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## HEAT TRANSFER

### I. MODES OF HEAT TRANSFER

Heat flows across temperature differences. There are three modes of heat transfer: conduction, radiation, and convection. Conduction and radiation are fundamental physical mechanisms, while convection is really conduction as affected by fluid flow.

Conduction is an exchange of energy by direct interaction between molecules of a substance containing temperature differences. It occurs in gases, liquids, or solids and has a strong basis in the molecular kinetic theory of physics. Conduction is often thought of as only occurring within the body of a material; however, the transfer of heat from the surface of, say, a solid to a fluid is also a conductive process. Convection is, therefore, a conductive heat transfer process wherein conductive heat transfer is assisted by flow to effect heat transfer from a material's surface into the body of a flowing fluid.

Radiation is a transfer of thermal energy in the form of electromagnetic waves emitted by atomic and subatomic agitation at the surface of a body. Like all electromagnetic waves (light, X-rays, microwaves), thermal radiation travels at the speed of light, passing most easily through a vacuum or a nearly "transparent" gas such as oxygen or nitrogen. Liquids, "participating" gases such as carbon dioxide and water vapor, and glasses transmit only a portion of incident radiation. Most other solids are essentially opaque to radiation. The analysis of thermal radiation has a strong theoretical basis in physics, beginning with the work of Maxwell and of Planck.

Convection may be described as conduction in a fluid as enhanced by the motion of the fluid. It may not be a truly independent mode, but convection is the most heavily studied problem in heat transfer: More than three-quarters of all published heat transfer papers deal with convection. This is because convection is a difficult subject, being strongly influenced by geometry, turbulence, and fluid properties.

### EXAMPLE: EXHAUST PIPE

The total heat rejected to the air ( $Q$ ) from an exhaust pipe is simply the sum of:

the heat convectively removed from the external surface of the pipe --

[  $q_{\text{conv}} = hA(T_{\text{Ex}} - T_{\text{Air}})$  ], where  $T_{\text{Ex}}$  is the temperature of the exhaust gas and  $T_{\text{air}}$  is the temperature of the surrounding air,

plus the heat emitted by radiation --

[  $q_{\text{rad}} = \epsilon\sigma A(T_{\text{H}}^4 - T_{\text{C}}^4)$  ], where  $\epsilon$  is the emissivity of the coating,  $\sigma$  is the Stefan-Boltzman constant,  $T_{\text{H}}$  is the temperature on the hot side of the coating, and  $T_{\text{C}}$  is the temperature at the interface of the

coating with the air.

At thermal equilibrium, which is when heat is being convectively removed from the pipe's exterior surface / air interface as fast as the air's convective heat transfer coefficient will allow [10 W/m<sup>2</sup>K for static air (10 J/m<sup>2</sup>K s) or 50 W/m<sup>2</sup>K for flowing air (50 J/m<sup>2</sup>K s) – which never changes] the difference in temperature ( $T_{Ex} - T_{Air}$ ) at the air interface of the coating will be determined by the thermal conductivity ( $\kappa$ ) of the coating [W/m K or J/m K s] , with a high thermal conductivity giving less of a difference in temperature (more heat gets through per unit time), and a low thermal conductivity giving more of a difference in temperature (less heat gets through per unit time). This difference determines the amount of heat that is supplied to the exterior surface of the pipe at the air interface per unit time that is available to be convectively rejected to the air [  $q_{conv} = hA(T_{Ex} - T_{Air})$  ].

The heat emitted by radiation is dependent on the emissivity of the coating at the interface of the exterior surface of the pipe at the air interface, and is simply determined by the relation:  $q_{rad} = \epsilon\sigma A(T_H^4 - T_C^4)$ .

So the two most important characteristics of a thermal coating are its thermal conductivity ( $\kappa$ ), which affects the amount of heat rejected to the surrounding air by convection at the air interface, and emissivity ( $\epsilon$ ), which affects the radiative transfer of heat out of the coating and into the surrounding air.

## II. CONDUCTION/CONVECTION:

Conductive / Convective Heat Transfer is a bulk material phenomenon.

Conduction per se occurs within the body of a material, while Convection is a conductive process that occurs at the surface of a material and results in transfer of heat from that material into the body of a flowing fluid. Thus, in a Convective process a continuous conductive heat transfer occurs, but at different rates depending on whether the conduction occurs solely within the body of one material or within the body of that material and then within the body of a fluid into which the heat is being transferred. The rate of conductive transfer by convection is enhanced by the continuous renewal of cooler fluid at the heat transfer interface caused by the flow of the fluid, maintaining a high temperature gradient at the surface.

The dominant carriers of heat in non-metallic crystalline materials are phonons, defined as quantized lattice vibrations. Specific heat, phonon group velocity and phonon mean free path (MFP)- the average distance a phonon travels between scattering events-determine a material's thermal conductivity.

Kinetic theory can be used to derive an approximate expression for thermal conductivity,  $k$ , as:

$$\kappa = 1/3 c_{p,v} v_{RMS} l \quad [ \kappa = (1/3)(3) v_{RMS} l ] = v_{RMS} l$$

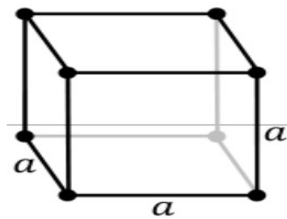
where  $c_{p,v}$  is the volumetric heat capacity ( $\rho c_{p,v} \sim 3 \text{ J/cm}^3\text{K}$ ),  $v_{RMS}$  is the root-mean-squared phonon velocity and  $l$  is the average mean free path (“MFP”) that a phonon travels between scattering

events. Generally, most materials that have a very low thermal conductivity also have a small specific heat.

### **Phonon Velocity ( $v$ ):**

A phonon is the quantum mechanical description of an elementary vibrational motion in which a lattice of atoms or molecules uniformly oscillates at a single frequency. In classical mechanics this designates a normal mode of vibration.

The lattice may be visualized as a system of balls connected by springs:



The potential energy of the lattice can be written as:

$$\sum_{\{ij\}(\text{nn})} \frac{1}{2} m \omega^2 (R_i - R_j)^2.$$

Where,  $\omega$  is the natural frequency of the harmonic vibrational potentials, which are assumed to be the same since the lattice is regular.  $R_i$  is the position coordinate of the  $i$ th atom, which is measured from its equilibrium position. The sum over nearest neighbors is denoted (nn).

Due to the connections between atoms, the displacement of one or more atoms from their equilibrium positions gives rise to a set of vibration waves propagating through the lattice. The amplitude of the wave  $\lambda$  is given by the displacements of the atoms from their equilibrium positions.

The study of phonon **dispersion** is useful for modeling the **directional** propagation of sound and thermal waves through solids, which is characterized by phonons. Phonon dispersion / dissipation occurs when waves of different wavelengths have different propagation velocities, so that a wave packet of mixed wavelengths tends to spread out in space. The dispersion relation can be written as:

$$v(\kappa) = \omega(\kappa) / \kappa$$

The energy of each phonon, is  $\hbar\omega$ . The velocity of the wave is given in terms of  $\omega$  and  $k$ , wherein  $\omega(k)$  is the angular frequency of lattice vibration ( $\omega = 2\pi f$ ) and  $k$  is the “wavevector” of the vibration related to its wavelength by  $k = 2\pi/\lambda$ . Thus, while ( $\omega$ ) relates to wave lattice vibration intensity,  $k$  gives the direction of the wave propagation.

The speed of propagation of a phonon, which is also the directional speed of the phonon in the lattice in the “ $k$ ” direction, is given by the slope of the dispersion relation,  $d\omega/dk$  (the ratio of the lattice vibrational frequency to the direction of phonon wave propagation the “ $k$ ” direction).

At low values of  $k$  (i.e. long wavelengths), the dispersion relation is almost linear, and the speed of sound is approximately  $\omega a$ , independent of the phonon frequency:

$$v(k) = \omega(k) / k = \omega(k)a \quad [k = 2\pi/\lambda = 2\pi/a, \text{ since } a \text{ is the limiting wavelength for propagation}]$$

wherein  $\omega$  is the natural vibrational frequency of the lattice, and  $a$  is the distance between atoms when the lattice is at equilibrium.

That is, the phonon velocity is the product of the natural vibrational frequency of the lattice,  $\omega$ , times  $a$ , the distance between atoms when the lattice is at equilibrium. The velocity of thermal waves is thus becomes independent of the thermal phonon frequency.

As a result, packets of phonons with different (but long) wavelengths can propagate for large distances across the lattice without breaking apart. This is the reason that sound and heat can propagate through solids without significant distortion. This behavior fails at large values of  $k$ , i.e. short wavelengths, due to the microscopic details of the lattice.

**Lattice vibrational frequencies ( $\omega$ )** themselves are determined by the type of vibration, the strength of the bond, the masses of the atoms, and by electronegativity.

The first factor is the type of vibration. If we were to consider the C- stretch versus the CH<sub>2</sub> bend, we see that the stretching vibration occurs at higher frequency. This tells us that stretching vibrations require more energy than bending vibrations.

The strength of the bond or bond order also has an impact on frequency. Consider a bond order of 1, we can have C-C, C-O, and C-N single bonds, with frequencies in the range of 1300-800 cm<sup>-1</sup>. Using the same atoms, but with a bond order of two, a C=C double bond, C=O double bond, and C=N double bond vibrate much higher, at 1900-1500 cm<sup>-1</sup>. Triple bonds, which are stronger than both double and single bonds, vibrate at even higher frequencies, roughly 2300-2000 cm<sup>-1</sup>. Thus, we can conclude that stronger bonds require more force to compress or stretch, which means that they will also vibrate faster than weaker bonds. Thus, frequency increases as bond strength increases. A third factor is the masses of the atoms. If we consider the C-H versus C-D stretch, we see that the C-H stretch is much more energetic than C-D.

Hydrogen is a small atom and can vibrate much faster than large atoms. We see this hold true for other atoms bound to hydrogen as well. OH, N-H, and C-H bonds have high vibrational frequencies. Thus, heavier atoms vibrate more slowly than lighter atoms, so frequency increases as weight decreases.

RULE OF THUMB 1: Since phonon velocity ( $v$ ) increases with increasing bond strength and decreases with atomic weight, thermal conductivity is increased with increasing bond strength and decreased with increasing atomic weight.

### Phonon Mean Free Path ( $l$ ):

$l$  is the mean phonon free path. At high temperatures it is close to the interatomic distance for complex oxides.

### Volumetric Heat Capacity ( $c$ ):

The Specific Heat Capacity ( $c_p$ ) of a substance is the amount of heat that must be added to one unit of mass of the substance in order to cause an increase of one unit in temperature (J/ g K).

Molecules have internal states that allow them to bend, vibrate, stretch, or twist in and of themselves. These extra ways of absorbing energy vary from one molecule to another ('degrees of freedom'), but they all absorb some of the energy that is added to the material.

If the material were made out of perfectly rigid, noninteracting spheres (basically, if the material were an ideal gas), then any energy you add would go to their movement, but real molecules don't work that way and so some of the energy you add -- for instance, as heat -- gets consumed in internal states of storage. The intermolecular forces between molecules in liquid or solid states also contribute additional degrees of freedom, as well. For each extra degree of freedom, the heat capacity goes up.

The other major component is that different molecules have different weights. Since each molecule constitutes an independent object that has to be moved around, the number of molecules in a given volume (density of molecules in a given volume) is relevant. For heavier molecules, there are fewer molecules per kilogram, meaning that it takes less energy to get all of its particles moving around and their heat capacities are low. The lighter a molecule is, the greater the number of molecules per unit of weight, and thus (in general and all else equal) the greater its heat capacity.

So the highest heat capacities come in things with some internal degrees of freedom and very light atoms. Hydrogen gas, for example, has an internal bond between two very light atoms, and thus has an exceptionally high specific heat. Water is also pretty high, since it has a couple bonds, lots of intermolecular forces, and isn't very heavy. On the other hand, the weak intermolecular forces and high weights of metals result in extremely low specific heat capacities.

The **volumetric heat capacity** of a material is the heat capacity ( $c_p$ ) of a sample of the

substance divided by the volume of the sample. It is the amount of energy that must be added, in the form of heat, to one unit of volume of the material in order to cause an increase of one unit in its temperature. The units of volumetric heat capacity are  $\text{J}/\text{cm}^3 \text{K}$ .

The volumetric heat capacity can also be expressed as the specific heat capacity (heat capacity per unit of mass, in  $\text{J}/\text{g K}$ ) times the density of the substance ( $\text{g}/\text{cm}^3$ )

In 1818, Dulong and Petit predicted that the product of solid substance's density and specific heat capacity ( $\rho c_p$ ) would be constant for all solids. This amounted to a prediction that the volumetric heat capacity ( $c_{p,v} = \text{g}/\text{cm}^3 \times \text{J}/\text{g K} = \text{J}/\text{cm}^3 \text{K}$ ) in all solids would be the same. This value is about  $3 \text{ J}/\text{cm}^3 \text{K}$ .

In 1819 they found that volumetric heat capacities were not quite constant, but that the most constant quantity was the heat capacity of solids ( $c_p$ ) adjusted by the atomic weight of the atoms of the substance.. This quantity was proportional to the heat capacity per atomic weight (or per molar mass), which suggested that it is the heat capacity *per atom* (not per unit of volume) which is closest to being a constant in solids. Meaning that the more *atoms (molecules)* per unit volume the higher the volumetric heat capacity. However, since the *size* of all atoms is about the same, even though their atomic weights vary greatly, the approximate  $3 \text{ J}/\text{cm}^3$  volumetric heat capacity for all solids still holds and this parameter does not highly affect the thermal conductivity of a material.

The volumetric heat capacity of solid materials at room temperatures and above varies from about  $1.2 \text{ MJ}\cdot\text{K}^{-1}\cdot\text{m}^{-3}$  for Bismuth to  $3.4 \text{ MJ}\cdot\text{K}^{-1}\cdot\text{m}^{-3}$  for Iron. This is mostly due to small differences in the physical size of the atoms, despite the fact that all atoms have roughly the same physical size.. However, atoms vary greatly in density, with the heaviest often being more dense, and thus are closer to taking up the same minimal volume in solids than their masses alone would predict. An additional factor for all types of specific heat capacities (including molar specific heats) then further reflects degrees of freedom available to the atoms composing the substance, at various temperatures.

As stated, the volumetric heat capacities for all solids is approximately the same, in accordance with the Dulong-Petit law. The Dulong-Petit law states that the ratio of volumetric specific heats for two solid materials are the same as the ratios of their atomic masses. The reason is that this ratio holds is that each atom, no matter what the material, can hold only the same thermal energy as any other, and thus their specific heats follow the ratio of their atomic masses. For ordinary solids at or above room temperature, the atomic heat capacity is approximately three times the gas constant, or about  $25 \text{ J}/\text{K}$ . This value is the sum of potential and kinetic energy per atom, which is  $3k_B T$ . So atomic mass has a lot to do with specific heat.

RULE OF THUMB 3: For a series of solid materials, those with the highest volumetric specific heat have the highest thermal conductivities.

### **SUMMARY FOR THE FACTORS THAT GIVE HIGH THERMAL CONDUCTIVITY:**

$$k = 1/3 c_{p,v} v l$$

Regarding volumetric heat capacity ( $c_{p,v}$ ):

1. on a per atom basis, the higher the number of degrees of freedom available to an atom – energy storage modes, the higher the heat capacity,
2. the higher the number of atoms per unit volume (which doesn't vary much despite atomic weight) the higher the heat capacity, and
3. larger molecules have higher heat capacities on a per-mole basis [vibrational frequency of atoms when the lattice is at equilibrium] [interatomic distances in the lattice]

High Thermal Conductivity results from:

1. Tightly packed lattice with many energy storage modes (vibrational, rotational, bend, wag, etc.) “degrees of freedom”
2. High vibrational bond frequencies (high Young's Modulus) “strong bonds”
3. Long interatomic distances

Thermal Diffusivity =  $\kappa / \rho c_{p,v} l$

Thermal Diffusivity =  $1/3 c_{p,v} v l / \rho c_{p,v}$

Thermal Diffusivity =  $1/3 v l / \rho$

Thermal Diffusivity =  $1/3$  (phonon velocity)(phonon MFP) / density

Thermal Diffusivity =  $1/3$  (vibrational frequency)(bond length) / (density → small atoms give high diffusivity)

To get High Thermal Conductivity you want High Bond Strength but Long Bond Length, generally with Lighter Atoms

As a General Rule of Thumb:

High Thermal Conductivity results in High Conductive Heat Transfer but Low Radiative Heat Transfer.

Low Thermal Conductivity results in Low Conductive Heat Transfer but High Radiative Heat Transfer.

### **III. RADIATION:**

Radiative / Emissive Heat Transfer is strictly a surface phenomenon.

It is the emission of heat energy that has been converted to electromagnetic radiation at or near the surface of a solid object and is then emitted into a fluid material. The emissivity ( $\epsilon$ ) of a material is indicative of the efficiency and speed that that material can convert heat near the surface of the material into electromagnetic radiation and radiate that energy to a fluid such as air.

If the wavelengths of the heat energy acting at or near the surface of a solid material at a solid/liquid interface is not such that it can be absorbed and then productively and efficiently converted to electromagnetic radiation by the mechanism described below, then that thermal energy is otherwise dissipated (such as through thermal conductivity into the body of the material) and the emissivity of the solid at those heat wavelengths is low. The opposite is also true. This explains why different materials have different emissivities at different temperatures, since heat wavelengths vary with temperature.

**Mechanism:** Thermal radiation is the emission of electromagnetic waves from all matter that has a

temperature greater than absolute zero. Thermal radiation reflects the conversion of thermal energy into electromagnetic energy.. Thermal energy is the kinetic energy of random movements of atoms and molecules in matter. All matter with a nonzero temperature is composed of particles with kinetic energy. These atoms and molecules are composed of charged particles, i.e., protons and electrons.. The kinetic interactions among matter particles result in charge acceleration and dipole oscillation. This results in the electrodynamic generation of coupled electric and magnetic fields, resulting in the emission of photons, radiating energy away from the body. Electromagnetic radiation, including visible light, will propagate indefinitely in vacuum.