Thermal Properties of Materials

- Response of a material to the application of heat

When a solid absorbs heat:

– Temperature increases

– Dimension increases

- Critical properties in practical utilization of solids
  - Heat capacity
  - Thermal expansion
  - Thermal conductivity

Heat capacity and Specific heat

Heat capacity (C):

- A property that is indicative of a material's ability to absorb heat from external surrounding
- Amount of energy required to produce a unit temperature rise

$$C = \frac{dQ}{dT}$$

Unit: J/mol.K, Cal/mol.K

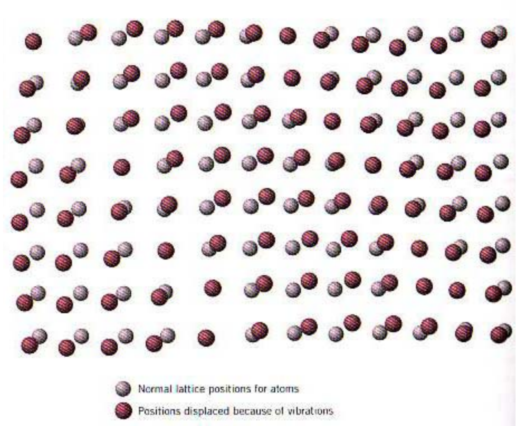
Specific heat (c):

- Heat capacity/unit mass
- Units: J/kg.K, cal/g.K

Material	c_p (*J/kg-K*)[a]
Aluminum	900
Copper	386
Gold	128
Iron	448
Nickel	443
Silver	235
Tungsten	138
1025 Steel	486
316 Stainless steel	502
Brass (70Cu-30Zn)	375
Kovar (54Fe-29Ni-17Co)	460
Invar (64Fe-36Ni)	500
Super Invar (63Fe-32Ni-5Co)	500
Alumina (Al_2O_3)	775
Magnesia (MgO)	940
Spinel ($MgAl_2O_4$)	790
Fused silica (SiO_2)	740
Soda–lime glass	840
Borosilicate (Pyrex) glass	850
Polyethylene (high density)	1850
Polypropylene	1925
Polystyrene	1170
Polytetrafluoroethylene (Teflon)	1050
Phenol-formaldehyde, phenolic (Bakelite)	1590–1760
Nylon 6,6	1670
Polyisoprene	—

Major energy-absorptive mechanism

- Vibrational heat capacity: energy absorbs by an increase in vibrational energy of atoms



•Atoms in solid vibrate at very high frequency and small amplitudes
•Adjacent atoms are coupled by atomic bonding
•Vibrations produce travelling lattice waves

Generation of lattice waves by atomic vibration (W.D. Callister, Jr., 2000)

Thermal Expansion

Solids: Heating→ expansion		Cooling→ contraction

For dimension changes, $$\frac{l_f - l_0}{l_0} = \alpha_l (T_f - T_0) \qquad \frac{\Delta l}{l_0} = \alpha_l \Delta T$$

α_l = linear coefficient of thermal expansion

unit of reciprocal T (°C^{-1}, F^{-1})

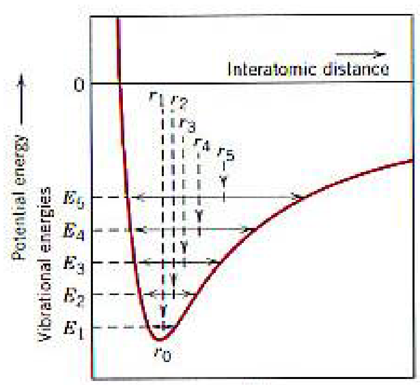
For volume changes, $$\frac{\Delta v}{v_0} = \alpha_v \Delta T$$

α_v = volume coefficient of thermal expansion (usually anisotropic)

Coefficient of thermal expansion is a material property indicate the extent to which a material expands upon heating

Thermal Expansion (cont.)

Atomic level: thermal expansion is reflected by an increase in the average distance between atoms



Increase in interatomic separation with rising T

T1→T2→T3…..

E1→E2→E3…..

r1→r2→r3…..

The greater the atomic bonding energy, the deeper and more narrow potential energy curve → increase in interatomic separation lower

Thermal Expansion: Ceramics

- Relatively strong interatomic bonding
- Low coefficient of thermal expansion
- Inorganic glasses, α depend on composition ex. Fused SiO_2 (high purity SiO_2 glass)
  - Small α due to low atomic packing density
  - Interatomic expansion produces small macroscopic dimensional changes

Ceramics used in T changes must have low α and isotropic (noncrystalline, cubic ceramics), otherwise, brittle materials may fracture due to nonuniform dimensional changes (thermal shock)

	α_l $[(°C)^{-1} \times 10^{-6}]^b$
Metals	
Aluminum	23.6
Copper	17.0
Gold	14.2
Iron	11.8
Nickel	13.3
Silver	19.7
Tungsten	4.5
1025 Steel	12.0
316 Stainless steel	16.0
Brass (70Cu-30Zn)	20.0
Kovar (54Fe-29Ni-17Co)	5.1
Invar (64Fe-36Ni)	1.6
Super Invar (63Fe-32Ni-5Co)	0.72
Ceramics	
Alumina (Al_2O_3)	7.6
Magnesia (MgO)	13.5[d]
Spinel ($MgAl_2O_4$)	7.6[d]
Fused silica (SiO_2)	0.4
Soda–lime glass	9.0
Borosilicate (Pyrex) glass	3.3
Polymers	
Polyethylene (high density)	106–198
Polypropylene	145–180
Polystyrene	90–150
Polytetrafluoroethylene (Teflon)	126–216
Phenol-formaldehyde, phenolic (Bakelite)	122
Nylon 6,6	144
Polyisoprene	220

Thermal conductivity

- **Thermal conduction** is a phenomenon by which heat is transported from high to low T regions of a substance
- **Thermal conductivity (k)** is a property that characterizes the ability of a material to transfer heat

$$q = -k\frac{dT}{dx}$$

q = heat flux or heat flow/unit time/unit area (W/m^2)
k = thermal conductivity (W/m.K)
dT = T gradient through the conducting medium
(-) = direction of heat flow from hot to cold (down the T gradient)

Mechanisms of heat conduction

1. Heat transfer in solid by lattice vibration waves (phonon)
   – Lattice vibration conductivity results from a net movement of phonon from high-low T regions
2. Heat transfer in solid by free electrons
   – Electronic thermal conduction
   – Free electron in hot region gain kinetic energy and migrate to colder areas, where some energy is transferred to atoms by collision → vibration

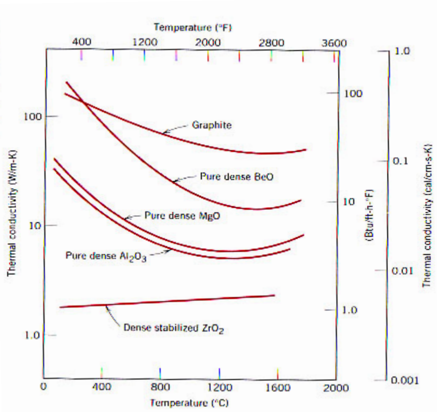
Thermal conductivity: Ceramics

- Nonmetallic, thermal insulators
  - a small number of free electron
  - Phonons are primarily responsible for thermal conduction
  - Heat transporting are not very effective
- Glass and amorphous ceramics have lower conductivity than crystalline ceramics
  - Higher phonon scattering in disorder and irregular atomic structure

Room T	k (W/m-K)
Aluminum	247
Copper	398
Gold	315
Iron	80
Nickel	90
Silver	428
Tungsten	178
1025 Steel	51.9
316 Stainless steel	15.9
Brass (70Cu-30Zn)	120
Kovar (54Fe-29Ni-17Co)	17
Invar (64Fe-36Ni)	10
Super Invar (63Fe-32Ni-5Co)	10
Alumina (Al_2O_3)	39
Magnesia (MgO)	37.7
Spinel ($MgAl_2O_4$)	15.0[c]
Fused silica (SiO_2)	1.4
Soda–lime glass	1.7
Borosilicate (Pyrex) glas	1.4
Polyethylene (high density)	0.46–0.50
Polypropylene	0.12
Polystyrene	0.13
Polytetrafluoroethylene (Teflon)	0.25
Phenol-formaldehyde, phenolic (Bakelite)	0.15
Nylon 6,6	0.24
Polyisoprene	0.14

Factors affect k of ceramics

- Temperature
  - T increase, scattering from lattice vibration increase, k of ceramics decrease
  - At higher T, k increase due to radiant heat transfer
- Porosity
  - Porosity increase, k decrease
  - Ceramics used for thermal insulation are porous
  - Heat transfer across pores is slow and inefficient
  - Internal pore containing air, which has extremely low k~0.02 W/m.K



Thermal stress

- Stress induced in a body as a result of changes in T
- Lead to fracture

1. Stress resulting from restrained thermal expansion and contraction

homogeneous and isotropic rod

↓ Heated or cooled uniformly (no T gradient)

If free expansion or contraction, **stress free**
If restrained by rigid end support, **thermal stress**

2. Stress resulting from T gradients

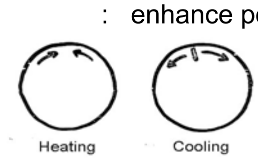
When solid body is heated or cooled, internal T distribution depends on size, shape, thermal conductivity and rate of T change

Rapid heating:
- -T changes: outside>inside
- -T gradients
- -Different dimensional changes restrain free expansion or contraction
- -Thermal stress

Thermal stress (cont.)

3. Thermal shock of brittle materials

Metal, polymer: ductile
: thermal stress accomplish by plastic deformation
Ceramic: brittle
: enhance possibility of brittle fracture from thermal stress



Rapid Heating: Compression on surface
Rapid Cooling: Tension on surface
Thus, rapid cooling cause failure in ceramics

Thermal shock resistance (TSR) = capacity of a material to withstand thermal shock failure

$$TSR \approx \frac{\sigma_f k}{E\alpha}$$

For ceramics, TSR depends on (1) magnitude of T change and
(2) mechanical and thermal properties of ceramics

For ceramic with high TSR: high fracture strength (σf) and k
: low Young's modulus (E) and α

Prevention of Thermal Shock

- Externally
  - Reduce cooling or heating rate
  - Minimize T gradients across a body
- Internally

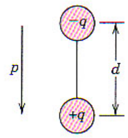
1. Modify parameters: fracture strength (σ_f), k, Young's modulus (E) and α
   - k is the most easily change and control
   - Ex soda-lime glasses has high thermal expansion, α_l~$9x10^{-6}$ (°C^{-1}), easy to fracture
     - Reduce CaO, Na_2O and add B_2O_3 to form borosilicate glass (pyrex)
     - Reduce α_l to $3x10^{-6}$ (°C^{-1})→ suitable for kitchen oven heating/cooling cycles
2. Introduce large pores or ductile 2nd phase to impede the propagation of crack

Remove thermal stress from ceramic by annealing heat treatment
•Cooling at a sufficiently slow rate
•To improve mechanical strength and optical characteristics

Dielectric material

- **A dielectric material** is electrically insulating and exhibits an electrical **dipole** structure
- **Dipole** is a separation of positive and negative electrical charges of equal magnitude on a molecular or atomic level

Dipole

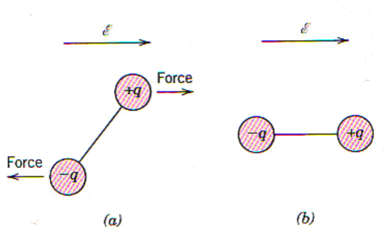


dipole moment,p (C.m)

$$p = qd$$

Polarization (P)

- Process of dipole alignment
- Total dipole moment/unit volume of dielectric material
- In presence of an electric field (E), a force (or torque) orients an electrical dipole to the direction of the applied field



- P (C/m^2) increases linearly with E (V/m)
- Dielectric susceptibility (χ) relates effect (P) to cause (E)

$$\chi = \frac{P}{\varepsilon_0 E}$$

$$\varepsilon_0 = \text{permittivity of a vacuum} = 8.85\text{x}10^{-12}\ \text{F/m}$$

Dielectric constant (ε_r)

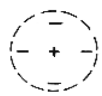
$$\varepsilon_r = 1 + \chi$$

Material	Dielectric Constant 60 Hz	Dielectric Constant 1 MHz
Ceramics		
Titanate ceramics	—	15–10,000
Mica	—	5.4–8.7
Steatite ($MgO-SiO_2$)	—	5.5–7.5
Soda–lime glass	6.9	6.9
Porcelain	6.0	6.0
Fused silica	4.0	3.8
Polymers		
Phenol-formaldehyde	5.3	4.8
Nylon 6,6	4.0	3.6
Polystyrene	2.6	2.6
Polyethylene	2.3	2.3
Polytetrafluoroethylene	2.1	2.1

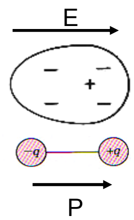
- If dipoles can be easily polarized with small E,
  - High χ
  - High ε_r

Type of Polarization

1. Electronic polarization: occur in all atoms



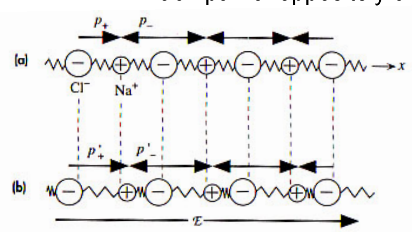
Net change=0
No net polarization



- Electron displaced by E
- Separation of negative charge center to positive charge center
→ dipole moment
→ polarization

2. Ionic polarization

- occur in ionic crystal ex. NaCl, KCl, LiBr
- Each pair of oppositely charged neighboring ions has a dipole moment



Net dipole moment/ion=0
Dipole moment of equal magnitude are lined up head to head and tail to tail

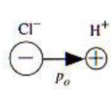
Ions slightly displaced
Na^+ in direction of E, Cl^- in opposite direction
Net dipole moment/ion≠0

Type of Polarization (cont.)

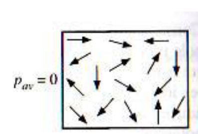
3. Orientaional (dipolar) polarization

- Molecules with permanent dipole moments
- Normally exhibit in polar liquid (water, alcohols acetone) and polar gas
- In solid (various glasses), dipolar orientation involves a discrete jump of an ion from one site to another

E=0

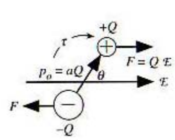


Permanent dipole moment

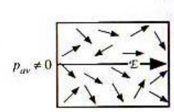


Random dipole moment
Net dipole moment/molecule=0

E≠0



A torque rotates a dipole to align with E



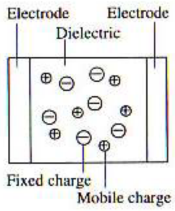
Net dipole moment/molecule≠0

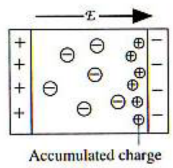
Type of Polarization (cont.)

4. Interfacial polarization

- Occur whenever there is an accumulation of charge at an interface between 2 materials or between 2 regions within a material

A crystal with equal no. of mobile positive ions and fixed negative ions



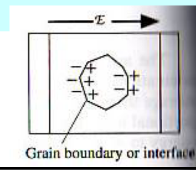


•E=0, no net charge separation

•E≠0: -Mobile positive ions migrate
-Overall charge separation
-Interfacial polarization

Interfacial polarization at grain boundaries and interfaces between different materials

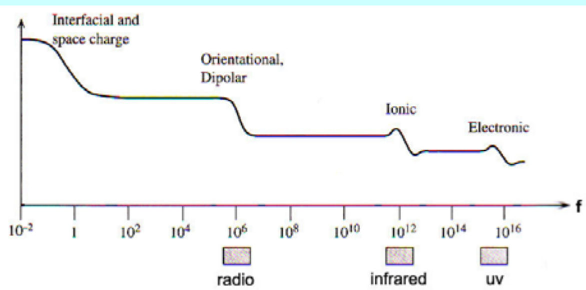
•Grain boundaries trap migrating charges
•Dipoles between trapped charges



Frequency dependence of dielectric constant

- AC field changes magnitude and direction continuously
- Dipoles under AC are lined up one way and then the other way and so on
- If AC field change too rapidly (too high frequency), dipoles cannot follow and remain randomly oriented
  - High frequency: polarization=0,
  - Low frequency: polarization=max=value under DC

The decrease in the induced dipole/molecule = relaxation process



Different types of polarization relax at different frequency

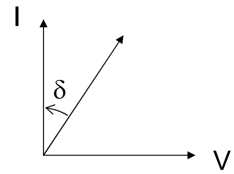
Dielectric loss

AC field: phase shift from 90°

:The filed is complex

:Polarization under AC is complex

:Dielectric constant under AC is complex



Dielectric constant under ac: $\varepsilon_r = \varepsilon' - j\varepsilon''$

Real part

Real part decrease from its max value (DC) to 1 at high frequency when P=0

Imaginary part

Imaginary part represents the energy lost in dielectric as dipoles are oriented by AC

Loss tangent or loss factor: relative magnitude of imaginary and real part

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Loss factor of Material

Material	loss factor (tan δ) at 1 MHz
Alumina	0.0002-0.01
Amber	0.015
Glass (pyrex)	0.008-0.019
Mica	0.0001
Neoprene (rubber)	0.04
Nylon	0.03-0.04
Paraffin wax	0.003
Polyethylene	0.0002-0.0005
Polystyrene	0.0001-0.001
Porcelain	0.003-0.02
Teflon	0.0002
PVC (rigid)	0.018-0.019
PVC (flexible)	0.1
Rubber (natural)	0.003-0.008
Titanium dioxide	0.0002-0.005
Titanates (Ba, Sr, Ca, Mg, Pb)	0.0001-0.02

Dielectric Strength & Dielectric breakdown

Dielectric breakdown occurs when dielectric material loss its insulating property and allow current to pass through

In solids, dielectric breakdown leads to permanent conducting channel (permanent damage)

Dielectric strength (E_{br}) is the maximum applied voltage that <u>will not</u> cause dielectric breakdown

$E > E_{br}$ → dielectric breakdown

Factors affecting E_{br} :

- Molecular structure
- Purity
- Defects
- Shape and size
- Electrode nature
- Temperature
- Humidity
- Duration and frequency of applied E
- Aging effect

Dielectric strength at T_{room} and 1 atm

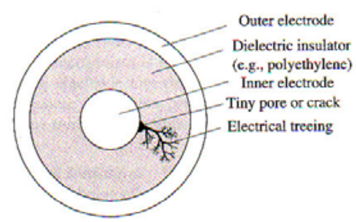
Dielectric Medium	Dielectric Strength	Comment
Atmosphere at 1 atm pressure	31.7 kV cm^{-1} at 60 Hz	1 cm gap. Breakdown by electron avalanche by impact ionization.
SF_6 gas	79.3 kV cm^{-1} at 60 Hz	Used in high voltage circuit breakers to avoid discharges.
Polybutene	>138 kV cm^{-1} at 60 Hz	Liquid dielectric used as oil filler and HV pipe cables.
Transformer oil	128 kV cm^{-1} at 60 Hz	—
Amorphous silicon dioxide (SiO_2) in MOS technology	10 MV cm^{-1} dc	Very thin oxide films without defects. Instrinsic breakdown limit.
Borosilicate glass	10 MV cm^{-1} duration of 10 μs 6 MV cm^{-1} duration of 30 s	Instrinsic breakdown. Thermal breakdown.
Polypropylene	295–314 kV cm^{-1}	Likely to be thermal breakdown or electrical treeing.

E_{br} is different under DC and AC

Dielectric Breakdown: Solids

- **Intrinsic or electronic breakdown**
  - Electron avalanche breakdown
  - Collision of a high energy, free electron with atoms produces more free electrons
  - Continuous process → a lot of free electrons → current in solid → dielectric breakdown
- **Thermal breakdown**
  - Heat generated in dielectric material increases conductivity (current in material)
  - Discharge
  - Conducting channel
- **Electromechanical breakdown and electrofracture**
  - Dielectric material between electrode with opposite charges are under compression
  - High voltage → high compression → breakdown
  - Electrofracture: Residual stress → crack and crack propagation

Dielectric Breakdown (cont.)



- **Internal discharges**
  - Discharge in voids, cracks and pores
  - Corrosion on internal surface
  - Electrical tree discharge
  - Conducting channel
- **Insulation aging**
  - Properties degrade after long-term used
  - Factors: thermal stress, mechanical stress, radiation, humidity, voltage nature
- **External discharges**
  - Accumulation of dust or humidity on surface
  - Discharge between electrodes
  - Surface tracking

Time and Electric Field for Dielectric Breakdown