1. Introduction

What is a glass?

- Conventionally: cooled oxide melts

Natural Glasses:

- Obsidian; viscous melts
  - Artifacts from 75,000 BC (Paleolithic Age)
    - Arrow tips, scrapers, etc.
- Pumice; gassy, low viscosity melts

Egyptians were making glasses ~9000 years ago; technological origins 'lost in the mists of time'

- Pliny (Roman historian) claimed that Phoenecian sailors cooking on blocks of *Natron* (alkali salts used for mummification) noticed primitive glass melts formed in beach sands around the cooking fires. Three basic components:
  - Sand (SiO_2)
  - Natron (Na_2O)
  - Sea Shells ($CaCO_3$)

  (Same three components in SLS compositions)

History of glass development: see www.pennynet.org/glmuseum/edglass.htm

- Through the 1500's, artisans dominate development
  - Venetian glass: Island of Murano
    - Well-guarded trade secrets; artisans held captive on island, death penalty for revealing trade information.

- Development of defect-free glass central to a variety of scientific revolutions:

  1. **Glass windows** replacing dark wooden shutters/oiled paper in Europe, 1400's and the development of **superior mirrors** → heightened awareness of cleanliness and hygiene.

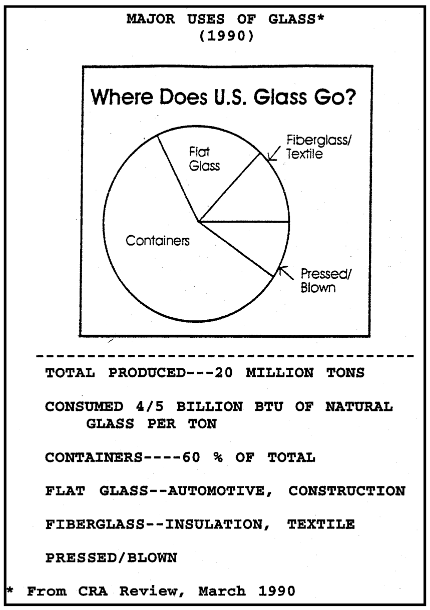
  2. **Optical glass** (1500's) → microscopes (Huygens) revolutionized *biology*
     → telescopes (Galileo) revolutionized *astronomy*

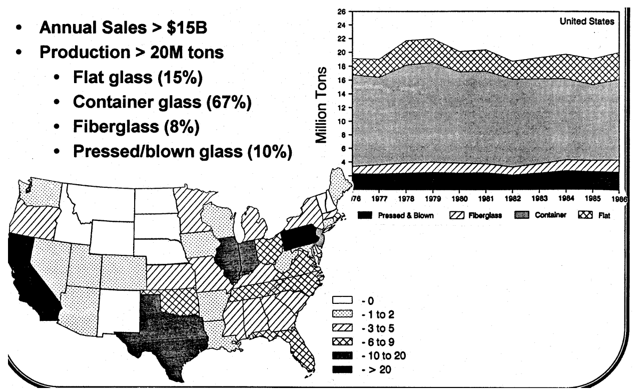
  3. **Thermometer Glasses** (1800's): accurate/reproducible measurement of temperature responsible for experimental underpinnings of *thermodynamics.*

  4. **Laboratory Glass** (1800's): chemical revolution (Michael Faraday)

Today: >98% (by weight) of commercial glasses are silicates

- Soda-lime silicate glass:
  - ~72 wt% SiO_2 — sand
  - ~14 wt% Na_2O — soda ash (Na_2CO_3 mined in Wyoming)
  - ~11 wt% CaO — limestone ($CaCO_3$)
  - ~3 wt% other
- melted at 2800°F (1500°C)





>20 million tons annually; production locations across the country to reduce transportation costs (typical for commodity material).

- **Containers**, **flat glass**, **pressed/blown**: generally SLS compositions
- **Fiber glasses**: borosilicate compositions
- Other types of glasses include:
  - **Glazes** for *decoration (dinnerware, architectural applications, etc.)
    *protective coatings (strength, chemical resistance, scratch resistance, etc.
  - **Consumer ware** ***Pb-crystal
    *glass-ceramics (Corelleware, etc)

More recently, glass has been part of new scientific and technological revolutions

- Ultrapure SiO_2 for **optical fibers**
  - Transparency improved by 10^{100} times since 1965 (first 1000-m fiber transmitted virtually no light; now sub-Pacific cables transmit 120,000 simultaneous phone calls, M-bit/sec transmission rates (Encyclopedia Brittanica per second- see *Stuff*, I. Amato, p 109-110).

- Ultrapure SiO_2 for **photolithographic optics**
    - Submicron features for next generation chip manufacturing
        - 191 nm (free electron lasers)

- Rare-Earth soluble glasses; other **non-linear optical** glasses
    - Optical amplifiers, switches, lasers

- Semiconducting Chalcogenide Glasses
    - Xerox process

- New glasses are developed for:
    - Information displays/flat panels
    - Microelectronic packages (seals, protective layers, etc.)
    -

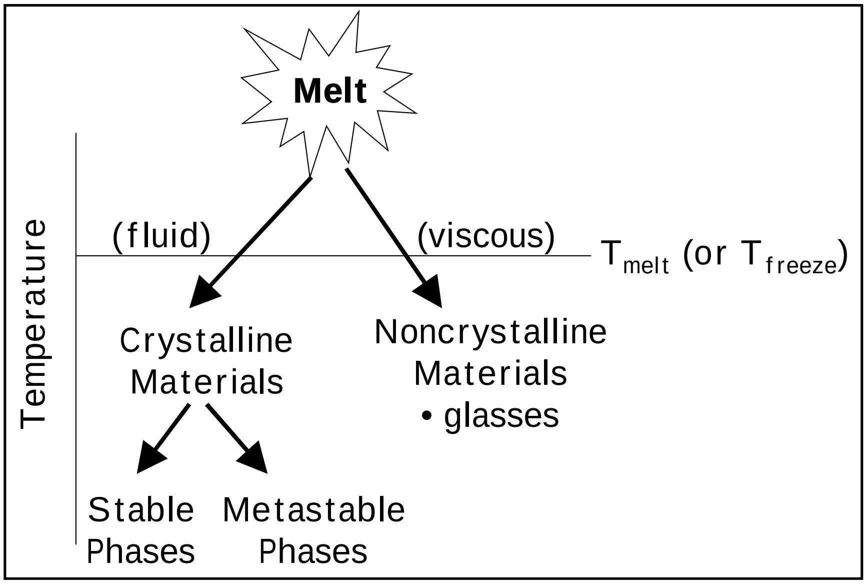
New Astronomical Optics:

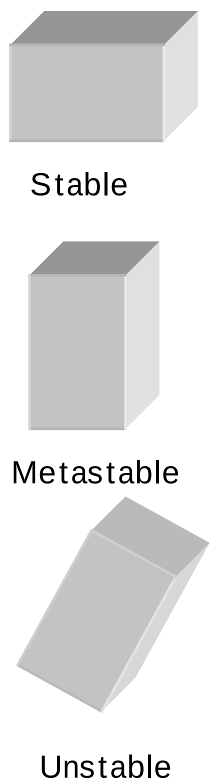
- 10-meter diameter low expansion glasses and glass-ceramics

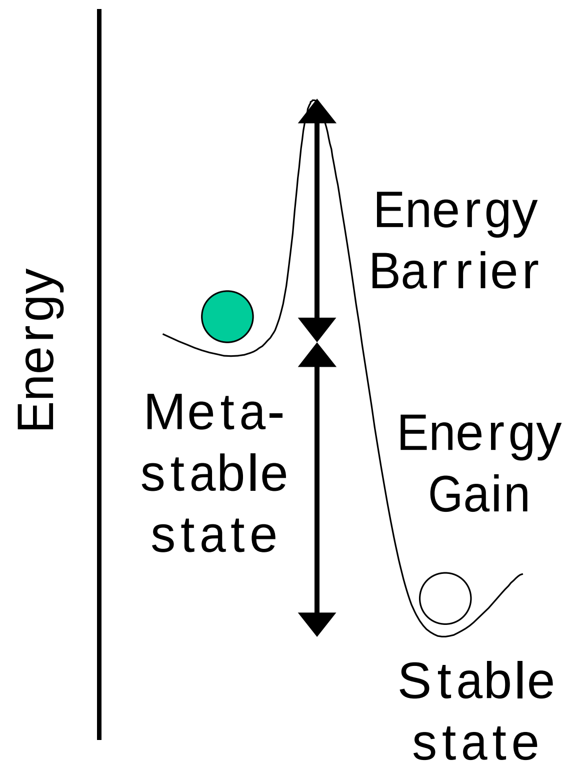
Rotating furnace to form meniscus

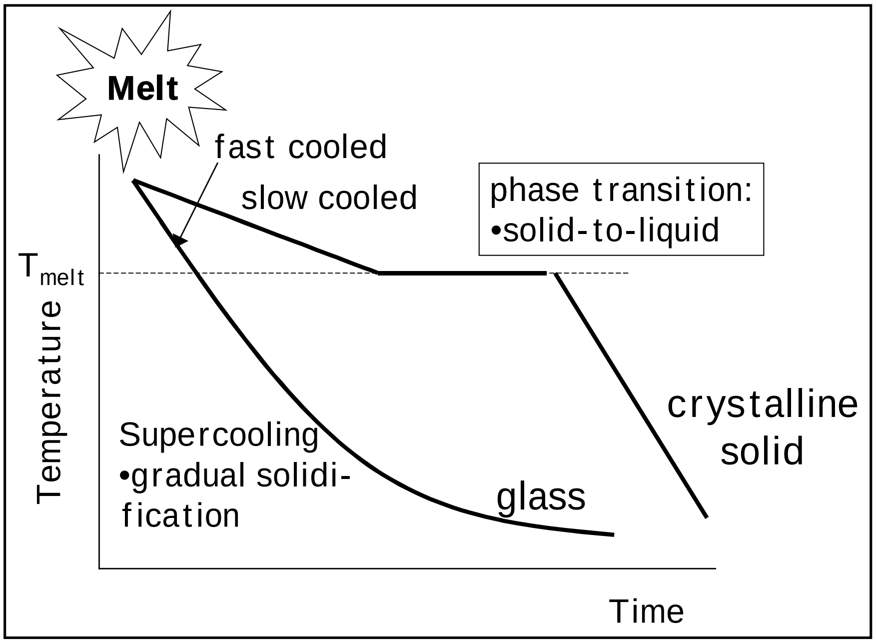
Arizona Mirror/Borosilicate glass

Classification of Solids









Crystalline solids follow a well-defined path:

- Thermodynamically stable path
- Lower energy
- Equilibrium conditions

Non-crystalline solids (glasses)

- Non-equilibrium path
- Favored by fast cooling & high viscosity
    - Slow atomic motion prevents long-range structural order that constitutes crystalline solids

Consider structures of liquids & solids:

Liquids: atoms/molecules moving rapidly; bonds breaking and reforming; fluid behavior.

Solids: local positions of atoms are fixed; bonds are intact; rigid behavior.

Difference between crystals and glasses? Positions of 'fixed' atoms are different. In a **crystal**, atoms have **ordered** positions, **long-range order.** In a **glass**, gradual solidification, 'freeze in' aspects of the '**liquid-like**' structure- **no long range order.**

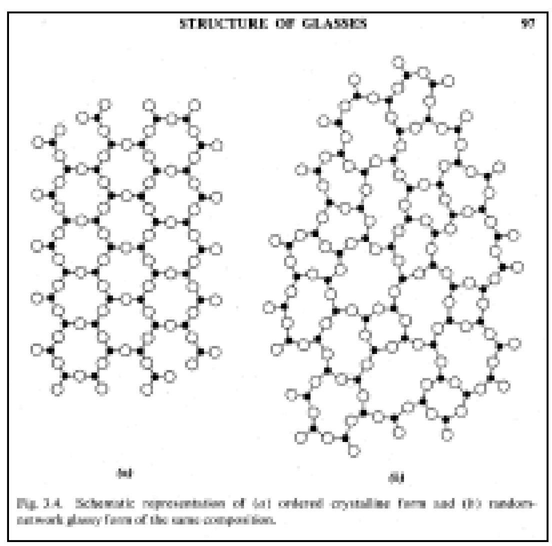
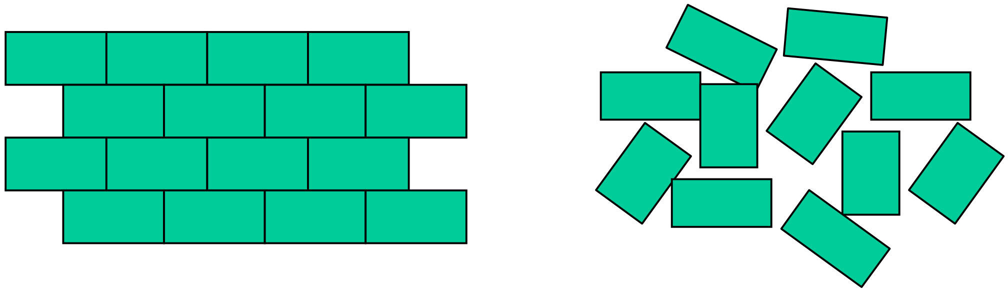


Fig. 3.4. Schematic representation of (a) ordered crystalline form and (b) random-network glassy form of the same composition.

Same polyhedral building blocks, different configurations:



Note: Two distinguishing characteristics of a glass:

- Gradual solidification kinetics
- No long-range atomic order

These characteristics form the basis for our definition of 'glass'.

Figure 1.1 from Shelby (y-axis can be enthalpy or volume)

Liquid-to-crystal transition at T_{melt}:

- Sharp, 1^{st} order phase transition

Liquid-to-glass transition (supercooling)

- Much more gradual, less distinct, over a range of temperatures. (*transformation range*)

Melt: liquid properties
Glass: solid properties

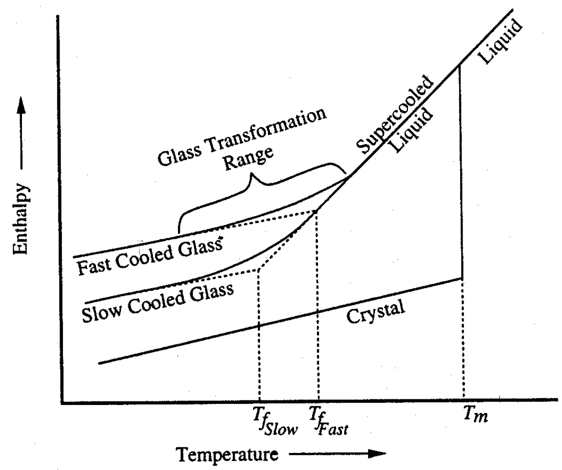


Figure 1.1 *Effect of temperature on the enthalpy of a glassforming melt*

Crystals: •ordered atomic structures mean smaller volumes & lower energies
•thermodynamically stable phase

Glasses: •lack of long-range order results in larger volumes, higher energies; atoms could rearrange to form denser structures if given enough thermal energy and time.
•thermodynamically metastable phase

Fictive Temperature: cross-over from supercooled liquid (equilibrium) behavior to solid glass behavior. A glass with 'T_f' possesses the 'frozen in' equilibrium structure of a supercooled liquid at T_f.

- *Rapid cooling:* fall out of equilibrium sooner as atoms cannot rearrange fast enough to reach lower densities → greater T_f → more open room temp. structure→lower room temperature density
- *Slow cooling:* atoms have more time to rearrange to reach lower energy, denser configurations→ lower T_f → less open room temp. structure→greater room temperature density

Glass Transformation Range: temperature range over which a melt becomes a rigid solid (glass) upon cooling.

- Defined as 'range' because cooling rate will affect the temperature at which a melt becomes a glass (and so cooling rate will affect macroscopic glass properties).

Glass transition temperature (T_g): experimental temperature at which glass properties change to melt properties.

- Not unique; experimentally sensitive
- Less precisely defined than T_f, but more useful because it is easy to measure.

Definitions: older ones are incomplete.

♦"Glass is an inorganic product of fusion that has cooled to a rigid condition without crystallization" ASTM (C-162-92):

- Accurate for most commercial materials (e.g., soda-lime-silica) but,
  - Ignores organic, metallic, H-bonded materials
  - Ignores alternate processing routes (sol gel, CVD, n-bombardment, etc.)

♦"Glass is an amorphous solid." (R. Doremus, *Glass Science*, 1994)

- Not all amorphous solids are glasses;
  - wood, cement, a-Si, thin film oxides, etc. are amorphous but do not exhibit the glass transition.

♦"Glass is an undercooled liquid."

- Problems: glasses have 'solid' properties (e.g., elastic material)
  No flow at room temperature

♦"***Glass is a solid that possesses no long range atomic order and, upon heating, gradually softens to the molten state.***"

- Non-crystalline structure
- Glass transformation behavior