MIT 3.071
Amorphous Materials

1: Fundamentals of the Amorphous State

Juejun (JJ) Hu

Contact Information

- Juejun (JJ) Hu, Rm 13-4054
- Research interests
  - We work with light
  - Optics & photonics
  - Novel optical materials (including amorphous materials)
  - Optical sensing, imaging, communications, solar energy, and many other topics related to light

References

- Fundamentals of Inorganic Glasses
  - Arun Varshneya, Academic Press (1994)
  - Arun Varshneya, John Mauro, Third Edition (2019)
  - Google Books, Google Books
- Introduction to Glass Science and Technology
  - James E. Shelby, Royal Society of Chemistry (2005)
  - RSC Publishing
- Glass Science, 2nd Edition
  - Robert H. Doremus, Wiley (1994)
- Springer Handbook of Glass
  - J. D. Musgraves, J. Hu, L. Calvez (Eds.), Springer (2020)

Class organization

- Modules
  - Lectures: MW 2:30-4 (virtual, will be recorded)
  - In-class demos
  - Guest Lectures (TBD)
  - Individual project meetings
  - Final project presentation
  - Pick-your-own-topic lectures
- Canvas site
  - Announcements, lecture slides, assignments, and solutions will be posted online
  - Spring 2021 Canvas Link

Pick-your-own-topic lectures

- You pick the topic, and I present
  - Submit your topic proposal by Apr. 15
  - Topics must be relevant to amorphous materials
  - Think about depth and breath
  - If there are more topics proposed than lecture slots available, we will set up a voting system

Grading policy

- Homework assignments: 30%
  - Three PSets
  - Discussions are allowed and encouraged; but you are supposed to complete the assignments independently
- Design review project: 70%
  - Project proposal: 20%
  - Term paper: 30%
  - Final presentation: 20%

Design Review Project

- Project proposal
  - Page limit: 5 (including figures, tables, and references); Font: Times New Roman 12; Page format: letter size with 1 inch margin
  - Motivation and significance; Brief review of state-of-the-art; Proposed technical approach; Anticipated outcome
  - 1 executive summary slide
- Project presentation
  - Time limit and format: TBD

Design Review Project

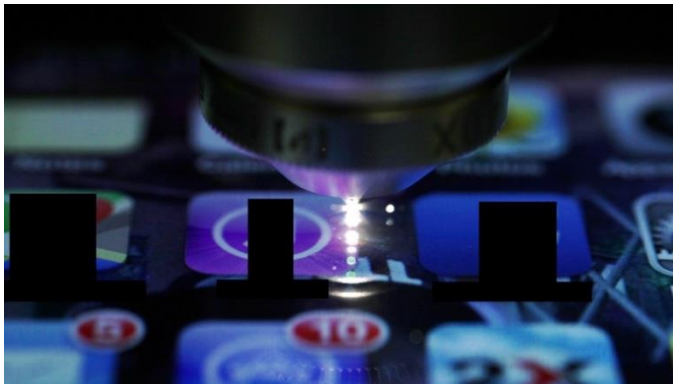
- TTerm paper
  - Page limit: 8 (including figures, tables, and references); Font: Times New Roman 12; Page format: letter size with 1 inch margin
  - Motivation and significance; Current state-of-the-art; Research methodology; Results and discussion; Conclusions
- Document templates are posted on the course site

Project topic examples



[Glass box cracks at 1,353 feet above: is it still safe?]

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Can we make smart phones smarter with built-in photonics?

Opt. Express **22**, 15473 (2014).

Courtesy of Jerome Lapointe, Mathieu Gagné, Ming-Jun Li, and Raman Kashyap. License: CC BY.



[Where is my metallic glass cased iPhone?]

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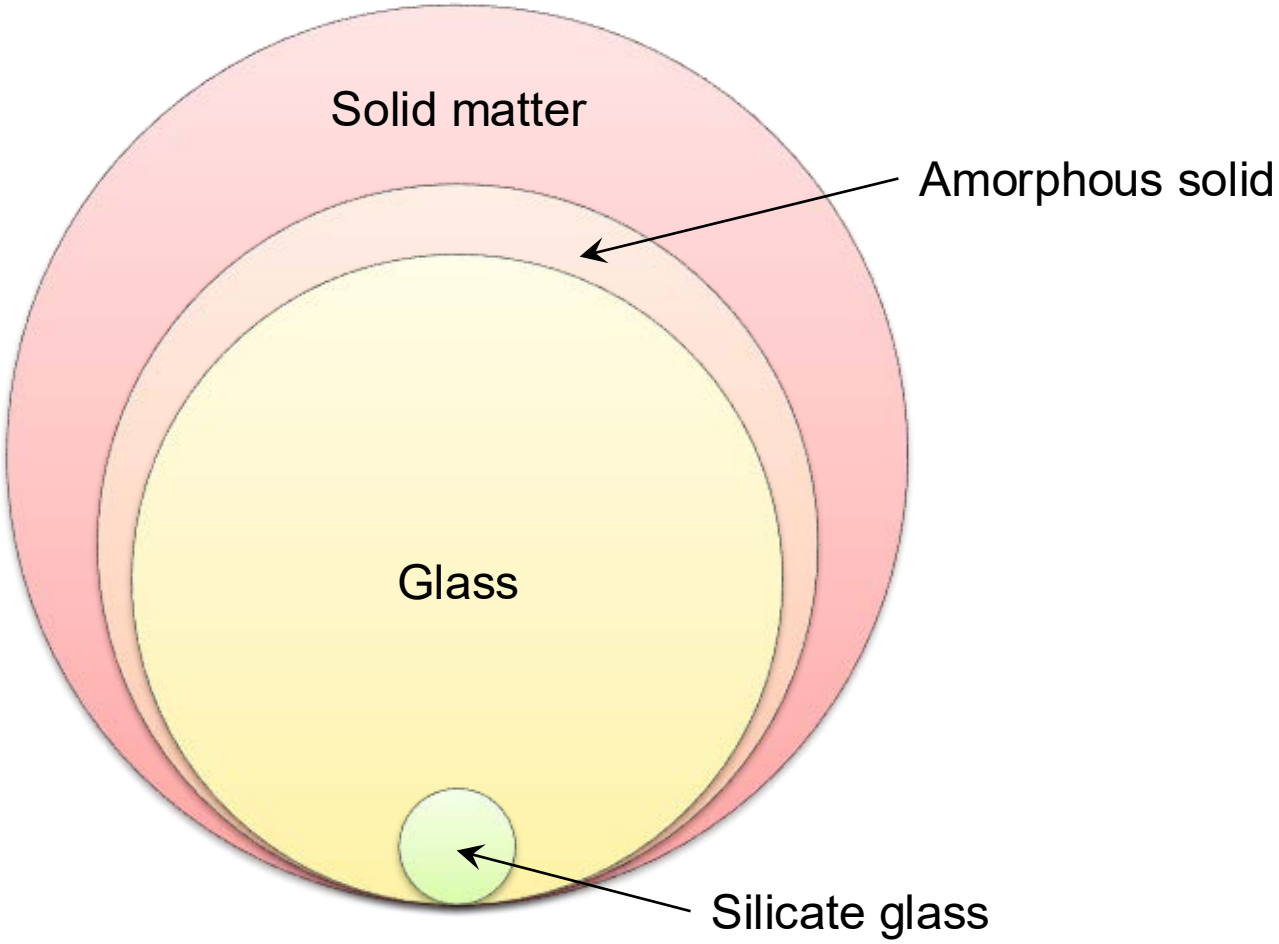


Are smart windows technologically and economically viable?

Evaluation criteria

- Proposals and papers
  - Intellectual merits (75%): soundness, depth, thoroughness, inventiveness
  - Presentation (25%): logical coherence, clarity, conciseness
- In-class presentation
  - Timing (20%)
  - Presentation (40%): logical coherence, clarity, conciseness
  - Intellectual merits (40%): soundness, depth, thoroughness, inventiveness

What is glass (amorphous solid)?





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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.

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What is glass (amorphous solid)?

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



Metallic glass

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The stone age… or the glass age?



Source: public domain



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"Obsidian is capable of producing an edge sharper than high quality steel razor blades…. What need could there be for a replacement material? The Aztecs didn't develop their use of metal because they couldn't see beyond obsidian."

An Obsession with Obsidian

Amorphous materials are ubiquitous



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

? Metallic glass case

? Phase change memory

? Solid state battery

and many more…

A modest proposal to update the textbooks

The new proposed definition of glass for non-specialists is:

'Glass is a non-equilibrium, non-crystalline state of matter that appears solid on a short time scale but continuously relaxes towards the liquid state.'

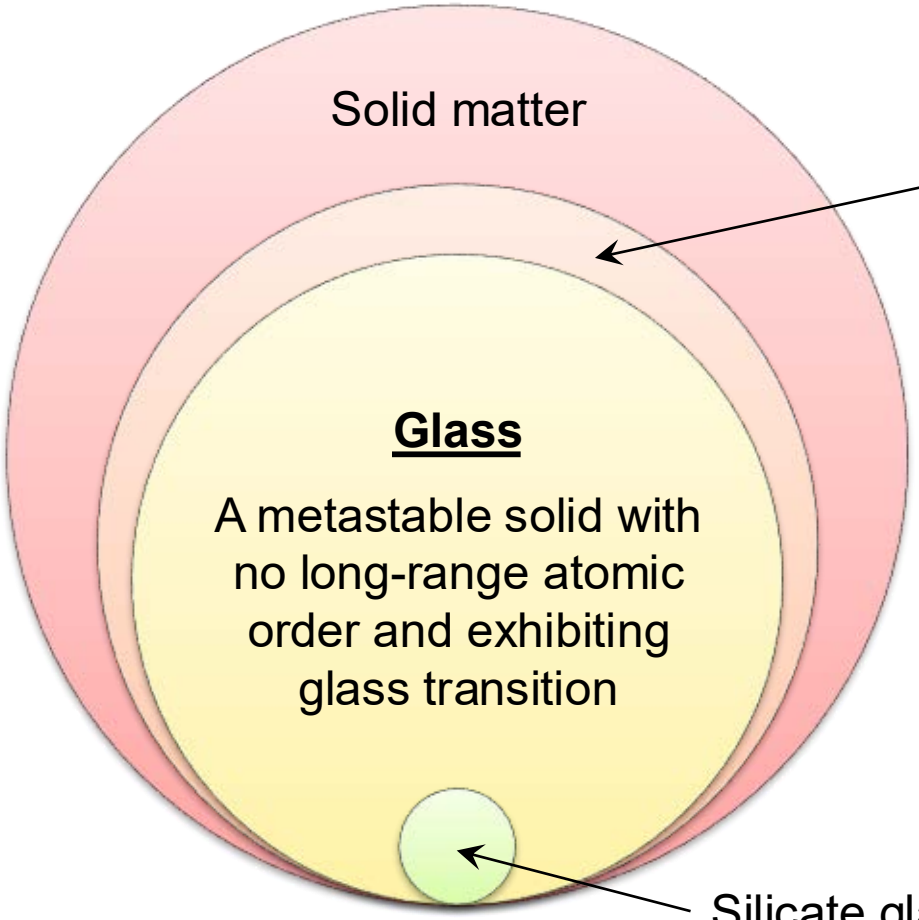
The two materials scientists also have a more detailed definition for experts:

'Glass is a non-equilibrium, non-crystalline condensed state of matter that exhibits a glass transition. The structure of glasses is similar to that of their parent supercooled liquids (SCL), and they spontaneously relax toward the SCL state. Their ultimate fate, in the limit of infinite time, is to crystallise.'

"The glassy state of matter: Its definition and ultimate fate," *J. Non-Cryst. Solids* **471**, 490 (2017)

Edgar D. Zanotto, John C. Mauro, "The glassy state of matter: Its definition and ultimate fate," *Journal of Non-Crystalline Solids*, Volume 471,2017, Pages 490-495. https://www.sciencedirect.com. Used with permission.

What is amorphous solid (glass)?

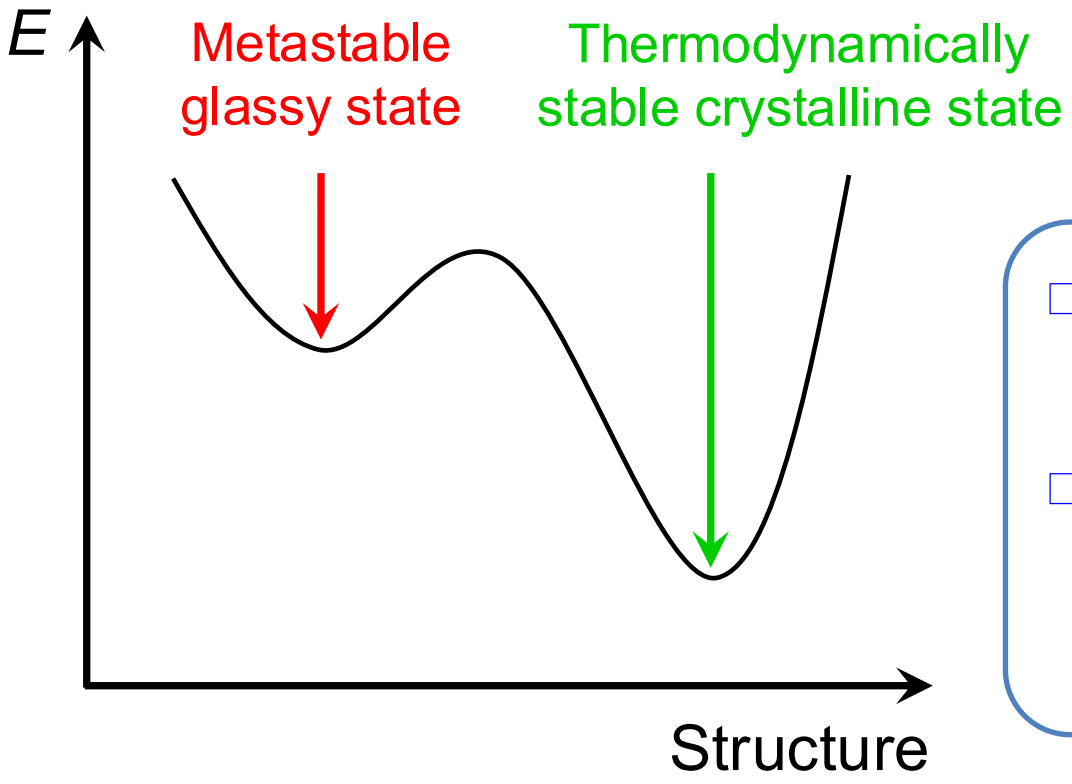


Amorphous solid

A metastable solid with no long-range atomic order

What is amorphous solid (glass)?

- A metastable solid with no long-range atomic order (and exhibiting glass transition)

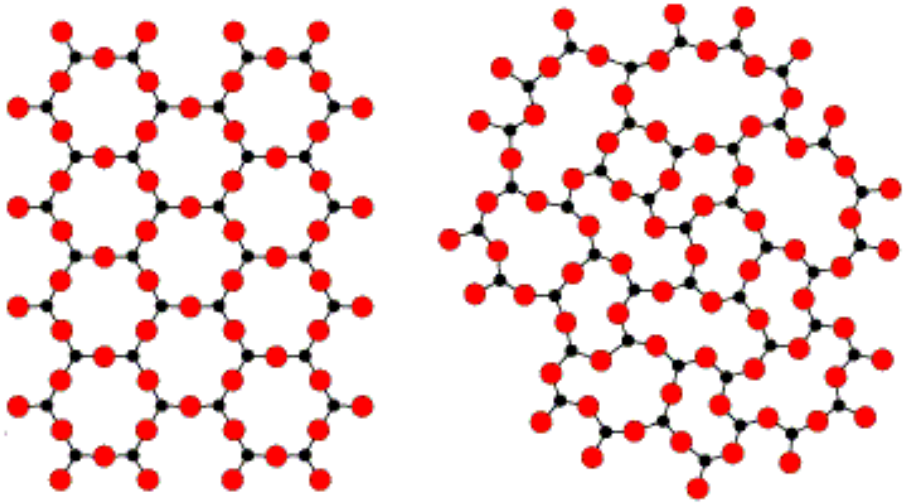


- Glasses are metastable with respect to their stable crystalline phase
- Atoms can rearrange to form a more stable state given enough time and thermal energy

What is amorphous solid (glass)?

- A metastable solid with no long-range atomic order (and exhibiting glass transition)

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

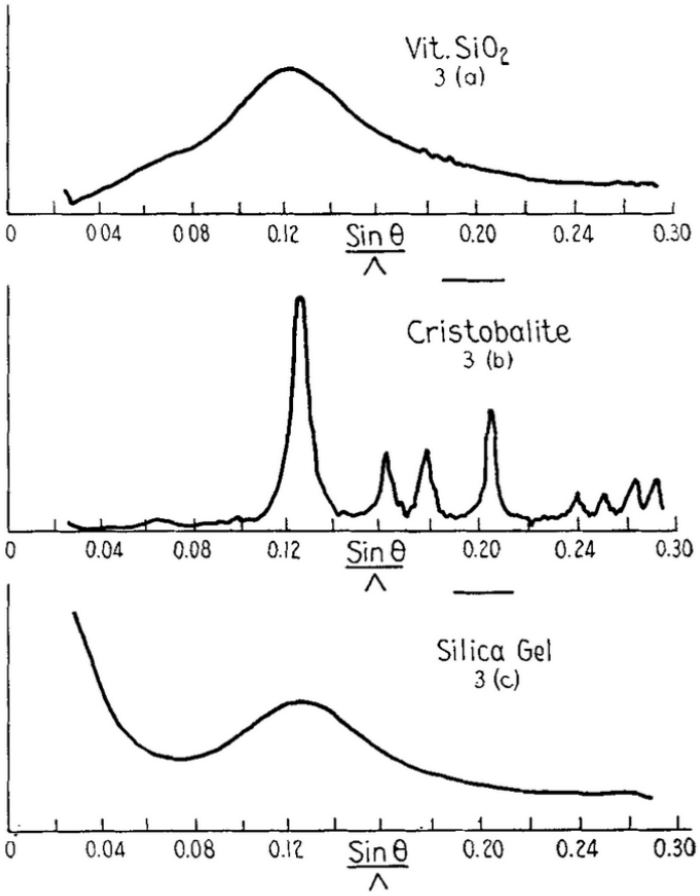


FIG. 3.—Microphotometer records of X-ray diffraction patterns; (*a*) vitreous silica, (*b*) cristobalite, and (*c*) dried commercial silica gel.

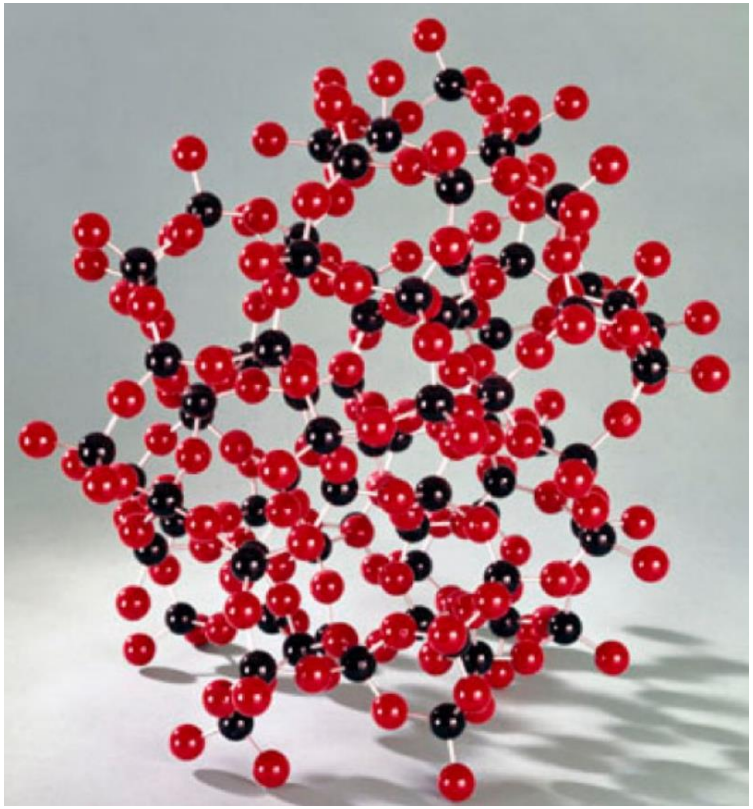
- Absence of small angle scattering
  - Continuous structure without micro-voids and micro-crystals
- Broad diffraction peak
  - Size of ordered region < 8 Å (Scherrer equation)
  - Unit cell size of cristobalite: 7.1 Å

Glass is NOT a collection of extremely small crystals

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

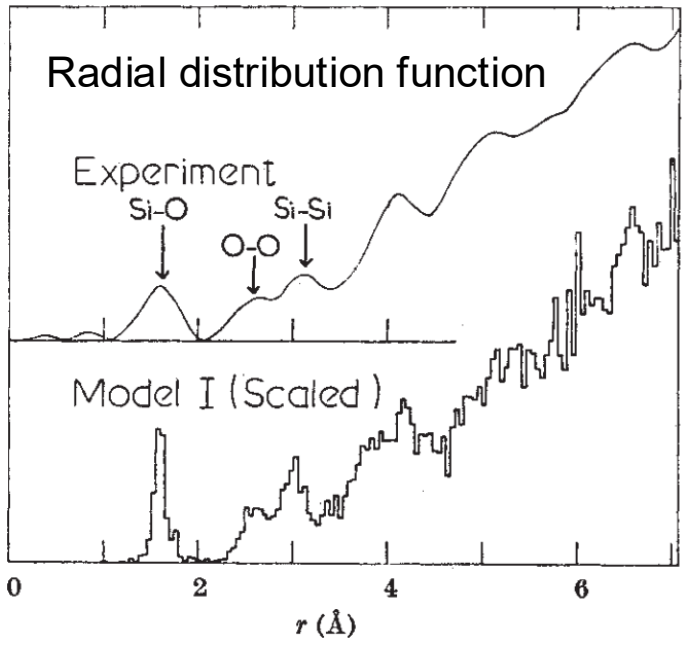
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Random network model of silica glass (SiO_2)



Nature **212**, 1353 (1966)

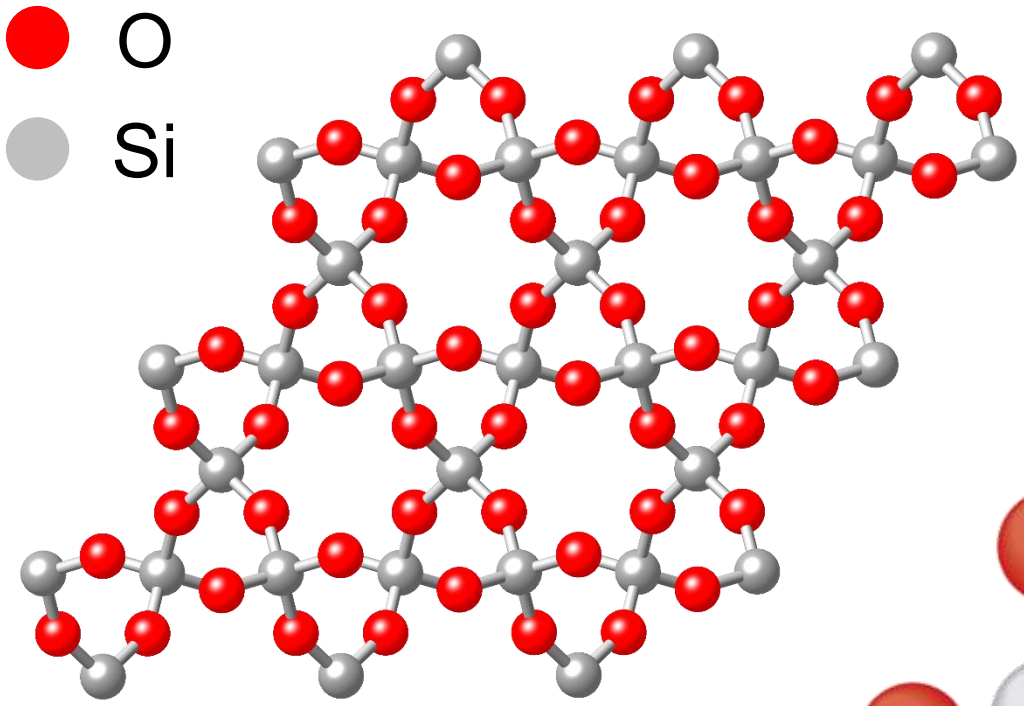
Now in the Science Museum, London



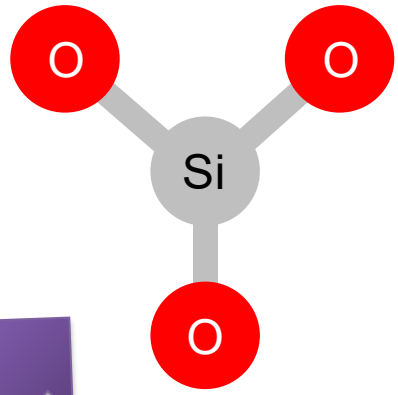
Excellent agreement between XRD and ball-and-stick model constructed according to the random network model

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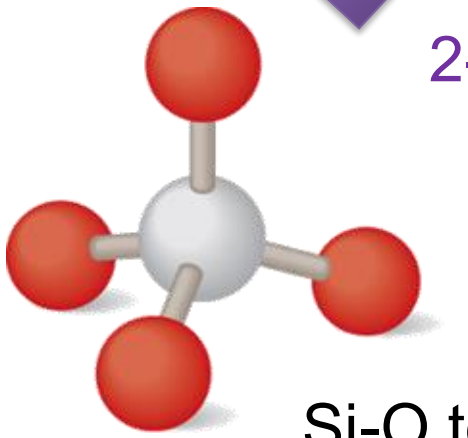
Direct atomic imaging of bilayer silica glass



Quartz crystal



2-D projection



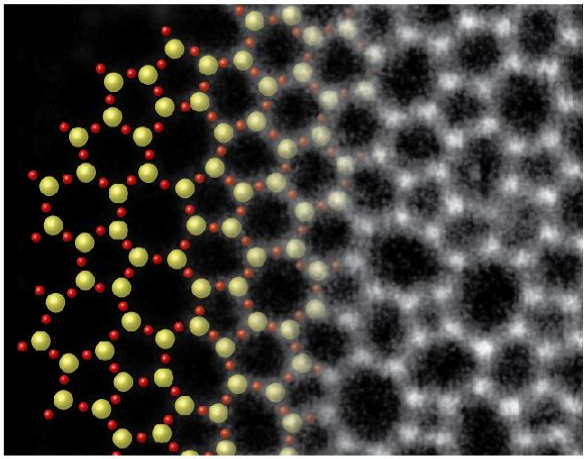
Si-O tetrahedron

Direct atomic imaging of bilayer silica glass



rds: Thinnest glass in Guinness book

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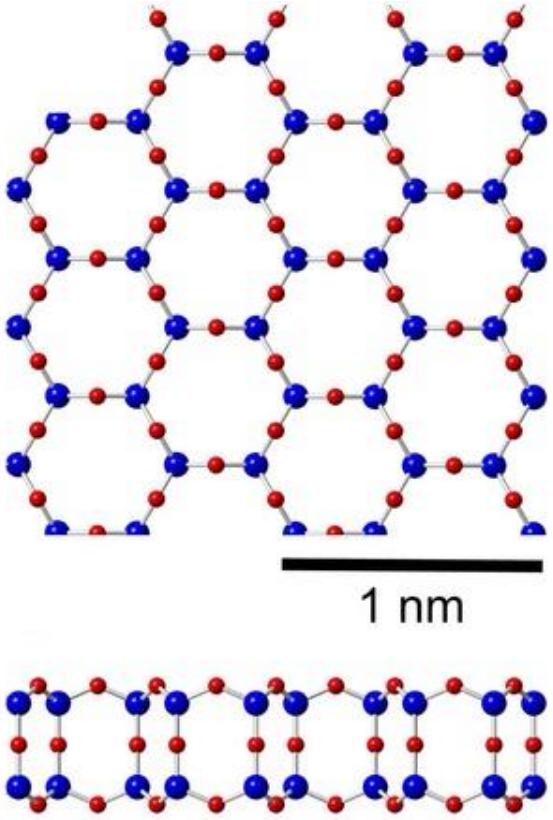
Most steps walked down by a dog facing forwards balancing a glass of water

es of 2-D silica crystal and glass

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

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Direct atomic imaging of bilayer silica glass

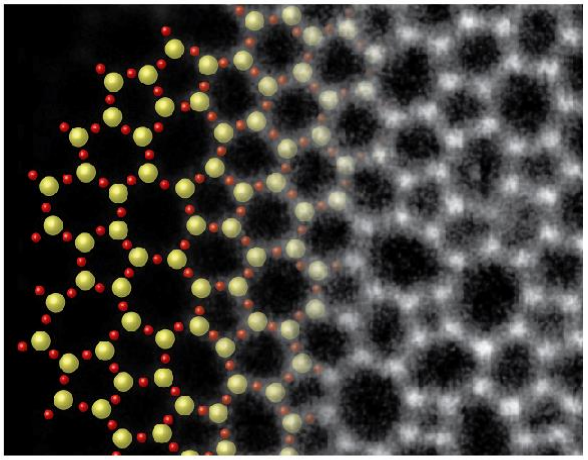


Sept. 12, 2013

Shattering records: Thinnest glass in Guinness book

By Anne Ju

At just a molecule thick, it's a new record: The world's thinnest sheet of glass, a serendipitous discovery by scientists at Cornell and Germany's University of Ulm, is recorded for posterity in the Guinness Book of World Records.



STEM images of 2-D silica crystal and glass

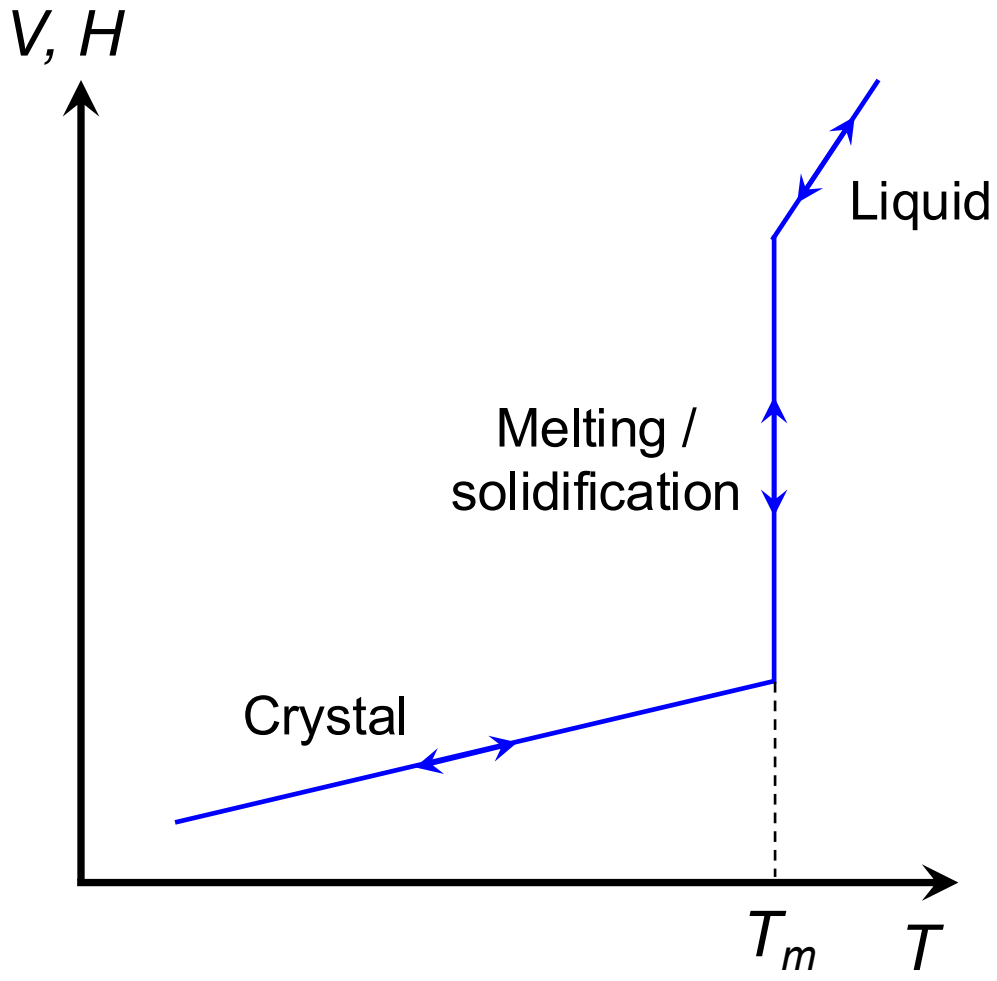
Sci. Rep. **3**, 3482 (2013)

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

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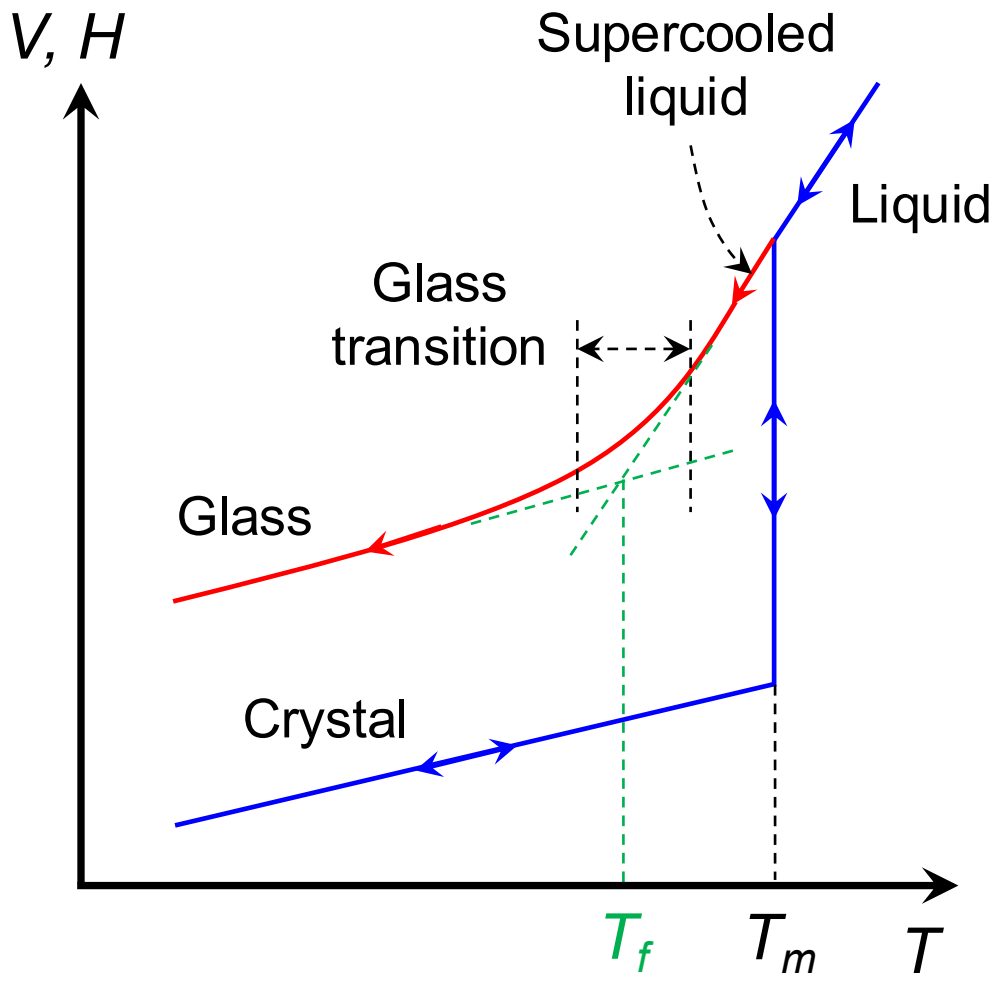
Glass formation from liquid



When the system is kept in thermal equilibrium:

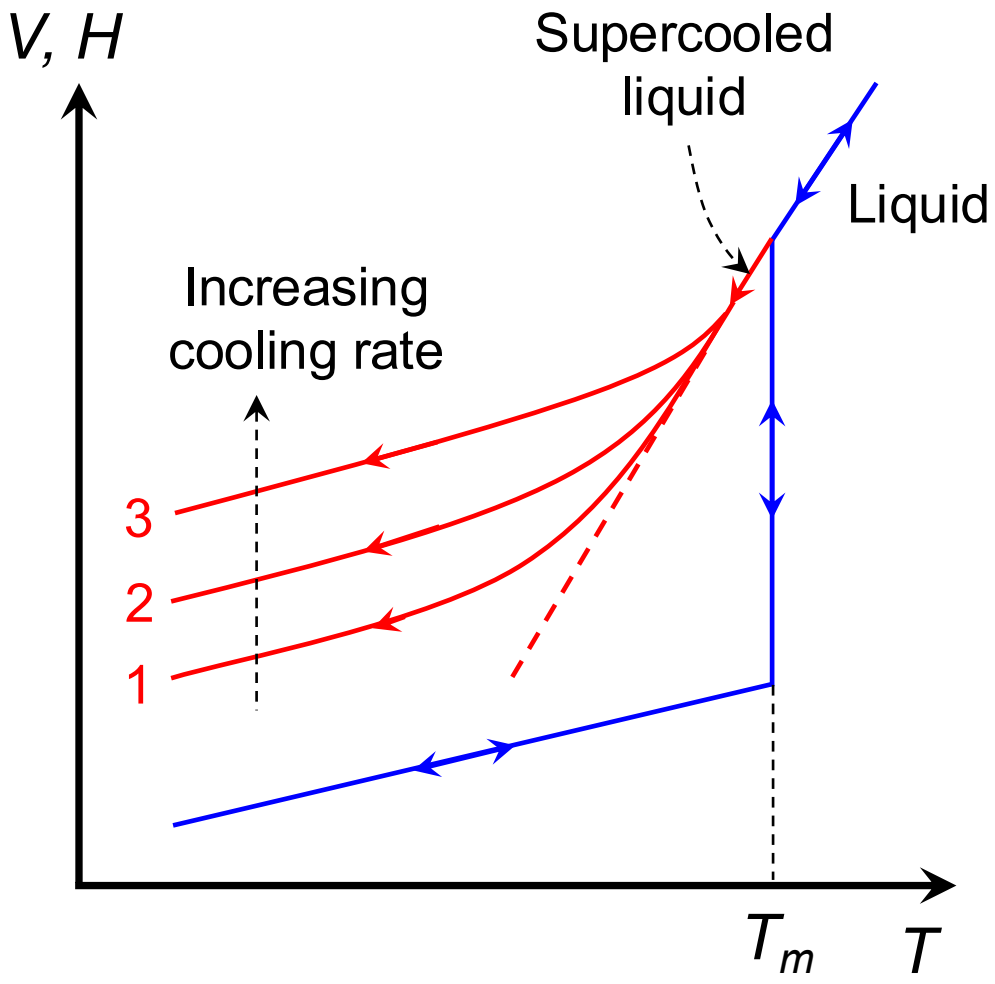
- First-order liquid-solid phase transition
- Discontinuity of extensive thermo-dynamic parameters (e.g., *V* and *H*)
- Reversible process

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

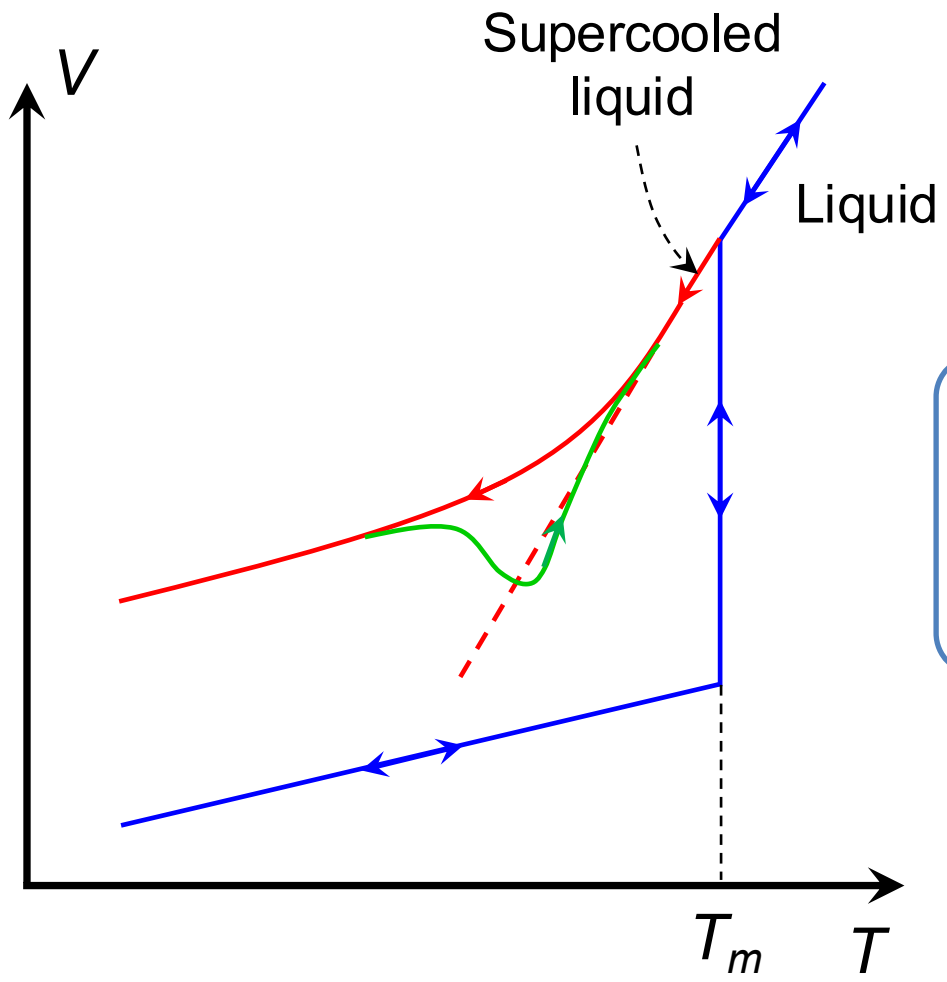


- Glasses obtained at different cooling rates have different structures
- With increasing cooling rate:
  - $V_1 < V_2 < V_3$

  Free volume increases
  - $H_1 < H_2 < H_3$

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

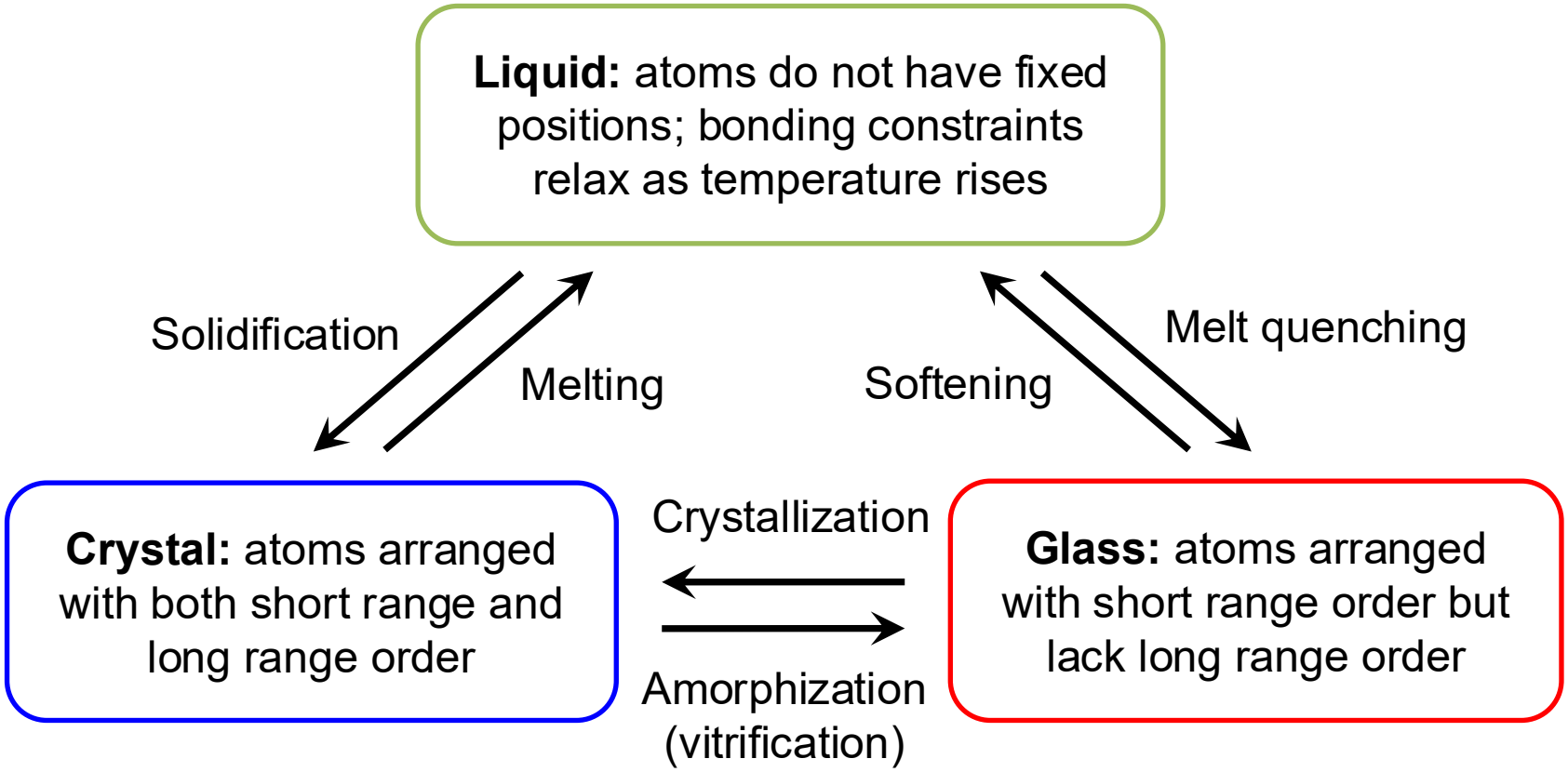
Glass formation from liquid



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

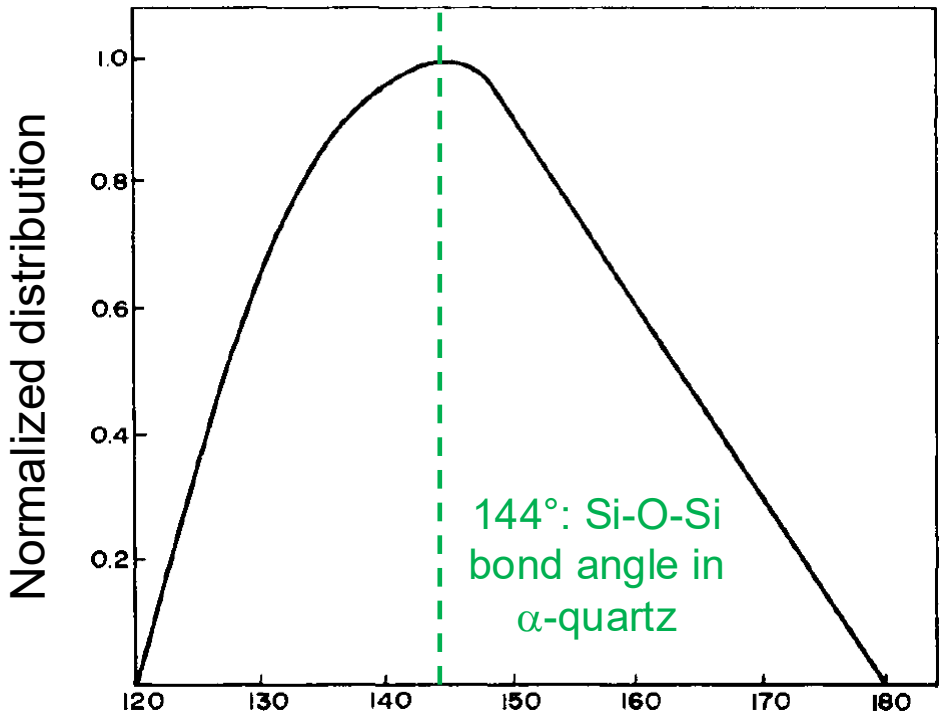
What is amorphous solid (glass)?

- A metastable solid with no long-range atomic order (and exhibiting glass transition)



What is amorphous solid (glass)?

- A metastable solid with no long-range atomic order (and exhibiting glass transition)



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

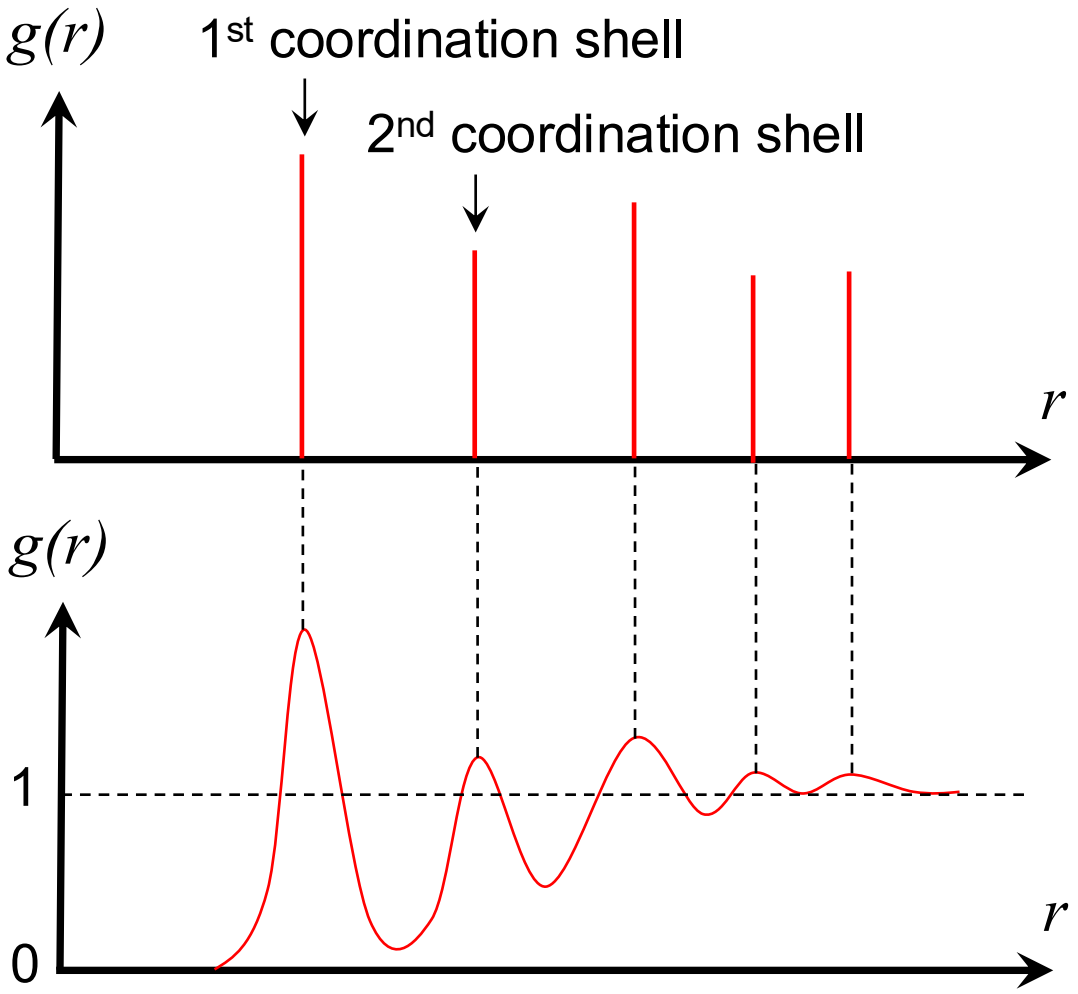
J. Appl. Cryst. **2**, 164 (1969)

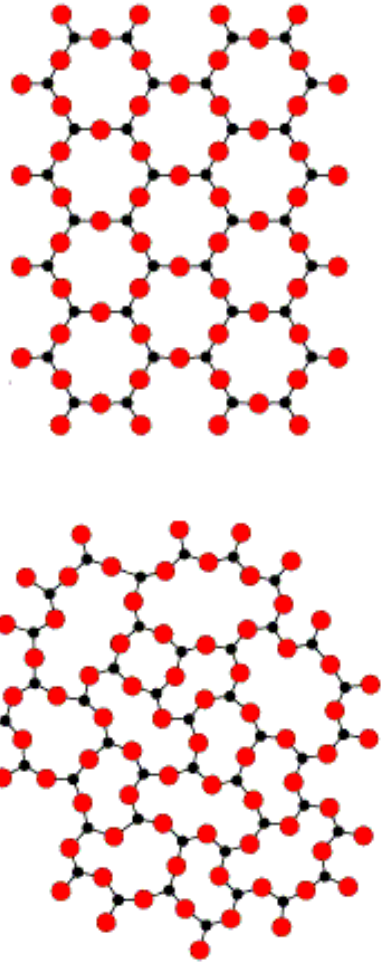
Quantitative description of glass structure

- 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:

    $\rho = n/V$ $\quad$ n : number of atoms $\quad$ 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

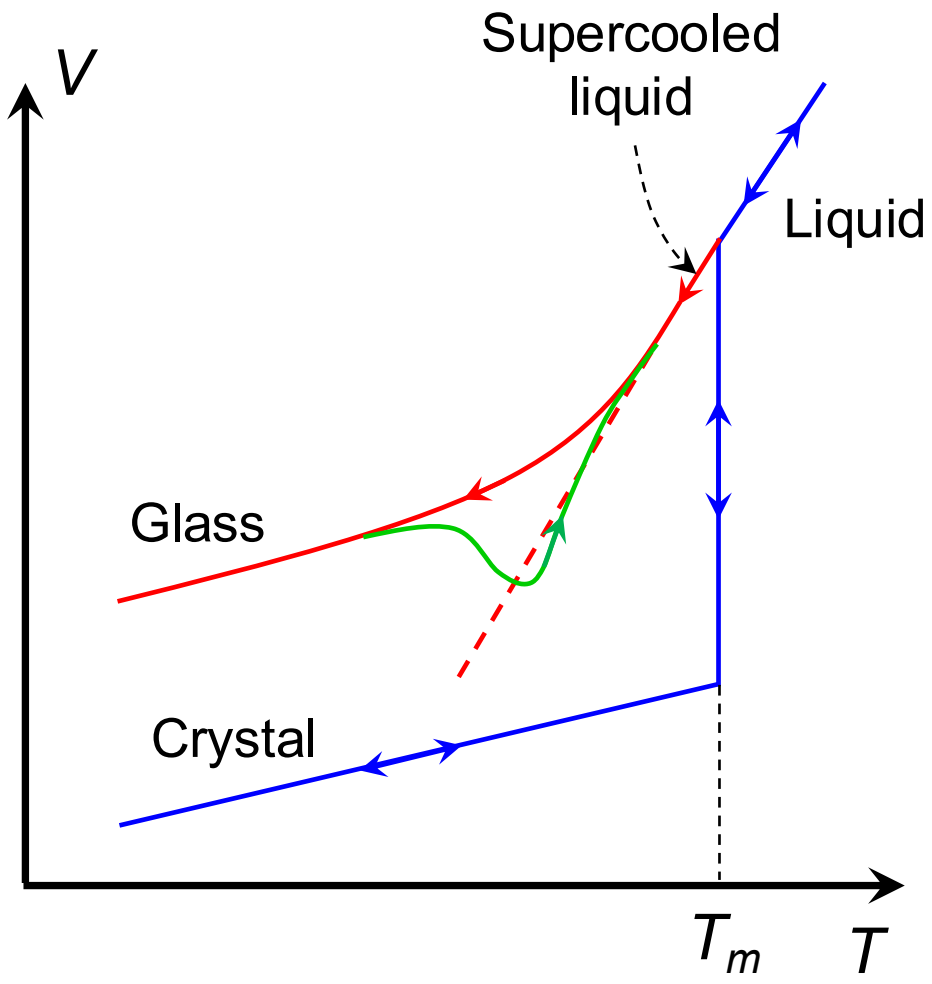




Quantitative description of glass structure

- 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

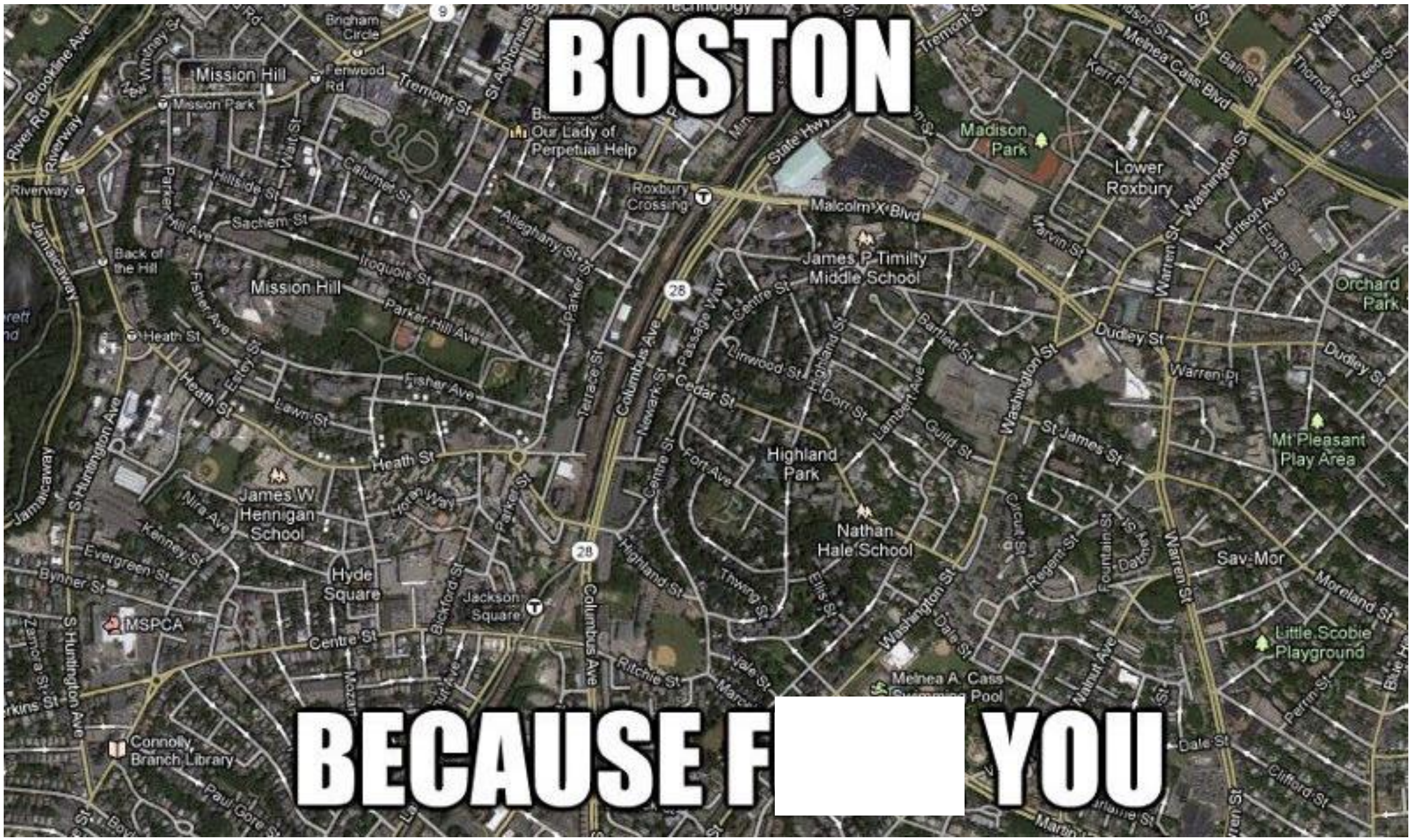


- The amorphous state is metastable
- Amorphous structures possess short-range order and lack long-range order
- Amorphous materials can be obtained from liquid by melt quench
- Melt quench is a continuous, irreversible process involving phase change
- Glass properties depend on their thermal history

Crystalline vs. amorphous



Crystalline vs. amorphous



After-class reading list

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

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3.071 Amorphous Materials
Spring 2025

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