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 (SiO2)
  - Natron (Na2O)
  - Sea Shells (CaCO3)

(Same three components in SLS compositions)

History of glass development: see [www.pennynet.org/glmuseum/edglass.htm](http://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
  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$_2$O soda ash (Na$_2$CO$_3$ mined in Wyoming)
  - ~11 wt% CaO limestone (CaCO$_3$)
  - ~3 wt% other
  - melted at 2800°F (1500°C)

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)*

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

- Annual Sales $\$15B
- Production >20M tons
  - Flat glass (15%)
  - Container glass (67%)
  - Fiberglass (8%)
  - Pressed/blown glass (10%)

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 Britannica per second- see Stuff, I. Amato, p 109-110).
- Ultrapure $\text{SiO}_2$ 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 Materials
  - Stable Phases
  - Metastable Phases
- Noncrystalline Materials
  - Glasses

Temperature

Melt

- (fluid)
- (viscous) $T_{\text{melt}}$ (or $T_{\text{freeze}}$)

Stable Metastable

Energy

- Energy Barrier
- Energy Gain
- Meta-stable state
- Stable state

Unstable
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.
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 $T_{\text{melt}}$:
- Sharp, 1st 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

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 'Tf' 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