

Chapter 9

The Structure and Transport Properties of Solids

Sections to be skipped in Chapter 9:

- Section 9.3 on Diffusion
- Section 9.4 on Electrical conduction.
- Solids are materials that hold their shape.
- The atoms or molecules in solids do not move about hence, $\frac{1}{2} m v^2 = 0$ (K.E. $\lll \Delta E$, the energy of association)
- However, the atoms/ molecules are not completely stationary:
 - They do vibrate around their fixed location

9.1 Macrostructure of Solids

Three classes:

- Crystalline: Salts, metals
- Amorphous or structure-less: glass
- Elastomers: rubbers, plastics (some of the characteristics of the other two)

9.1.1 Crystalline Solids

- Regular and repetitive pattern on long range, in which atoms/ molecules are arranged.
- A stable configuration – metals, ionic salts due to covalent and or ionic bonding.
- Sometimes there are imperfections such as empty spaces, holes or dislocations and these influence the properties as well.
- Atoms/ molecules may vibrate with varying amplitudes of vibration.

9.1.2 Amorphous solids

- Except over short distances, no repetitive pattern displayed in atomic/ molecular arrangement
- Glass is a typical example --> transforms into a crystalline state

9.1.3 Polymeric solids

- Long chain molecules (organic) which are bonded together. Rubber (latex, rubber from rubber trees) above a certain temperature, such compounds are elastic (stretchable)
- Below this temperature polymeric solids behave similar to amorphous solids.
- Polymers and plastics have both crystalline and amorphous regions, which depend on:
 - Chemical composition
 - Molecular configurations of monomers (units)
 - Processing history

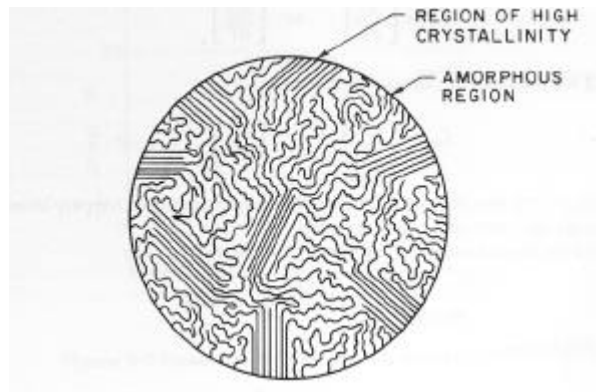


Figure 9-1 Combinations of crystallinity and amorphous regions

Elasticity of rubbers:

- Due to randomness of chain segments
- Show similarities to an ideal gas
- Rubber constant: Like R (gas constant)

9.2 Thermal Properties & Heat Conduction

In general, when we provide thermal energy to a solid (by heating it), the extent of molecular vibration increases. If there are “free” or mobile” electrons (such as in metals due to metallic bonding), then the kinetic energy of such “loosely bound” electrons increases as well. The increased vibration of molecules generally results in increased mean distance of separation. This is the reason why solids expand on heating. The energy is transmitted through solids by mechanism of collisions between the vibrating molecules and also by the movement of free electrons.

The important thermal properties are:

- Heat capacity (specific heat), C
- Thermal expansion, α (K^{-1})
- Thermal conductivity, k (W/mK)

9.2.1 Heat Capacity

Heat capacity is defined (as before)

$$C = \frac{\Delta Q}{\Delta T}$$

i.e heat energy needed to increase the temperature of a unit mass by one $^{\circ}\text{C}$.

For a constant volume process:

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V \quad \text{or,} \quad \left(\frac{\partial U}{\partial T} \right)_V \quad ; U \text{ denotes internal energy.}$$

For a constant pressure process

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p \text{ or, } \left(\frac{\partial H}{\partial T} \right)_p ; H \text{ denotes enthalpy. } H = U + PV.$$

For ideal gases:

$$C_p - C_v = R$$

For solids, C_v is only slightly smaller than C_p , and

$$C_p - C_v = \alpha_p^2 T V_m K$$

α_p = Coefficient of volume expansion (chapter 7)

T = Absolute temperature

V_m = Molar volume (m^3/kmol)

K = The bulk modulus --> a property to be discussed in Chapter 10)

Table 9-1 Heat Capacity of some Solids
(Lange's Handbook)

Substance	Heat Capacity kJ/kmol K	Temperature
Aluminum	24.51	50°C
	30.95	500°C
Copper	24.68	50°C
	33.49	900°C
Lead	26.45	50°C
	29.31	300°C
Silver	25.15	50°C
	34.31	800°C
Sodium Chloride	49.91	0°C
	53.09	100°C
Lead Oxide	61.98	0°C
	65.08	50°C
Ice	25.03	-100°C
	37.09	0°C

For calculations, C_v values are listed in Handbooks.

9.2.2 Thermal Expansion

Coefficient of linear expansion is defined as:

$$\alpha_L = \frac{1}{L} \frac{dL}{dT}$$

Typical values are listed in Table 9-2. The fact that the thermal coefficient of expansion is different for various solids has important consequences.

Bimetallic thermostats: Two metals of widely different coefficient of thermal expansion are bonded together in strips. The greater expansion of one metal leads to predictable bending of the strip with increase in temperature.

Fracture of Materials: Porcelain enamelled metal surfaces; porcelain cracks when the metal expands upon heating.

Table 9-2 Coefficient of Linear Thermal Expansion for Various Solid Materials

Material	Coefficient of Linear Thermal Expansion, $\alpha_L \times 10^{-6}, \text{K}^{-1}$
Copper	18
Aluminum	25
Graphite	2
Steel	12
Ceramics	7
Pyrex Glass	3
Soda Glass	9
Rubber	670
Polyurethane Foam	90
Invar (Iron-Nickel alloy)	1

Rivets and Fasteners can fail if the thermal expansion in the parts they are holding together is much different from their own thermal expansion.

9.2.3 Thermal Conductivity

- Thermal conductivity of a material is defined as:
$$k = \frac{Q/A}{-(dT/dx)}$$
- i.e. Amount of energy flowing per unit area at a temperature gradient of one °C per unit length.
- Gases and liquids --> κ is low
- Solids --> κ can be low or high.
- Low κ --> materials are poor conductors of heat; or good insulators.
- High κ --> materials are good heat conductors; or poor insulators.
- The mode of heat conduction in low- κ and high- κ materials is different.
- **Heat flow in poor conductors (e.g. wood, concrete, rubber, plastics)**
- Thermal energy travels by molecular vibration - like waves.
- The waves can be viewed as particles possessing energy and momentum – called "Phonons."
- The phonons move with the velocity of sound and travel an average distance λ before they collide with molecules in the lattice structure and transfer the energy.
- In certain ways, the phonons behave like molecules in a gas and the kinetic theory can be used to estimate the thermal conductivity.

$$k = \frac{u_s I r C_V}{2M}$$

Values of κ are listed in handbooks for various materials. Also in Table 9-3

Heat Flow in Good Conductors (metals, graphite, certain salts)

- Movement of "free" or unbound electrons is the primary mechanism for heat conduction.
- Good conductors have κ values 100 to 1000 times higher than the poor conductors.
- Positive ions occupy fixed lattice locations but are submerged in the electron cloud formed by "free" electrons.
- The electrons in the electron-cloud behave like ideal gas molecules. Kinetic theory can be

used to get

$$k = \frac{n_e I (C_V / N_A) \bar{C}}{2} \quad \text{where,}$$

n_e = number of electrons/m³

(C_V / N_A) = heat capacity per electron = $3k/2$ (as in a monoatomic gas)

$$k = \frac{3n_e I k \bar{C}}{4}$$

gives a reasonable estimate.

9.2.4 The Rate of Heat Conduction

The rate of heat flow in solids depends on:

- Geometry of the solid (plate, cylinder, sphere)
- Temperature distribution
- Thermal conductivity, κ

We will look at the simpler case of steady-state heat flow only. Steady-state means the temperature distribution is not changing with time. The simplest geometry is that of a flat plate in which the cross-sectional area for heat flow remains constant.

$$Q = -kA \frac{dT}{dx} = -kA \frac{\Delta T}{\Delta x}$$

If you know κ , A and the temperature gradient, the amount of heat energy flowing through the surface can be calculated.