MIT 3.071
Amorphous Materials

1: Fundamentals of the Amorphous State

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What is glass (amorphous solid)?

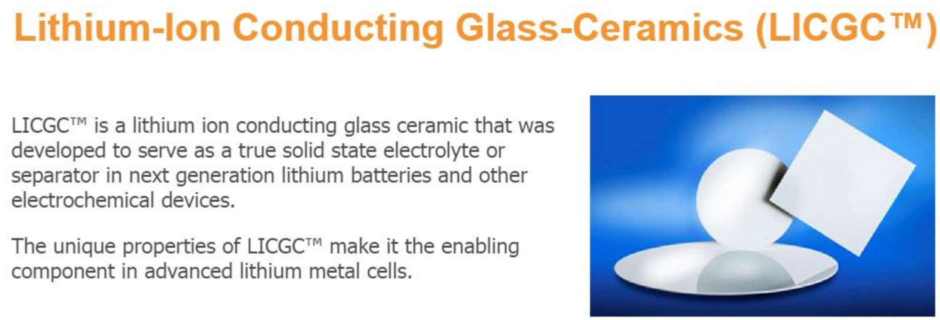
- Mechanical properties
  - Brittle, fragile, stiff
- Optical properties
  - Transparent, translucent

"A room-temperature malleable glass" ($As_{60}Se_{40}$)

Video courtesy of IRradiance Glass Inc.

What is glass (amorphous solid)?

- Electrical properties
  - Insulating
- Chemical properties
  - Durable, inert
- Man-made
  - Obsidian (volcanic activity)
  - Tektite (meteorite impact)
  - Fulgurite (lightning strike)



Amorphous materials are ubiquitous

- Glass cover
- Camera lens
- TFT display
- Dielectrics
- Circuit packaging

? Metallic glass case

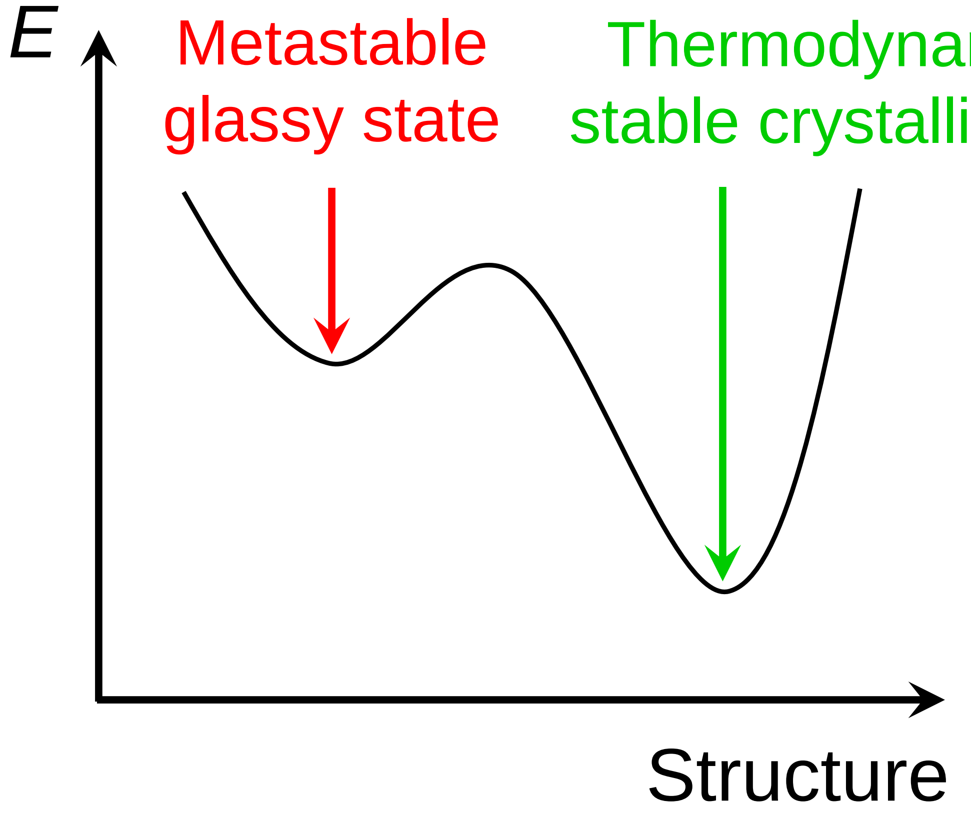
? Phase change memory

? Solid state battery

and many more…

What is glass (amorphous solid)?

- A metastable solid with no long-range atomic order

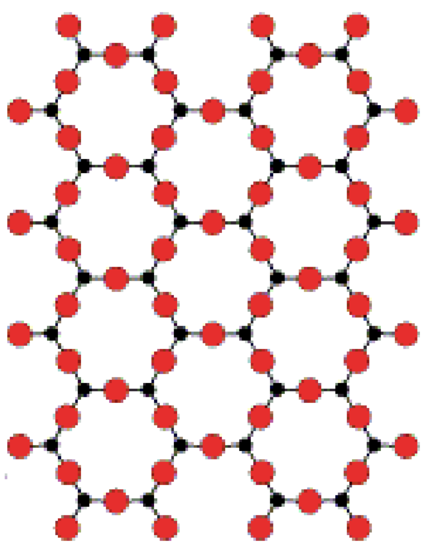


- ✓ Glasses are metastable with respect to their stable crystalline phase
- ✓ Atoms can rearrange to form a more stable state given enough time and thermal energy

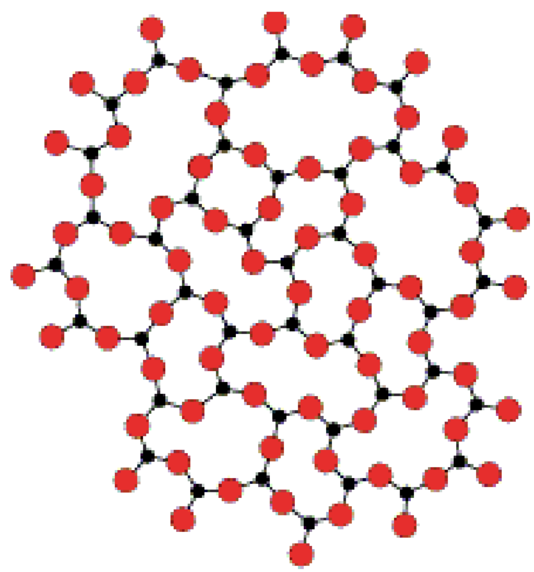
What is glass (amorphous solid)?

- A metastable solid with **no long-range atomic order**

Consider a fictitious A_2O_3 2-D compound:



A_2O_3 crystal



A_2O_3 glass

- ✓ Short-range order is preserved (AO_3 triangles)
- ✓ Long-range order is disrupted by changing bond angle (mainly) and bond length
- ✓ Structure lacks symmetry and is usually isotropic

Zachariasen's Random Network Theory (1932)

Glass consists of a continuous atomic network

Figure of Microphotometer records of X-ray diffraction patterns removed due to copyright restrictions. See Figure 3: Warren, B.E., and J. Biscce. "The Structure of Silica Glass by X-ray Diffraction Studies." *J. Am. Cer. Soc.* 21 (1938): 49-54.

- Absence of small angle scattering
  - Continuous structure without micro-voids
- Broad diffraction peak
  - Size of ordered region < 8 Å (Scherrer equation)
  - Unit cell size of cristobalite: 7.1 Å

Glass is NOT a collection of extremely small crystals

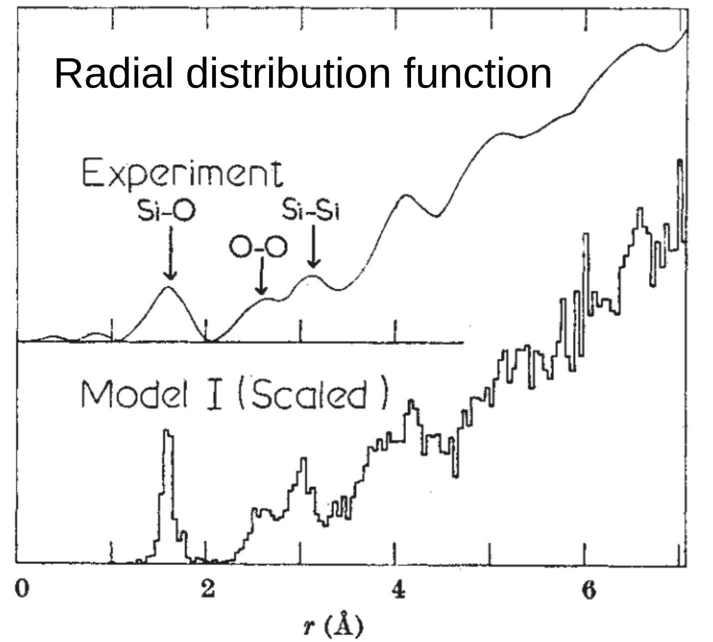
J. Am. Cer. Soc. **21**, 49-54 (1938).

Random network model of silica glass (SiO_2)

Image of vitreous silica model removed due to copyright restrictions. See Getty Images.

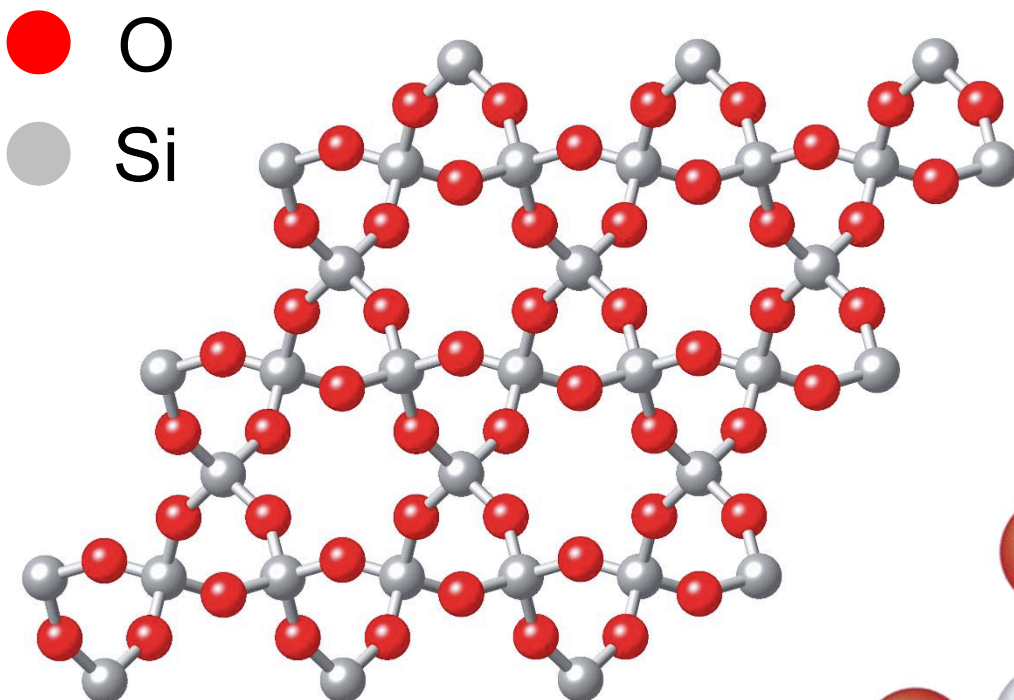
Nature **212**, 1353 (1966).

Now in the Science Museum, London

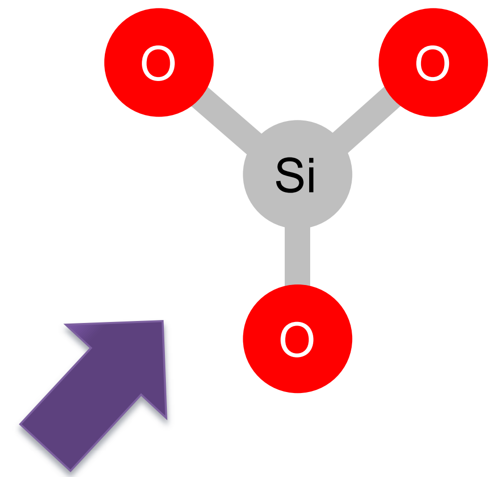


Excellent agreement between XRD and ball-and-stick model constructed according to the random network model

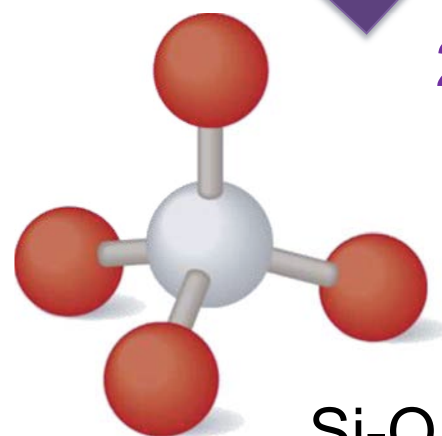
Direct atomic imaging of bilayer silica glass



Quartz crystal



2-D projection



Si-O tetrahedron

Direct atomic imaging of bilayer silica glass

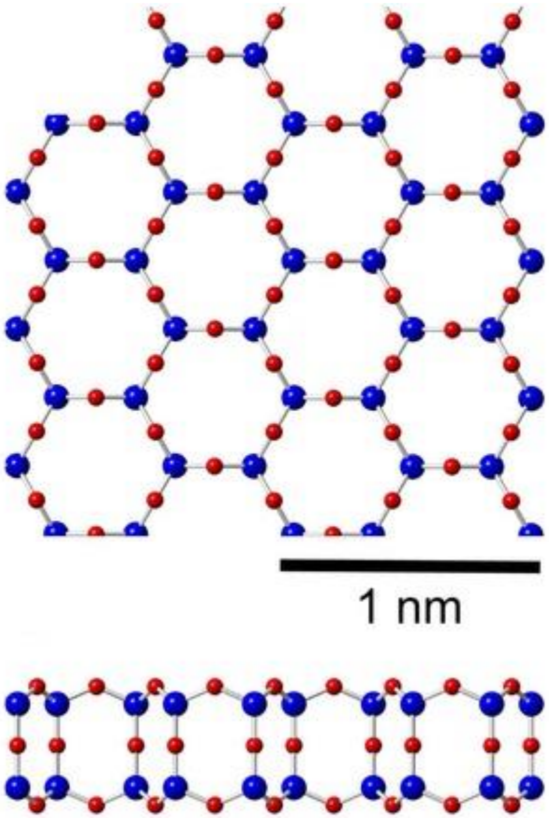


Figure removed due to copyright restrictions. See Figure 1: Huang, P.Y., et al. "Direct Imaging of a Two-Dimensional Silica Glass on Graphene." *Nano Lett*. 12 (2012): 1081-1086.

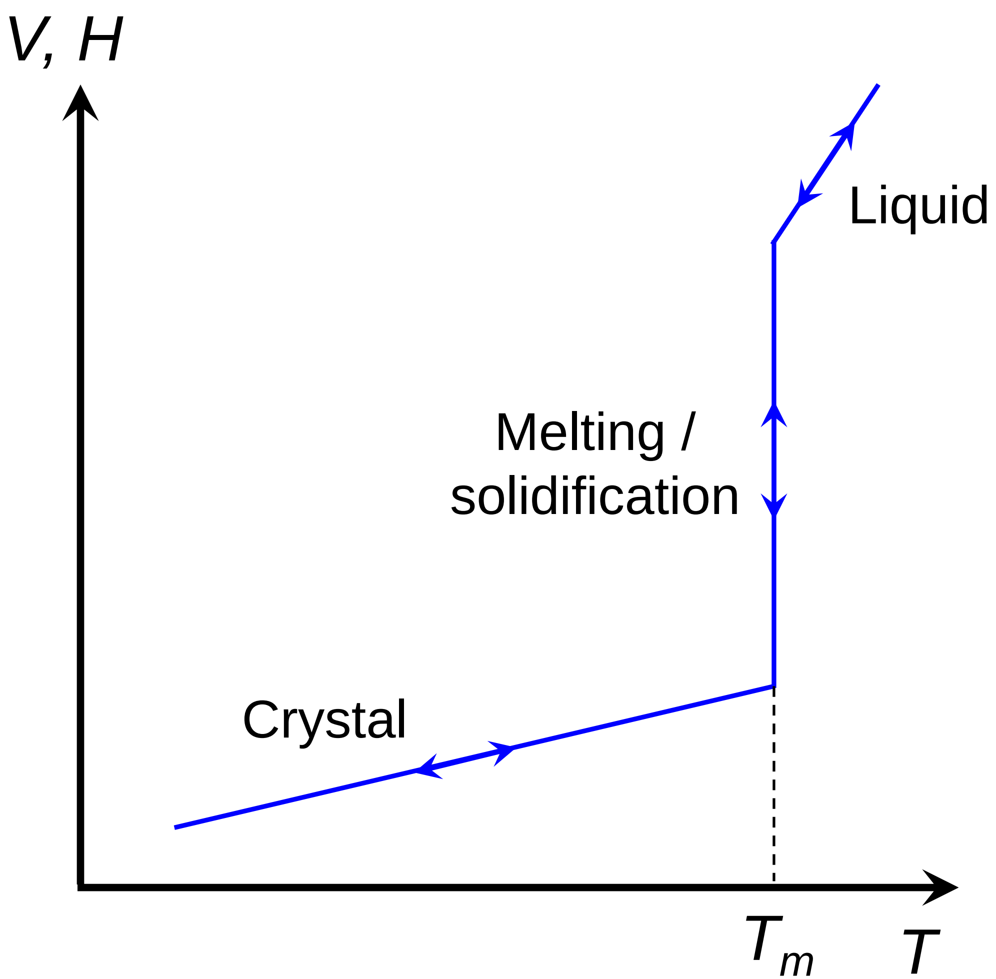
STEM images of 2-D silica crystal and glass

Sci. Rep. **3**, 3482 (2013).

Nano Lett. **12**, 1081-1086 (2012).

- Article: Anne Ju "Shattering records: Thinnest glass in Guinness book." *Cornell Chronicle*. September 12, 2013.

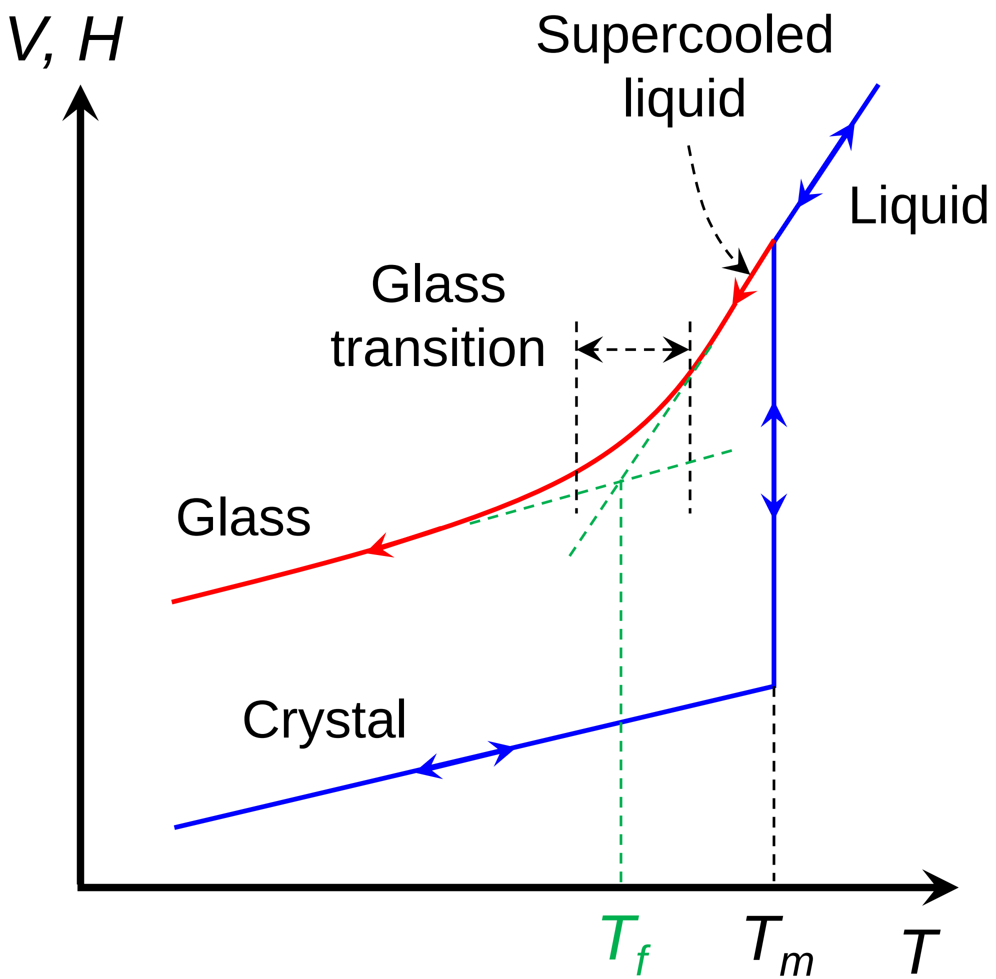
Glass formation from liquid



When the system is kept in thermal equilibrium:

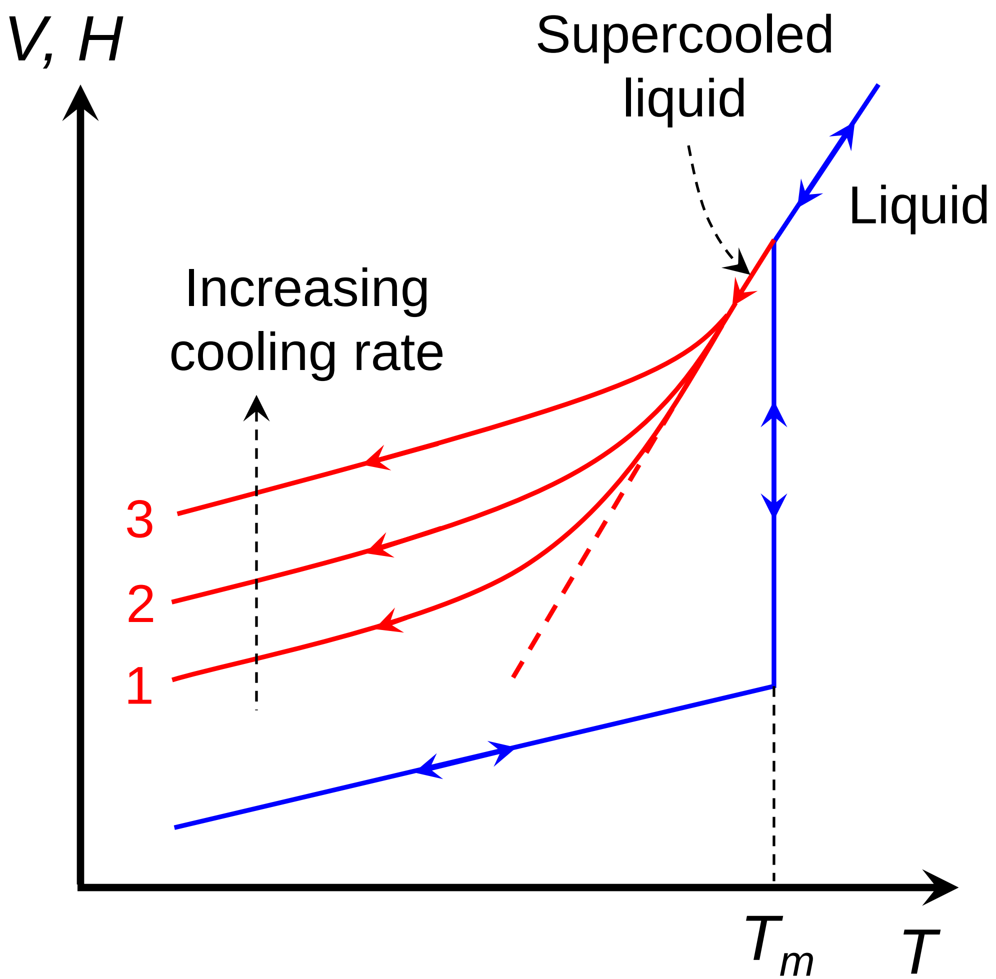
- ✓ First-order liquid-solid phase transition
- ✓ Discontinuity of extensive thermo-dynamic parameters (e.g., *V* and *H*)
- ✓ Reversible process

Glass formation from liquid



- Supercooled liquid transforms to the glassy state when crystallization is kinetically suppressed
- Extensive variables remain continuous during glass transition
- The glassy state is different from super-cooled liquid
- T_f : Fictive temperature

Glass formation from liquid

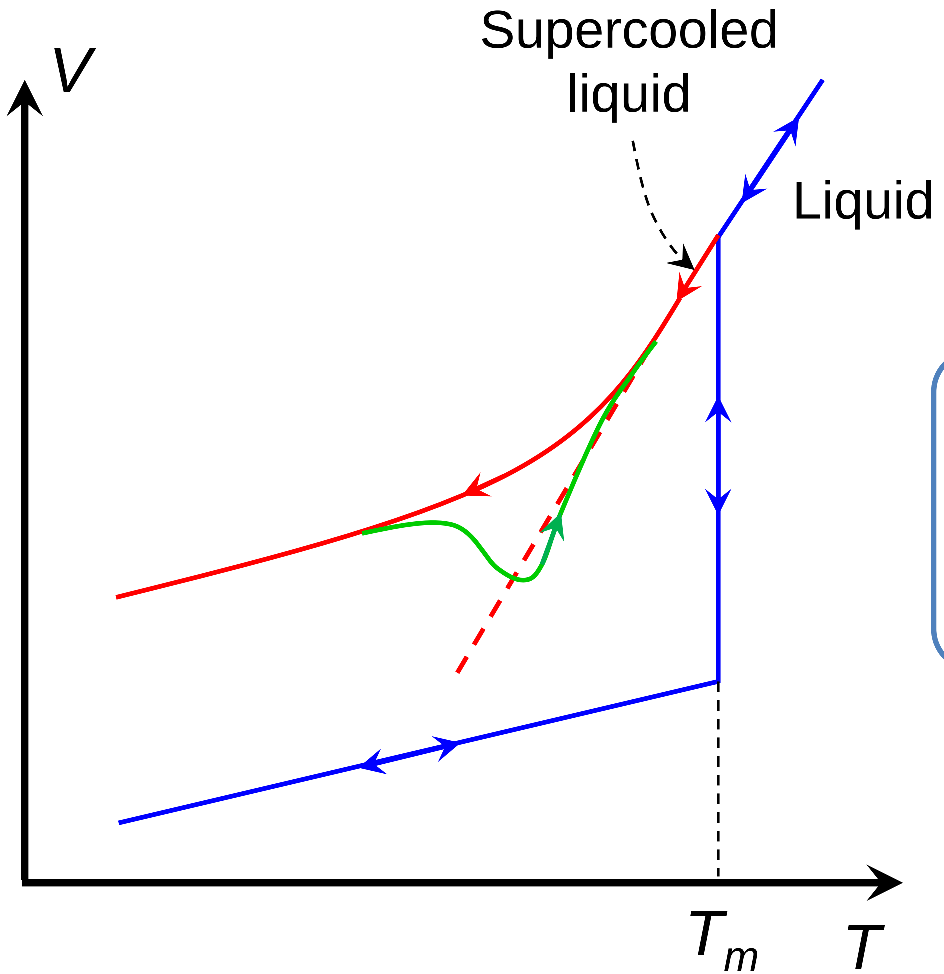


- ✓ Glasses obtained at different cooling rates have different structures
- ✓ With increasing cooling rate:
  - ❖ $V_1 < V_2 < V_3$

    Free volume increases
  - ❖ $H_1 < H_2 < H_3$

    Configurational entropy increases
  - ❖ $T_{f,1} < T_{f,2} < T_{f,3}$

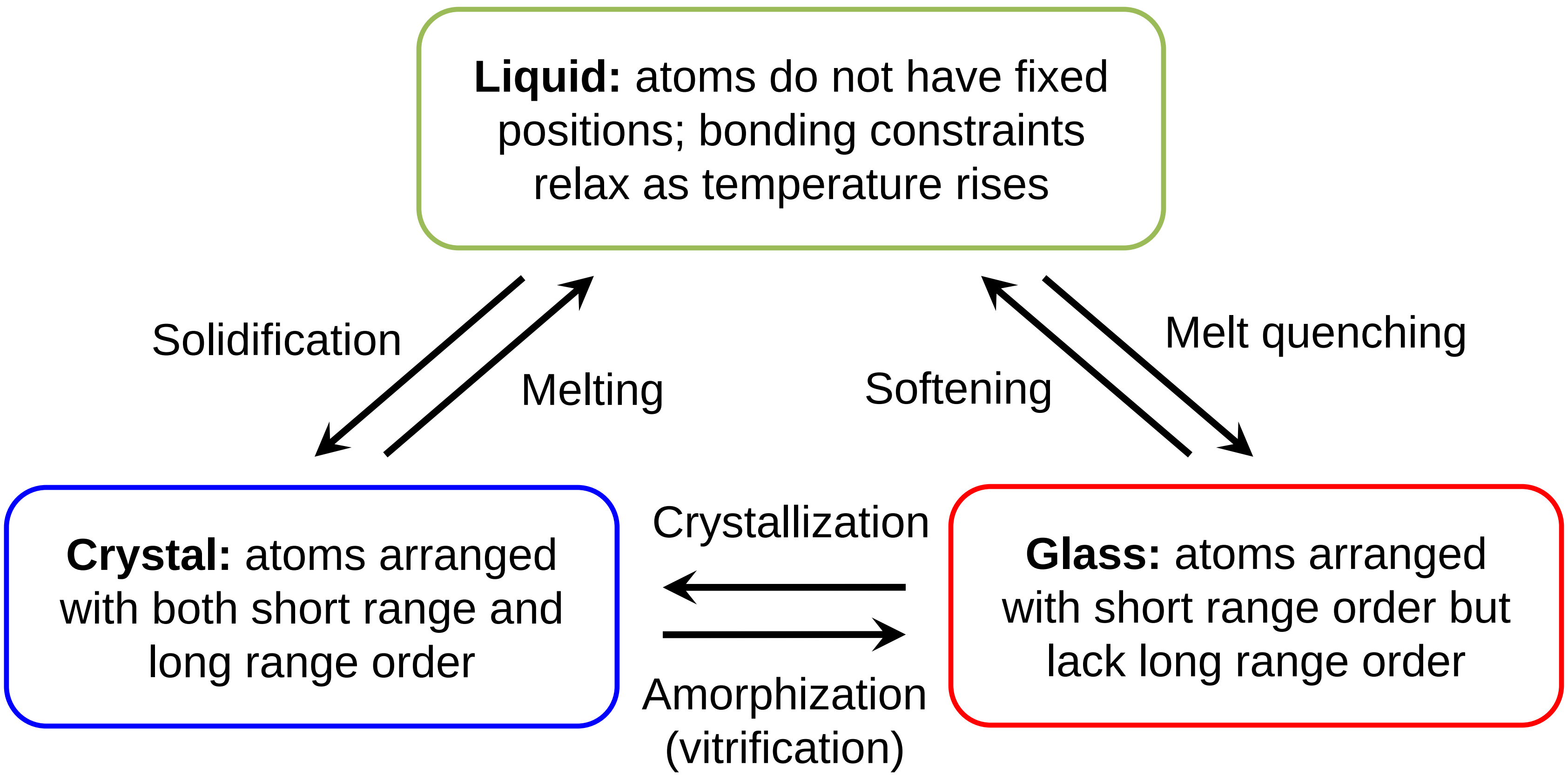
Glass formation from liquid



The heating curve never retraces the cooling curve during glass transition due to structural relaxation

What is glass (amorphous solid)?

- A metastable solid with no long-range atomic order



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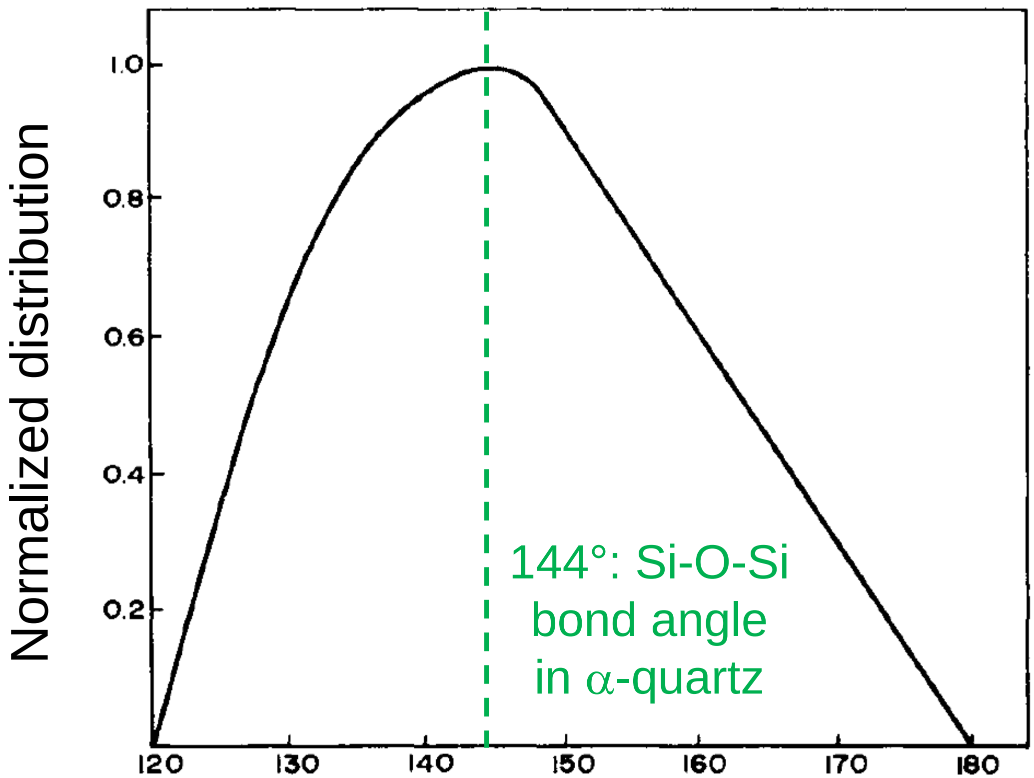


Si-O-Si bond angle in silica glass

Si-O-Si bond-bending constraint is relaxed at the forming temperature of silica glass

Si-O-Si bond angle distribution in silica glass measured by XRD

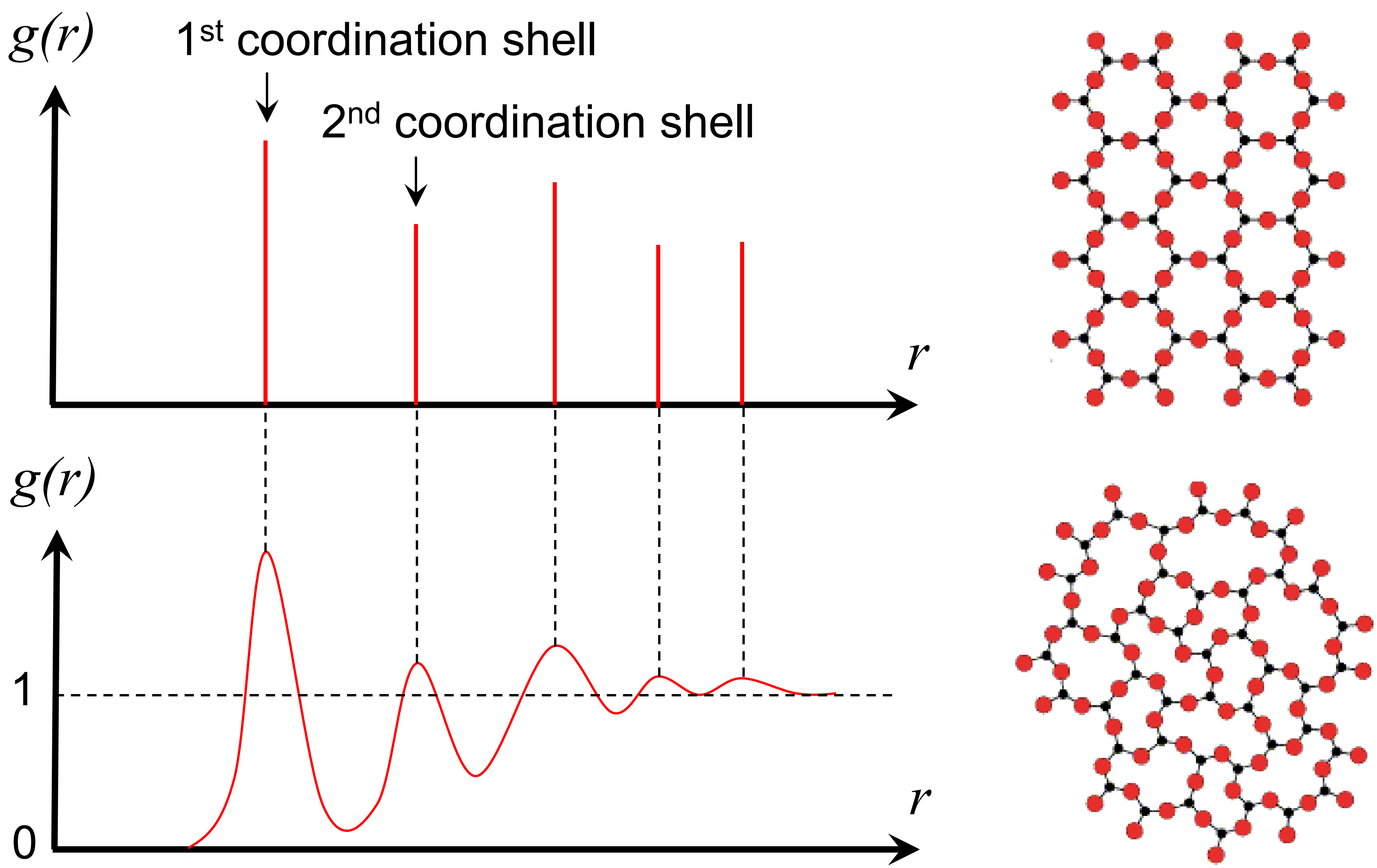
J. Appl. Cryst. **2**, 164 (1969)

Quantitative description of glass structure

- Structural descriptions of amorphous materials are always statistical in nature
- Pair distribution function (PDF): $g(r)$
  - Consider an amorphous material with an average number density of atom given by:

    $\rho = n/V$ n : number of atoms V : material volume
  - The number density of atoms at a distance r from an origin atom is given by $\rho \cdot g(r)$
  - When $r \to 0, g \to 0$
  - When $r \to \infty, g \to 1$

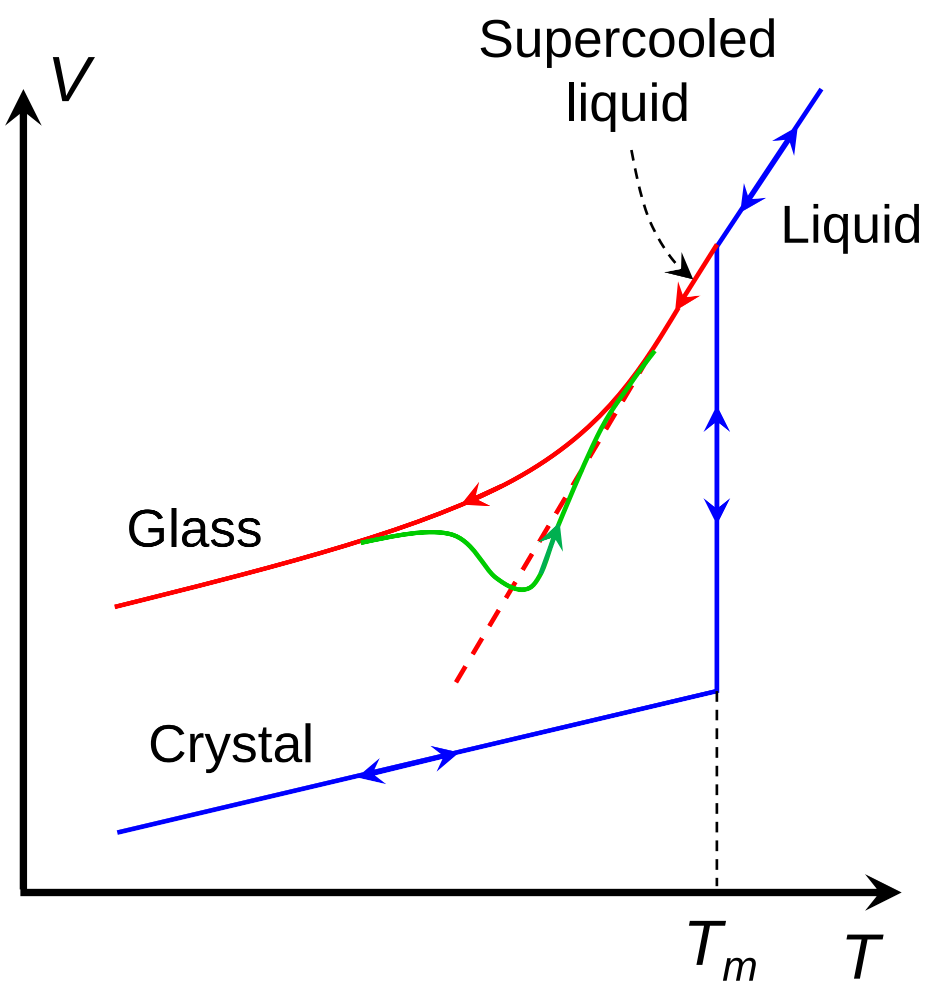
PDFs of ideal (hard sphere) crystals vs. glasses



Quantitative description of glass structure

- Pair correlation function $h(r)$
  - $h(r) = g(r) - 1$
- Radial distribution function (RDF): $J(r)$
  - $J(r) = 4\pi r^2 \rho \cdot g(r)$
  - $J(r)dr$ gives the number of atoms located between r and $r + dr$ away from the origin atom
  - The area under the RDF curve gives the number of atoms
- Reduced radial distribution function (rRDF): $G(r)$
  - $G(r) = 4\pi r^2 \rho \cdot [g(r) - 1] = 4\pi r^2 \rho \cdot h(r)$

Summary



- The amorphous state is metastable
- Amorphous structures possess short-range order and lack long-range order
- Amorphous materials can be obtained from liquid by melt quench
- Melt quench is a continuous, irreversible process involving phase change
- Glass properties depend on their thermal history

After-class reading list

- Fundamentals of Inorganic Glasses
  - Ch. 1 & 2
- Introduction to Glass Science and Technology
  - Ch. 1