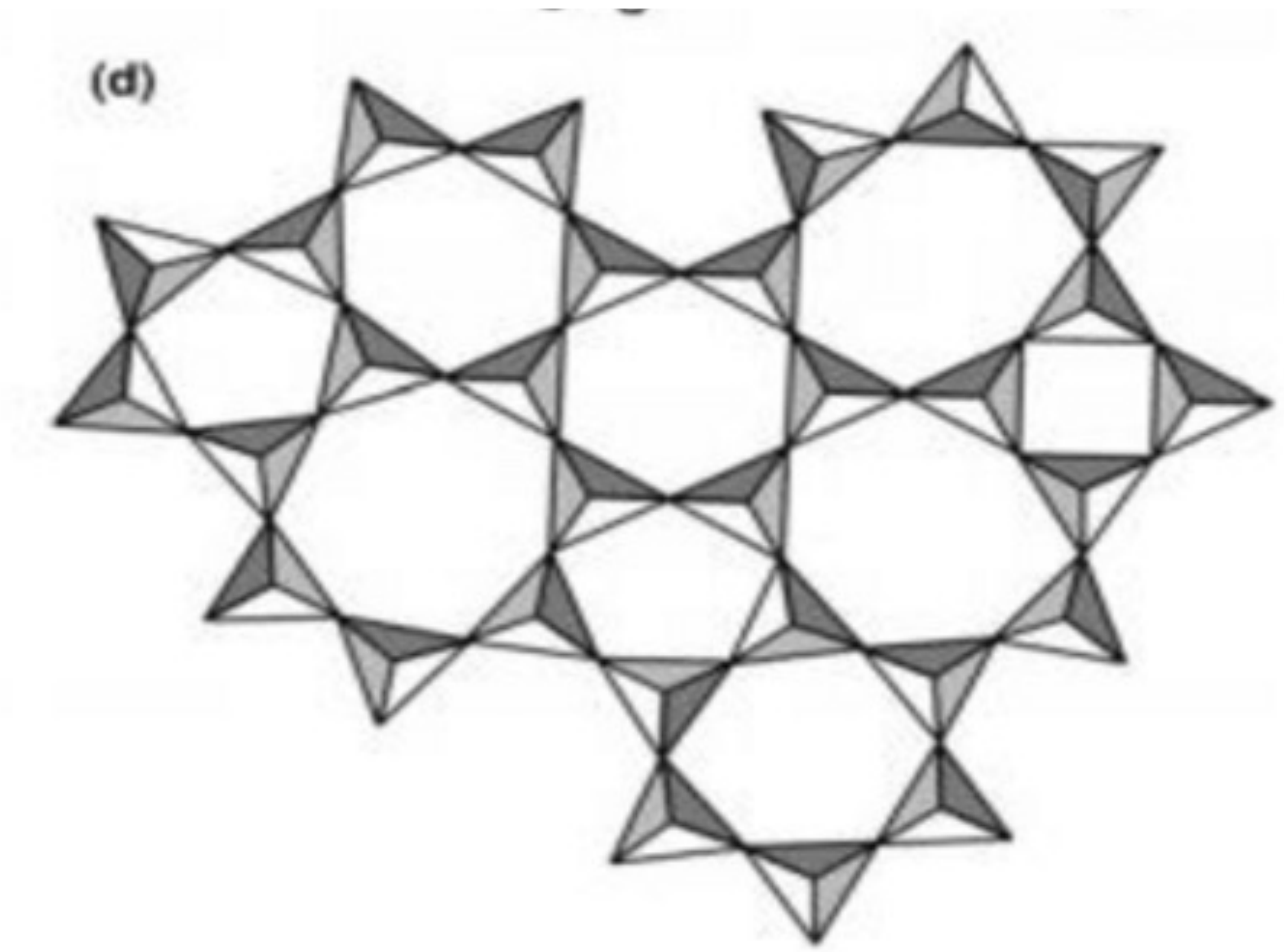
Crystalline

Slow cooling



Amorphous

Fast cooling



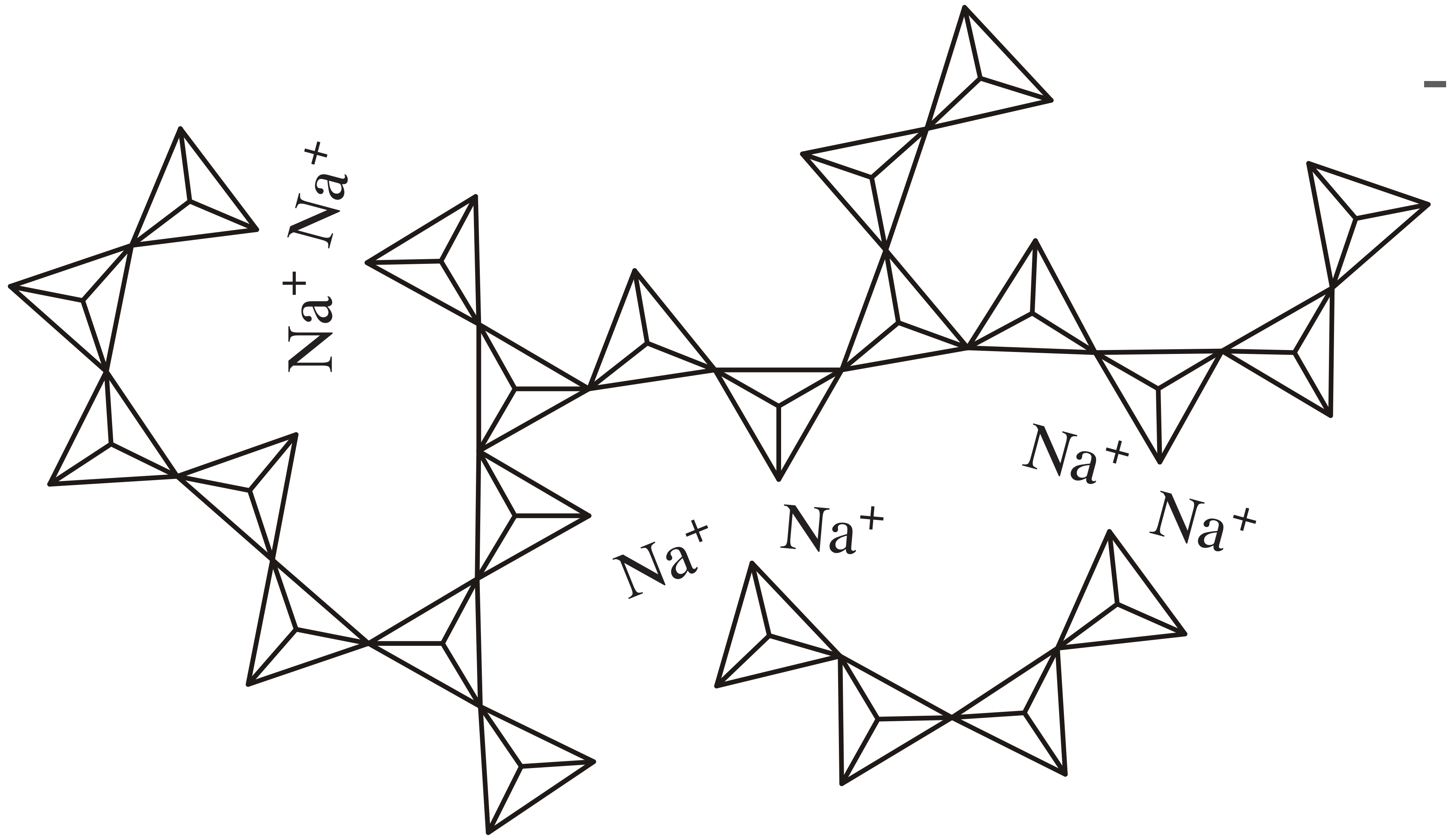
Glass without any additives is called FUSED GLASS

https://doi.org/10.1073/pnas.1803919115

Another non-crystalline silicate: soda lime glass

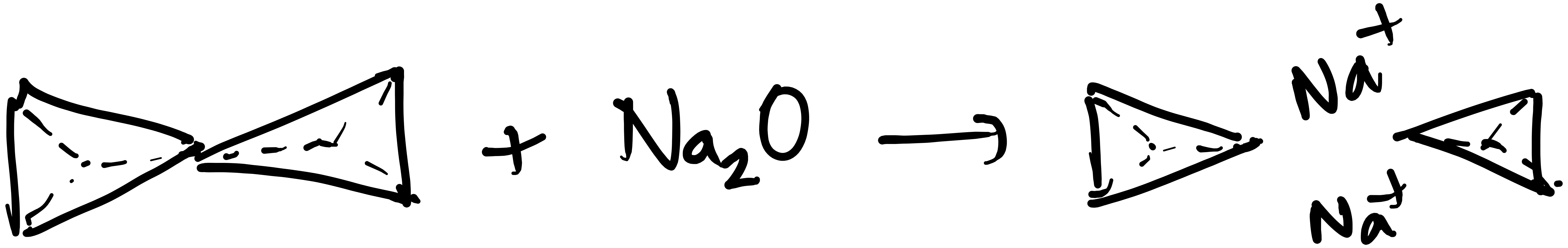
lime : CaO

Sodium oxide and calcium oxide are added

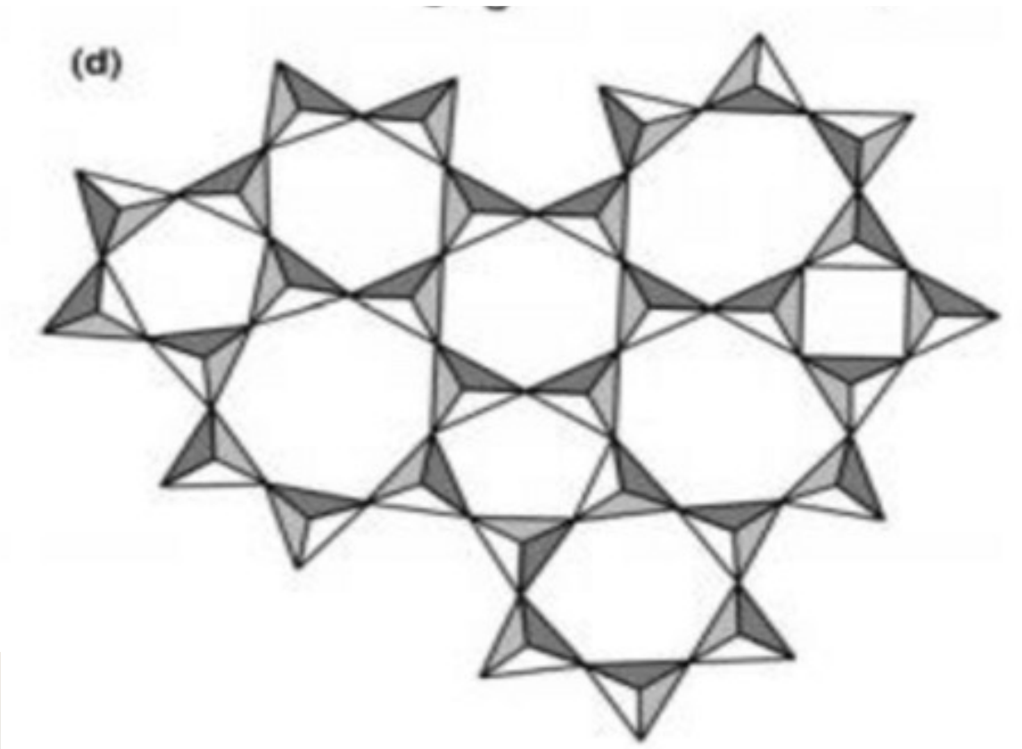


- The alkali cations break break up the network of the silicate tetrahedra
- For each Na2O introduced, one Si–O bridge is disrupted and the extra oxygen atom from Na2O splits up one common corner into separate corners

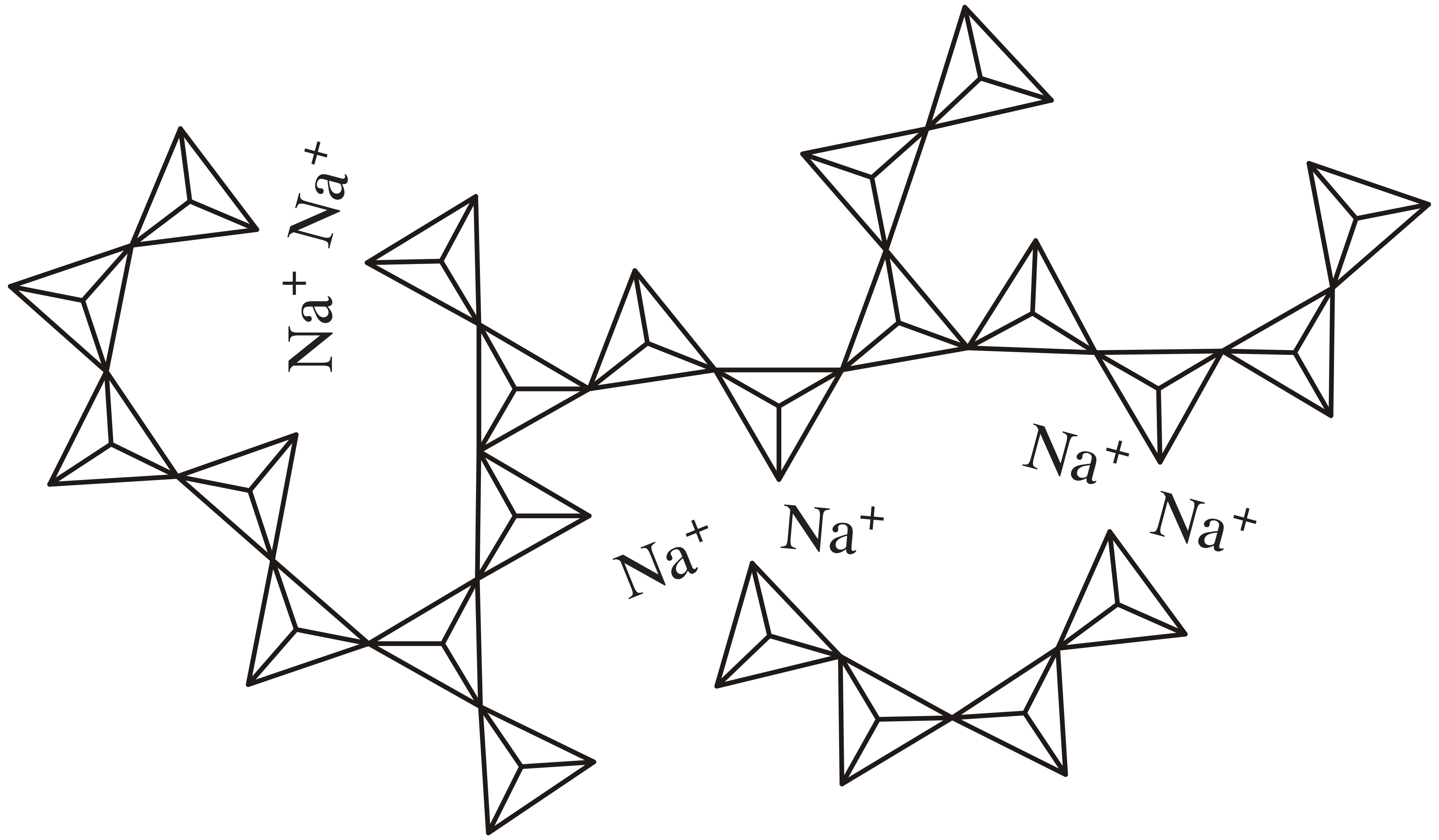
Soda : Na_2O



Soda lime glass is used in daily applications.



Cut the spaghetti into smaller pieces!



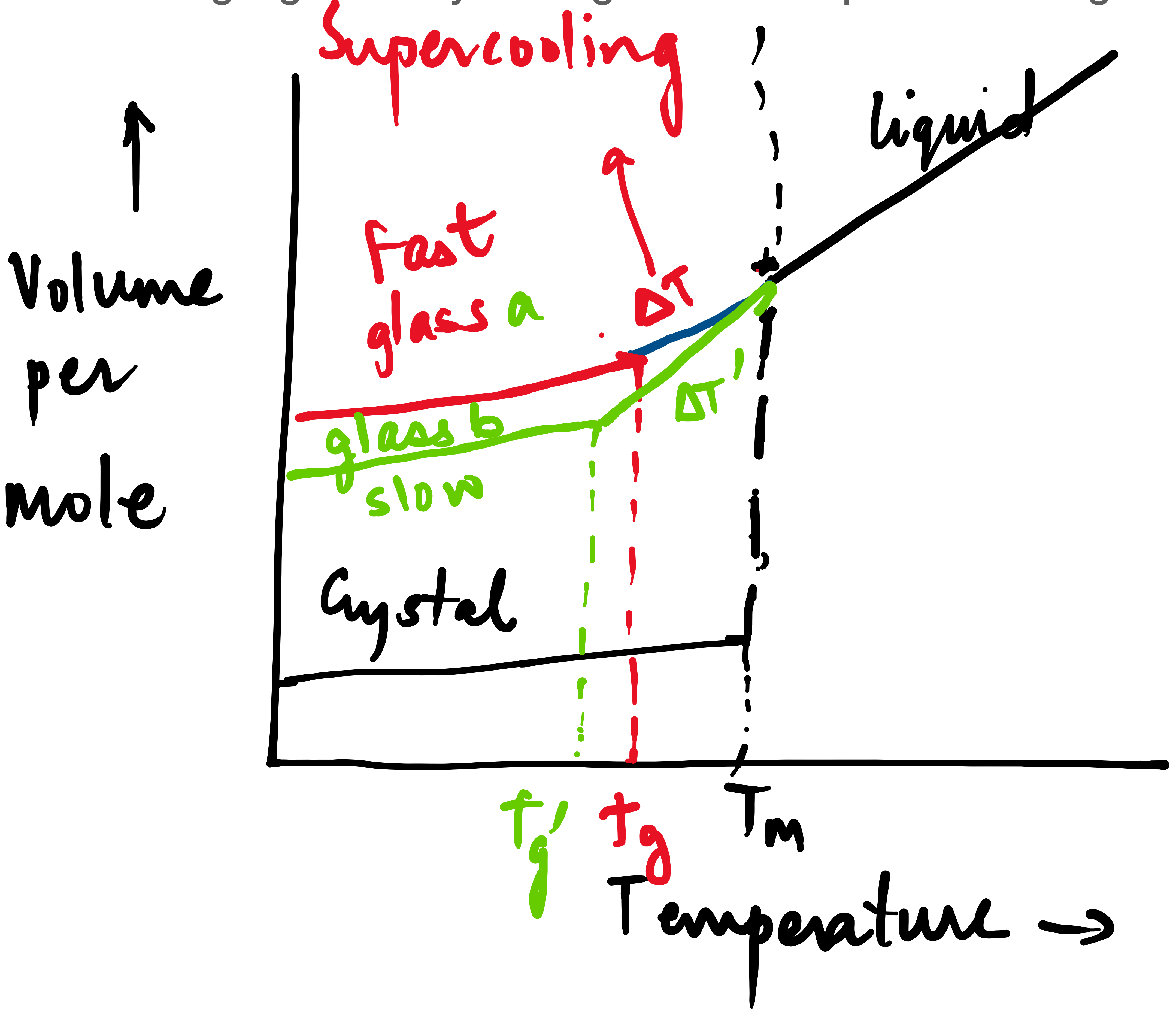
Highly viscous

10^4 to 10^6 Ns/m ^{2}

Less viscous and other properties change

How is glass formed?

Glasses are disordered materials that lack the periodicity of crystals but behave mechanically like solids. The most common way of making a glass is by cooling a viscous liquid fast enough to avoid crystallization called Supercooling.



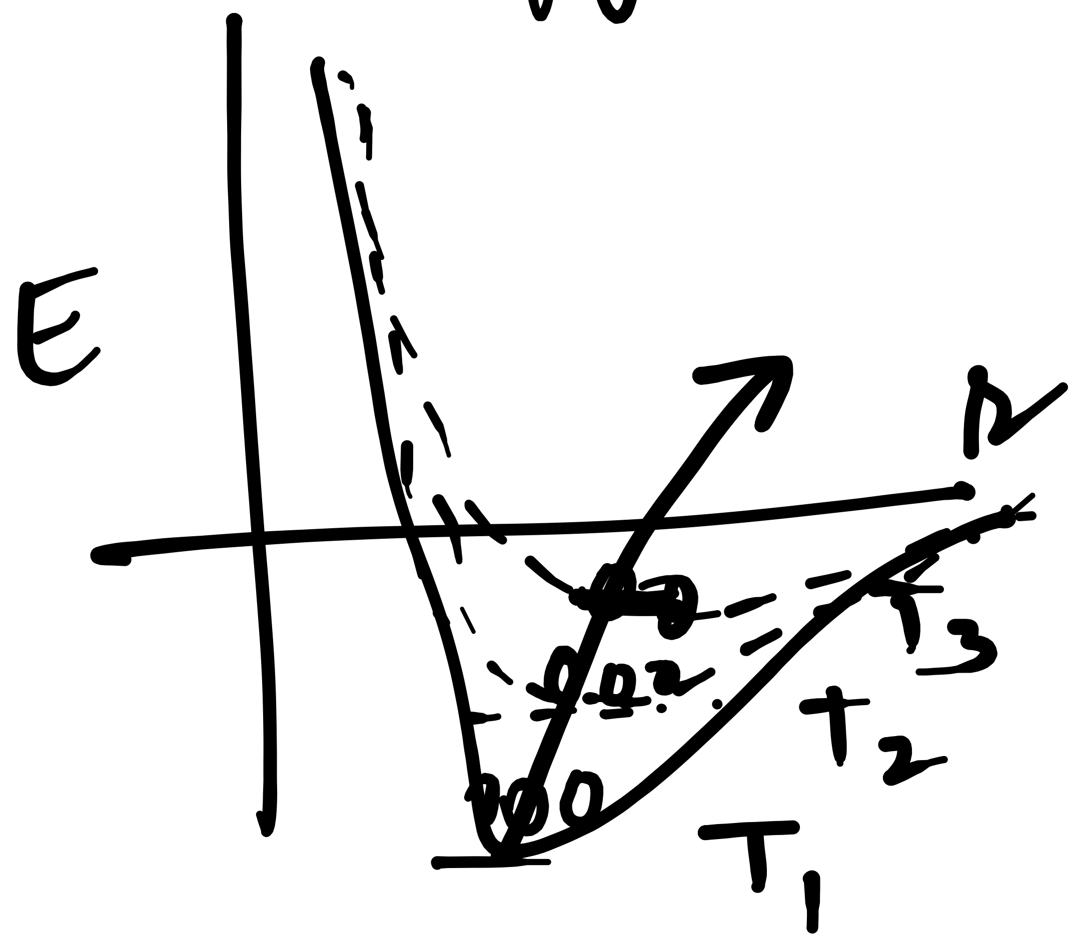
Melting : First order phase transition

$$\text{Slope} = \left(\frac{\partial \ln V}{\partial T}\right)_P = \alpha$$

"Thermal expansion coefficient"

Glass transition

T_g : Glass transition temp.



The glass transition

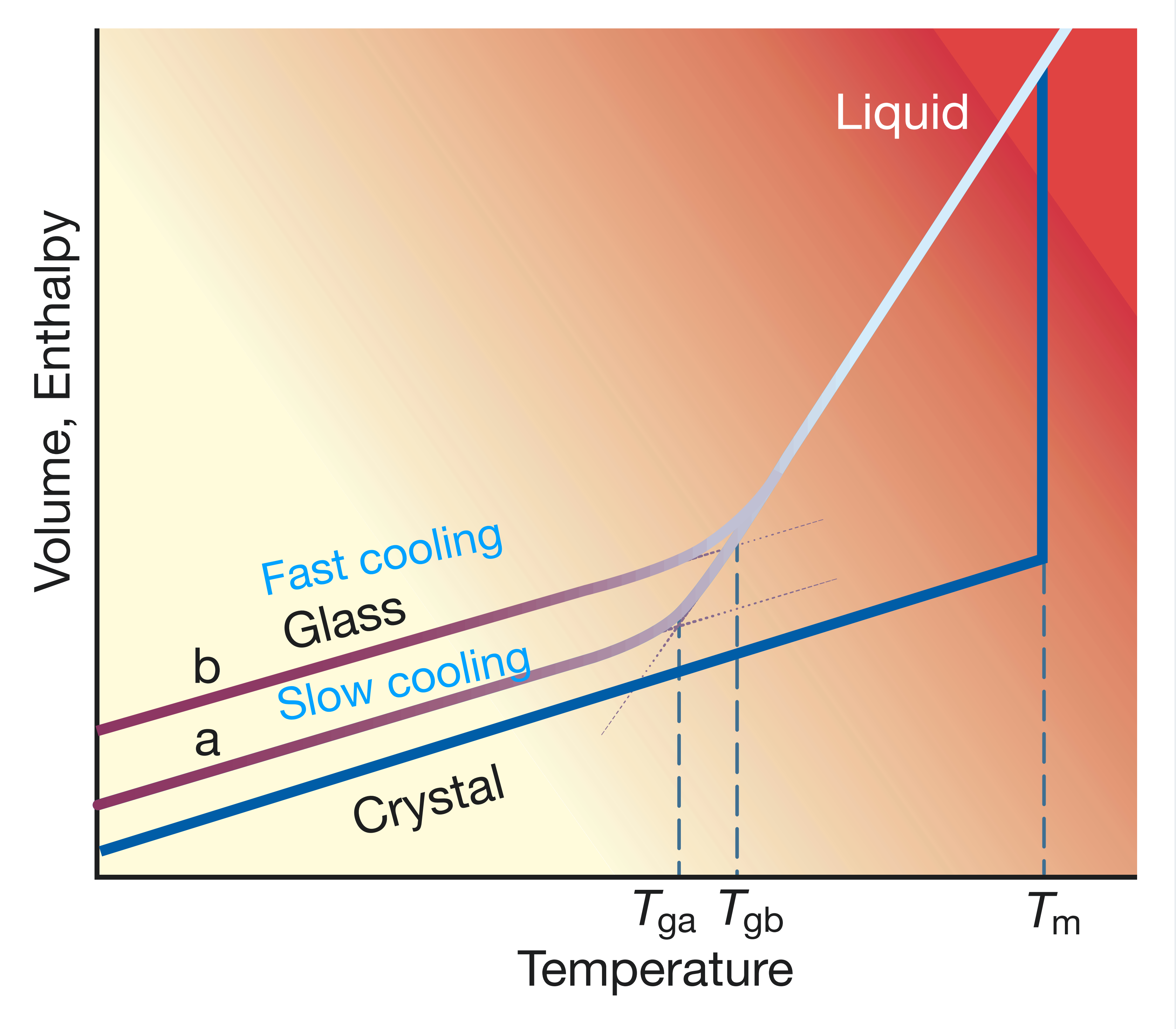


Figure 1 Temperature dependence of a liquid's volume v or enthalpy h at constant pressure. T_m is the melting temperature. A slow cooling rate produces a glass transition at T_{ga}; a faster cooling rate leads to a glass transition at T_{gb}. The thermal expansion coefficient $\alpha_p = (\partial \ln v/\partial T)_p$ and the isobaric heat capacity $c_p = (\partial h/\partial T)_p$ change abruptly but continuously at T_g.

Upon cooling below the freezing point *T*m, molecular motion slows down. If the liquid is cooled sufficiently fast, crystallization can be avoided. Eventually molecules will rearrange so slowly that they cannot adequately sample configurations in the available time allowed by the cooling rate. The liquid's structure therefore appears 'frozen' on the laboratory timescale (for example, minutes). This falling out of equilibrium occurs across a narrow transformation range where the characteristic molecular relaxation time becomes of the order of 100 seconds, and the rate of change of volume or enthalpy with respect to temperature decreases abruptly (but continuously) to a value comparable to that of a crystalline solid. The resulting material is a glass.

The glass transition point, Tg, (temperature at which a supercooled liquid becomes a glass) is for glasses what the melting point, Tm, is for crystalline solids.

Debenedetti and F. H. Stillinger. "Supercooled liquids and the glass transition". *Nature*, Vol 410, 8 March 2001.

Musical chairs= glass formation

People: silicates, chairs: lattice points

1. Speed around chairs (MOBILITY): high mobility, finding lattice sites is easier→ crystal. If high viscosity, slow to find lattice sites (getting stuck)→ glass
2. Arrangement of chairs (LATTICE COMPLEXITY): higher complexity→ glass
3. How fast the music stops (COOLING RATE): sudden stop or fast cooling→ glass

Rate of supercooling for nucleation

$$\text{Rate of Nucleation, } I = \frac{\overbrace{dN}^{\dot{N}}}{dt} \Rightarrow I = \underbrace{N_t \exp\left(-\frac{\Delta G^*}{k_B T}\right)}_{\text{No. of critical sized particles}} s^* \nu \underbrace{\exp\left(-\frac{\Delta H_d}{k_B T}\right)}_{\text{frequency with which they become supercritical}}$$

No. of critical sized particles $\Downarrow$ n^*

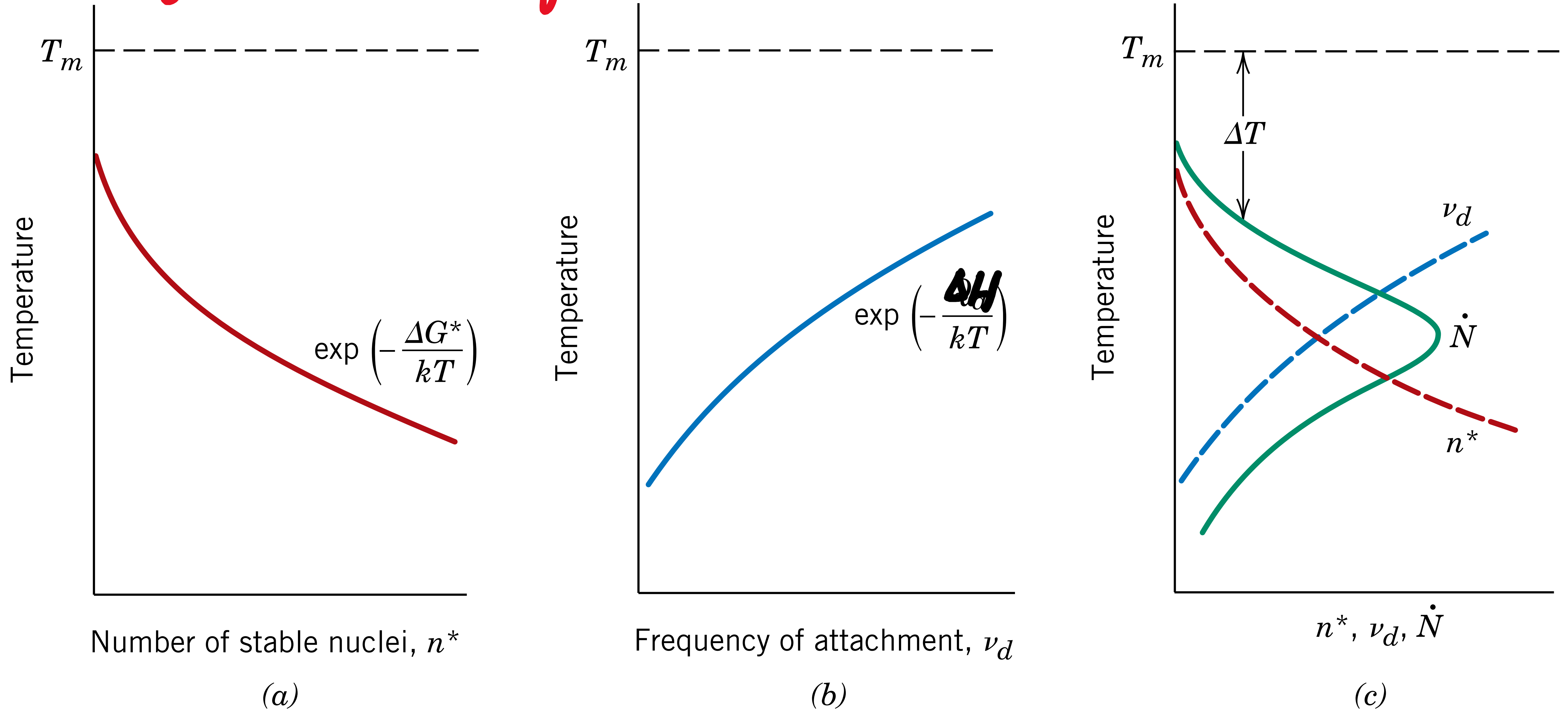
frequency with which they become supercritical $\Downarrow$ ν_d

N_t = no. of particles per unit vol.

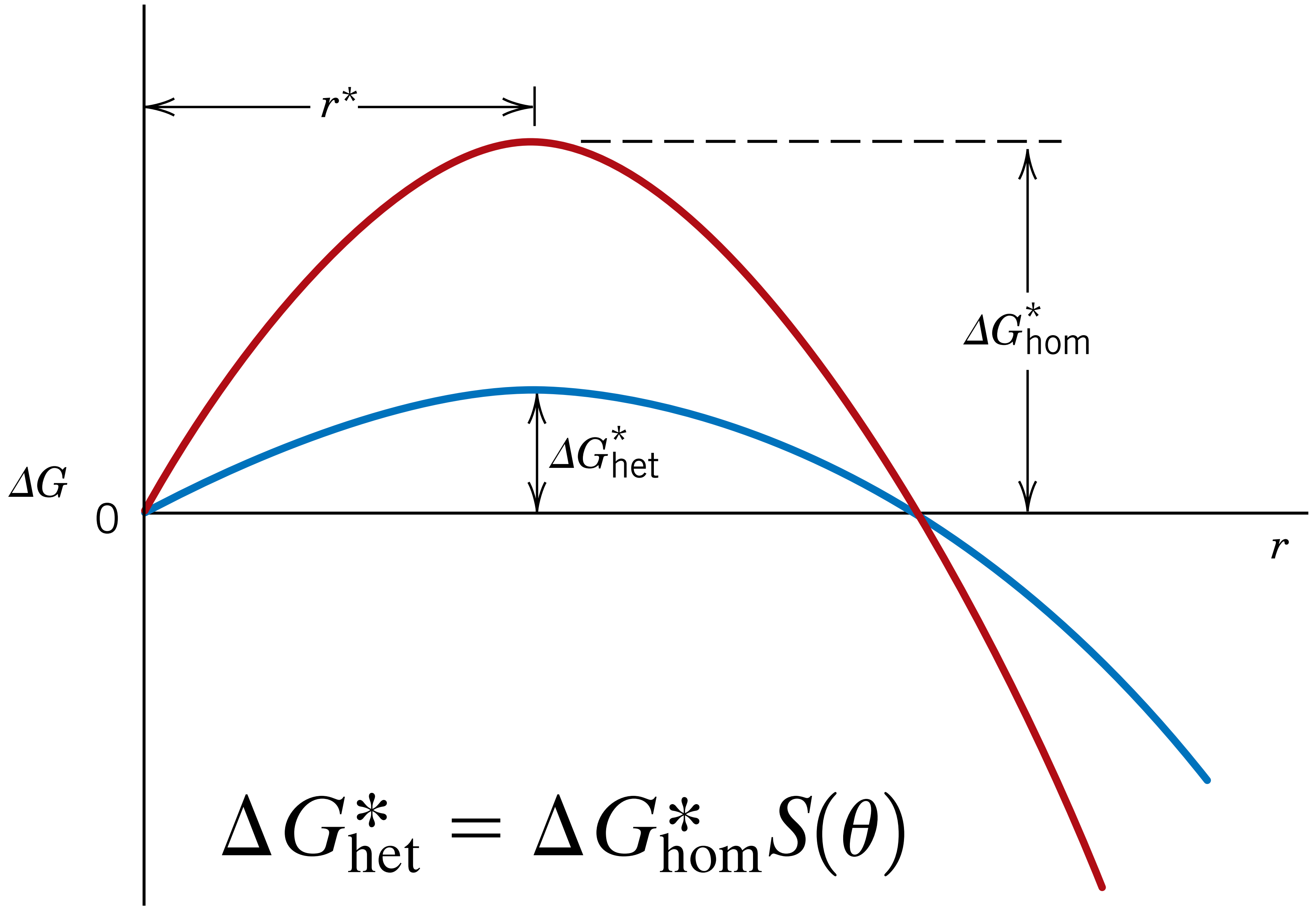
ν = lattice vibration frequency

ΔH_d = activation barrier to jump into nucleus

ΔG^* = freeenergy to form critical nucleus

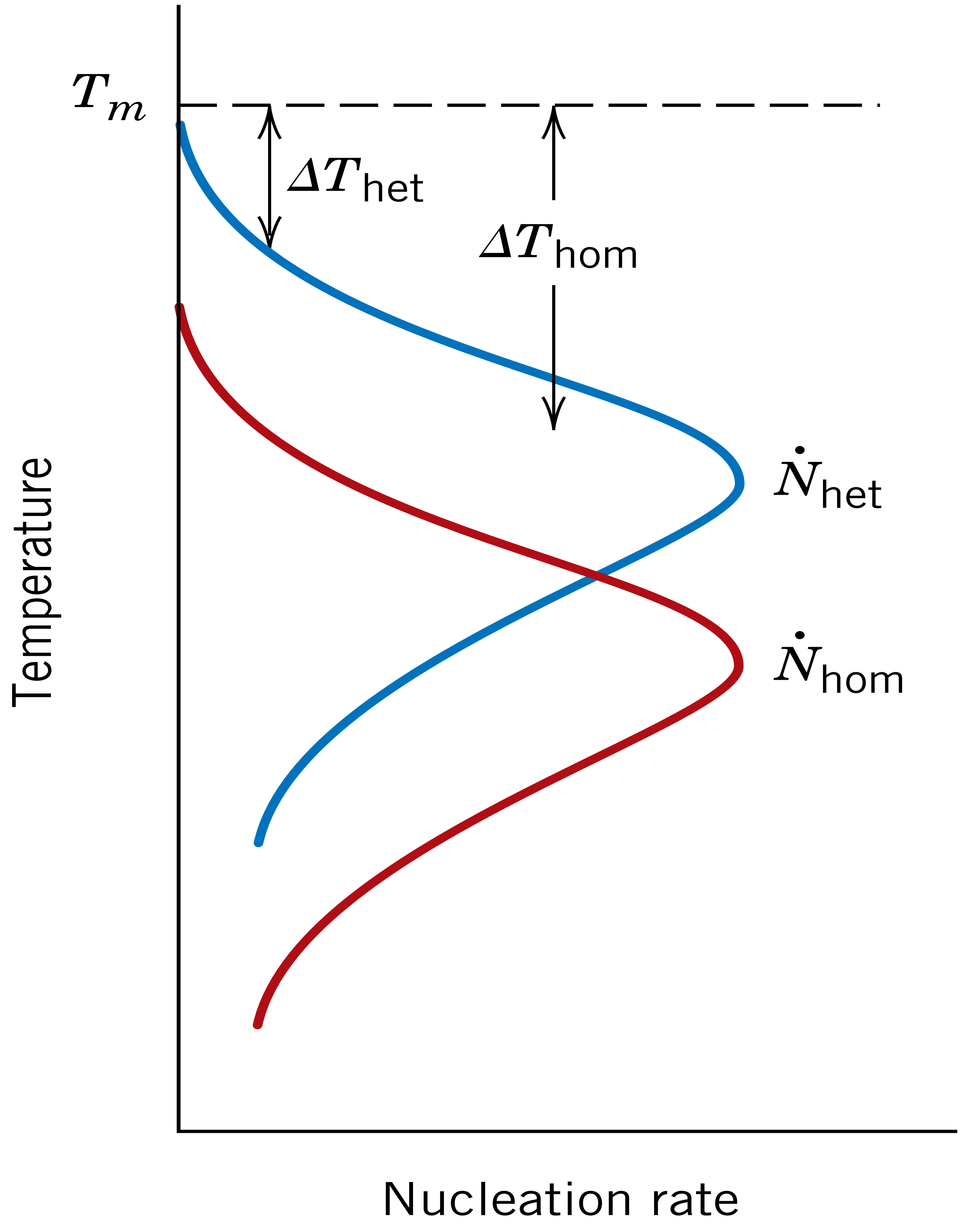


Smaller rate of supercooling for heterogeneous nucleation



$$\Delta G^*_{het} = \Delta G^*_{hom} S(\theta)$$

Heterogeneous nucleation occurs more readily due to lower free energy to form critical nucleus



ΔT= supercooling rate

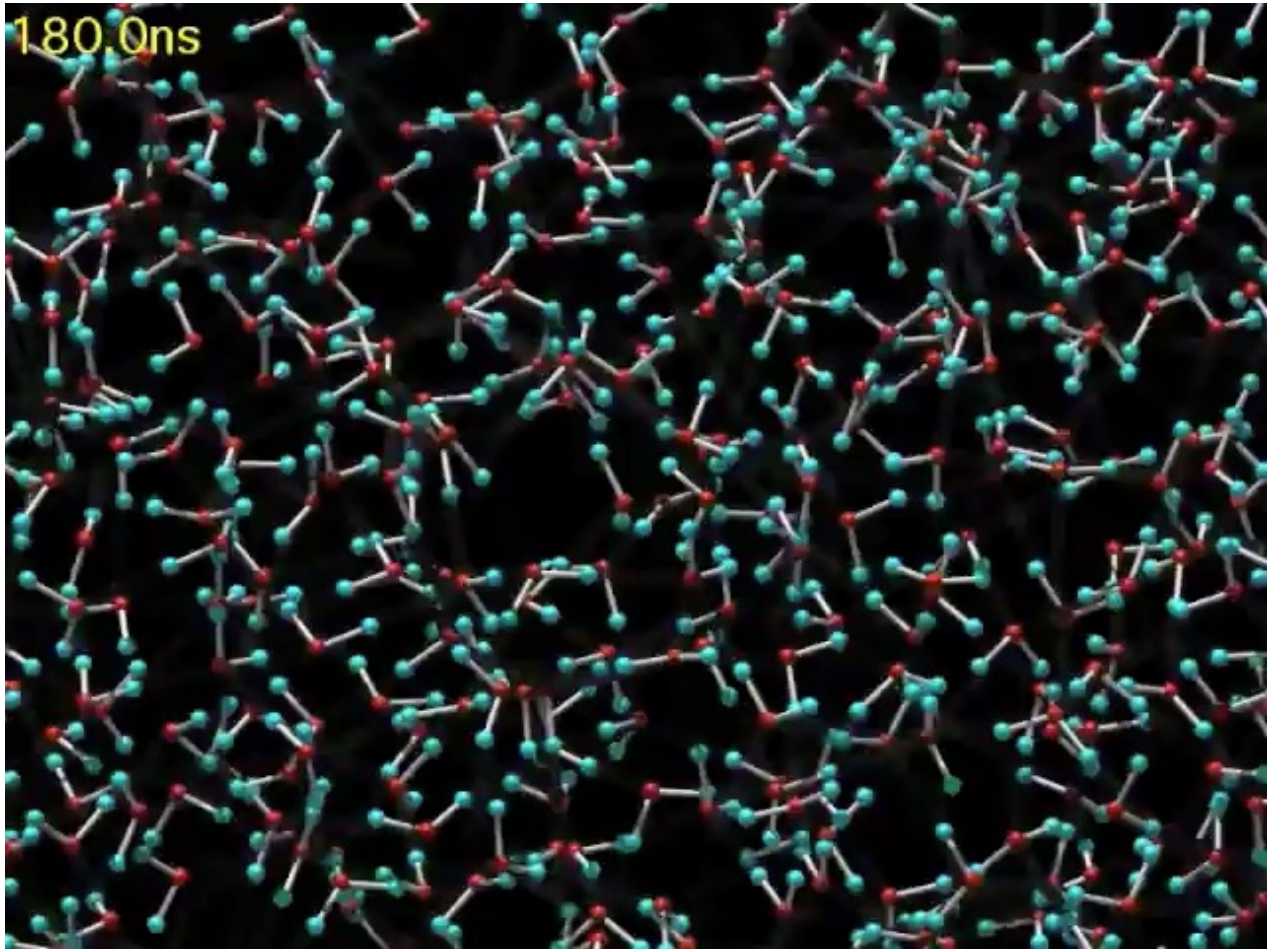
Energy landscape of glasses

DOI: 10.2320/matertrans.45.1163

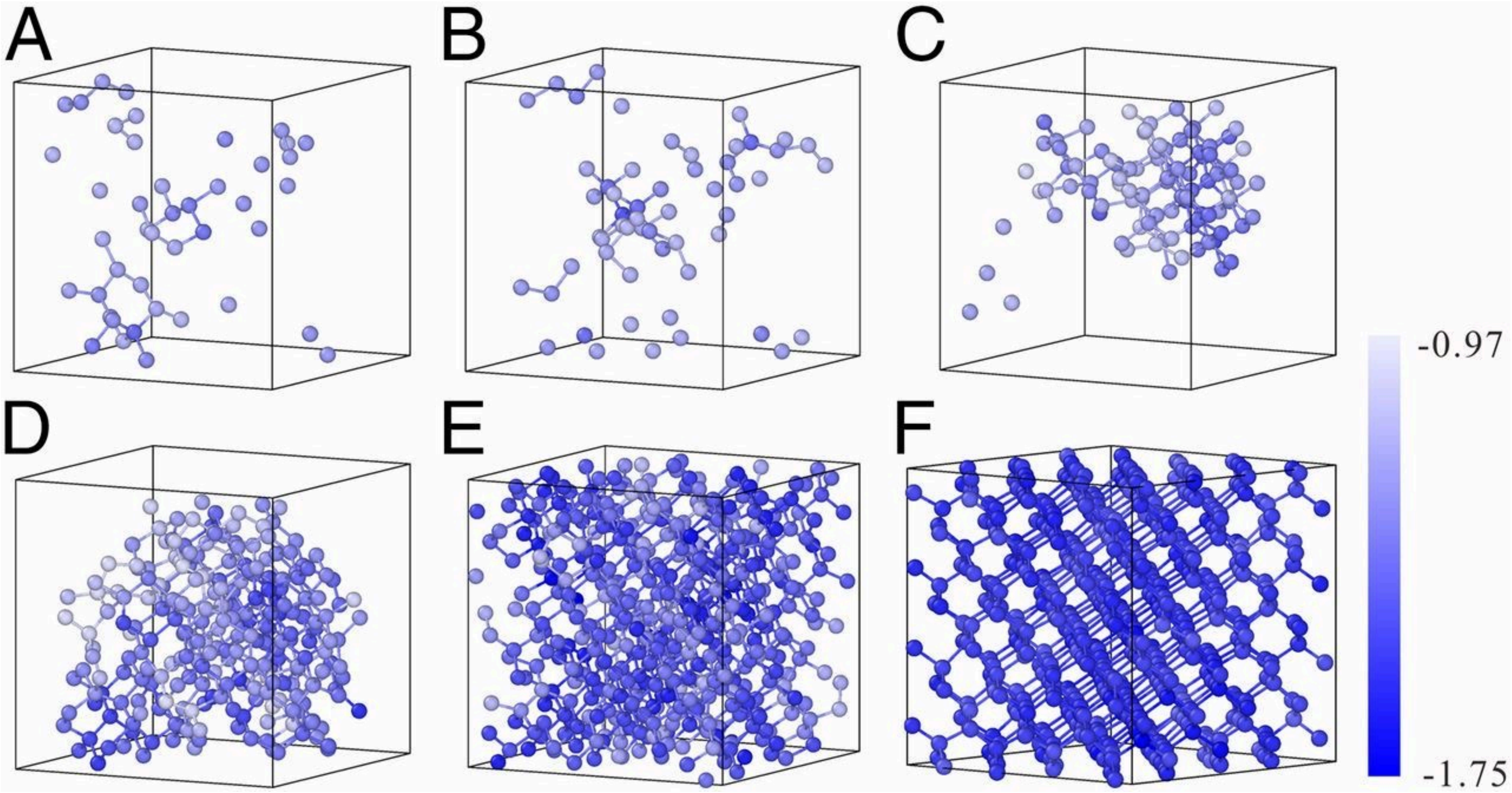
A video on supercooled water

You can try this experiment at home…

Molecular dynamics simulation of water crystallizing into ice



Molecular dynamics simulations of crystallization of silicate



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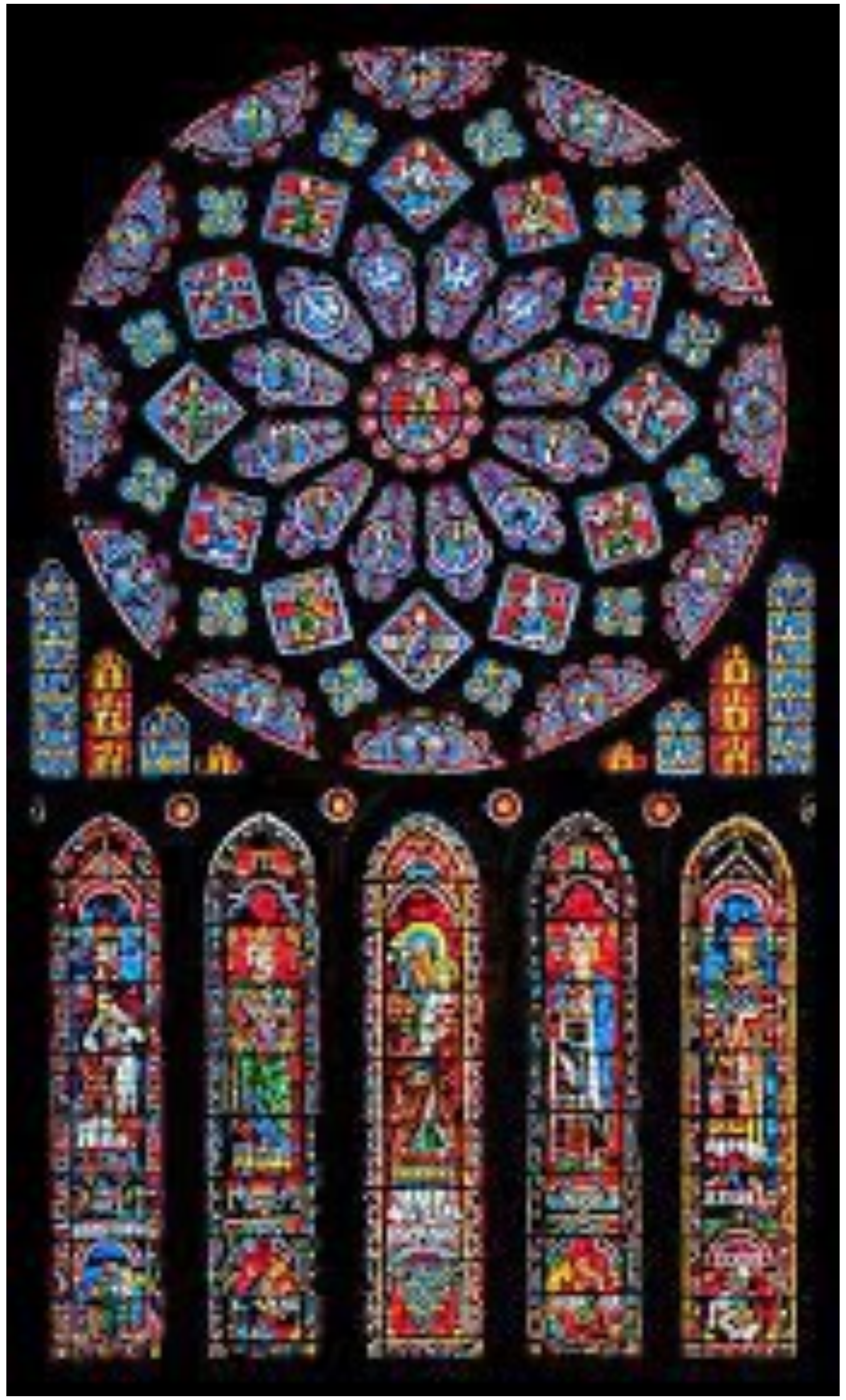
Are medieval windows melting?



Glass does not flow

https://www.scientificamerican.com/article/fact-fiction-glass-liquid/