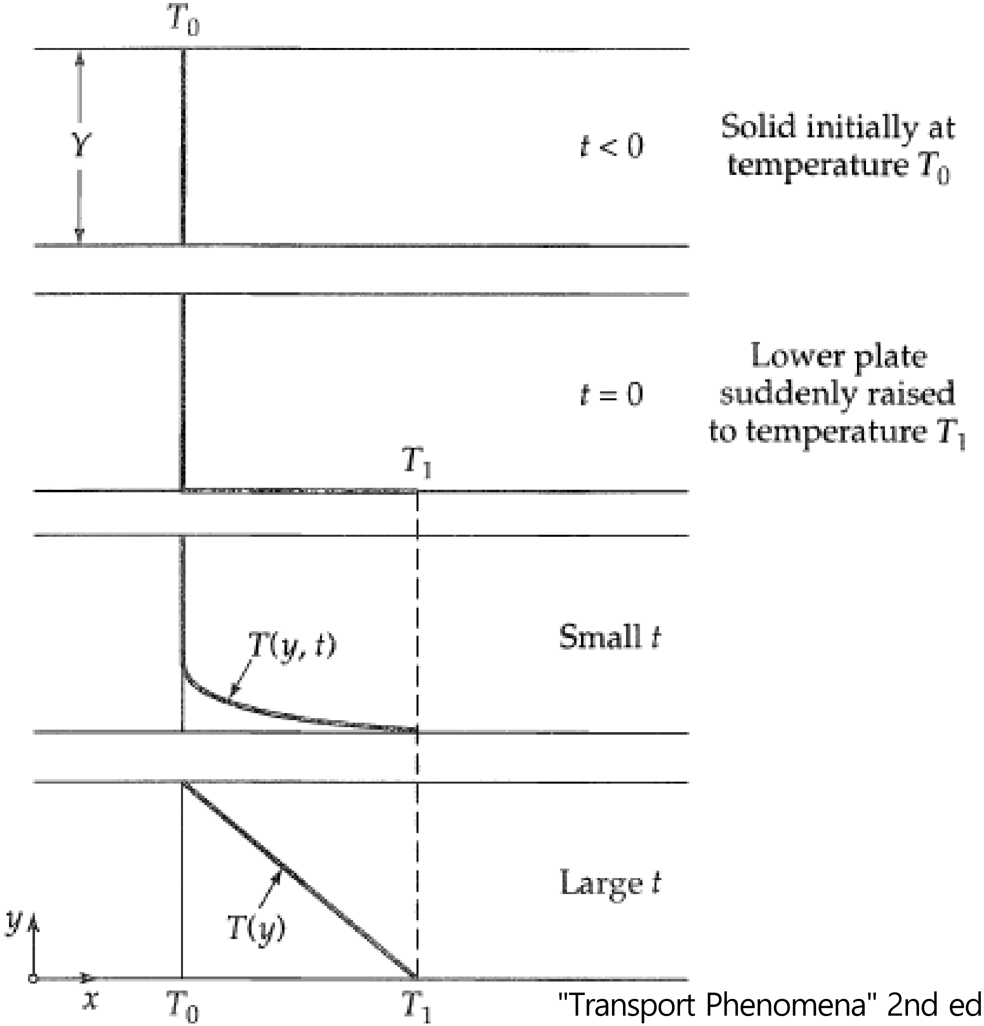
Chapter 9. Thermal conductivity and the mechanisms of energy transport

- Fourier’s law of heat conduction (molecular energy transport)
- Temperature and pressure dependence of heat conductivity
- Theory of thermal conductivity of gases at low density, of solids, and of composite materials
- Convective transport of energy
- Work associate with molecular motions

Fourier's law of heat conduction (molecular energy transport)



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- At steady state

$$\frac{Q}{A} = k\frac{\Delta T}{Y}$$

- Fourier's law of heat conduction

$$q_y = -k\frac{dT}{dy}$$

Thermal conductivity

- k = Thermal conductivity
- q_y = Heat flux in y-direction

$$q_x = -k\frac{\partial T}{\partial x} \qquad q_y = -k\frac{\partial T}{\partial y} \qquad q_z = -k\frac{\partial T}{\partial z}$$

$$\boxed{\mathbf{q} = -k\nabla T}$$

- Anisotropy

$$\mathbf{q} = -[\underset{\substack{\downarrow \\ \textit{thermal conductivity tensor}}}{\boldsymbol{\kappa}} \cdot \nabla T]$$

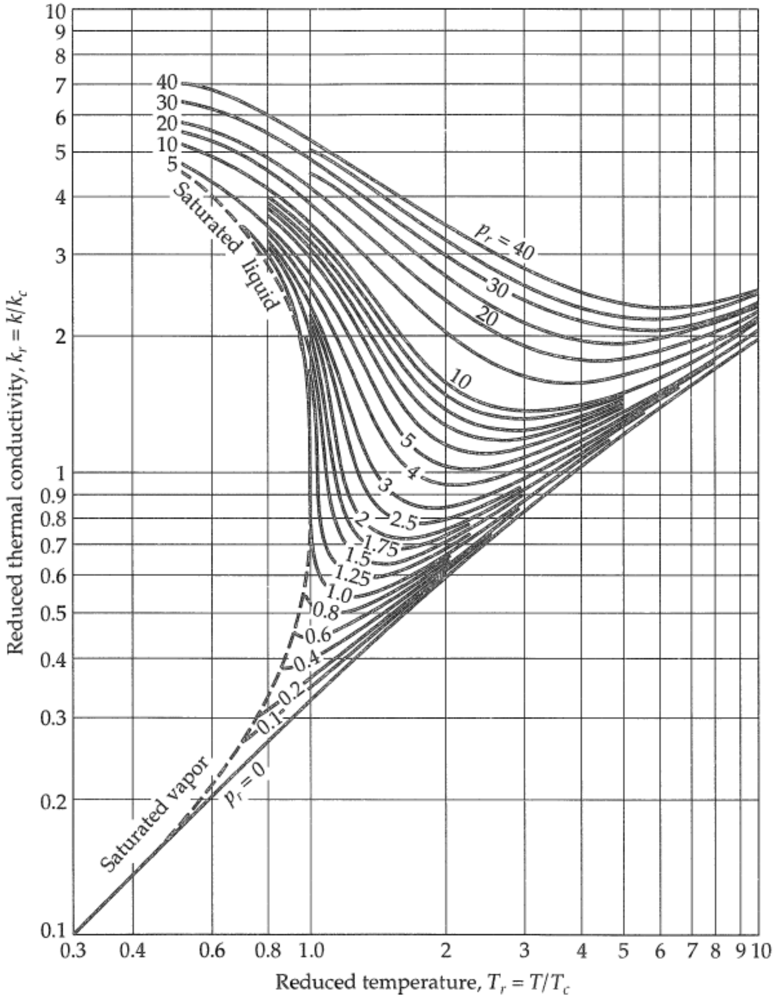
Thermal diffusivity

- α = Thermal diffusivity, m^2/s

$$\alpha = \frac{k}{\rho \hat{C}_p} \qquad \mathrm{Pr} = \frac{\nu}{\alpha} = \frac{\hat{C}_p \mu}{k}$$

- Pr = Prandtl number
- ν = kinematic viscosity

9.2 Temperature and pressure dependence of thermal conductivity



- Reduced thermal conductivity as a function of reduced temperature and pressure

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Temperature and pressure dependence of thermal conductivity

- Thermal conductivities of gases at low density increases with increasing temperature
- Thermal conductivities of most of the liquid decreases with increasing temperature

9.3 Theory of thermal conductivity of gases at low density

- Using mean molecular velocity and mean free path

$$\bar{u} = \sqrt{\frac{8\kappa T}{\pi m}} \qquad \lambda = \frac{1}{\sqrt{2}\pi d^2 n}$$

- And considering exchange of energy in the collisions, for mono-atomic gases

$$k = \frac{\sqrt{m\kappa T/\pi}}{\pi d^2}\frac{\kappa}{m} = \frac{2}{3\pi}\frac{\sqrt{\pi m\kappa T}}{\pi d^2}\hat{C}_V$$

Theory of thermal conductivity of gases at low density

- Using Chapman-Enskog, mono-atomic gases at low density

$$k = \frac{25}{32} \frac{\sqrt{\pi m \kappa T}}{\pi \sigma^2 \Omega_k} \hat{C}_V \quad \text{or} \quad k = 1.9891 \times 10^{-4} \frac{\sqrt{T/M}}{\sigma^2 \Omega_k}$$

- Polyatomic gases at low density

$$k = \left(\hat{C}_p + \frac{5}{4} \frac{R}{M} \right) \mu$$

9.5 Thermal conductivity of solids

- For pure metals, the thermal conductivity k and the electrical conductivity k_e are related approximately

$$\frac{k}{k_e T} = L = \text{constant}$$

Wiedemann–Franz–Lorenz equation

Heat capacity of metals – electronic contribution

In addition to atomic vibrations (phonons), thermal excitation of electrons can also make contribution to heat capacity.

To contribute to bulk specific heat, the valence electrons would have to receive energy from the thermal energy, ~kT. Thus, only a small fraction of electrons which are within kT of the Fermi level makes a contribution to the heat capacity. This contribution is very small and insignificant at room temperature.

Mechanisms of heat conduction

Heat is transferred by phonons (lattice vibration waves) and electrons. The thermal conductivity of a material is defined by combined contribution of these two mechanisms:

$$k = k_l + k_e$$

where k_l and k_e are the lattice and electronic thermal conductivities.

Lattice conductivity: Transfer of thermal energy phonons

Electron conductivity: Free (conduction band) electrons equilibrate with lattice vibrations in hot regions, migrate to colder regions and transfer a part of their thermal energy back to the lattice by scattering on phonons.

The electron contribution is dominant in metals and absent in insulators.

Since free electrons are responsible for both electrical and thermal conduction in metals, the two conductivities are related to each other by the Wiedemann-Franz law:

$$L = \frac{k}{\sigma T}$$

where σ is the electrical conductivity and L is a constant

Heat conduction in nonmetallic materials

In insulators and semiconductors the heat transfer is by phonons and, generally, is lower than in metals. It is sensitive to structure:

- glasses and amorphous ceramics have lower *k* compared to the crystalline ones (phonon scattering is more effective in irregular or disordered materials).
- Thermal conductivity decreases with porosity (e.g. foamed polystyrene is used for drinking cups).
- Thermal conductivity of polymers depends on the degree of crystallinity – highly crystalline polymer has higher *k*

Quest for good thermoelectric (TE) materials

Thermoelectric conversion: conversion of thermal to electrical energy

An applied temperature difference ΔT causes charge carriers in the material (electrons or holes) to diffuse from the hot side to the cold side, resulting in current flow through the circuit and producing an electrostatic potential ΔV.

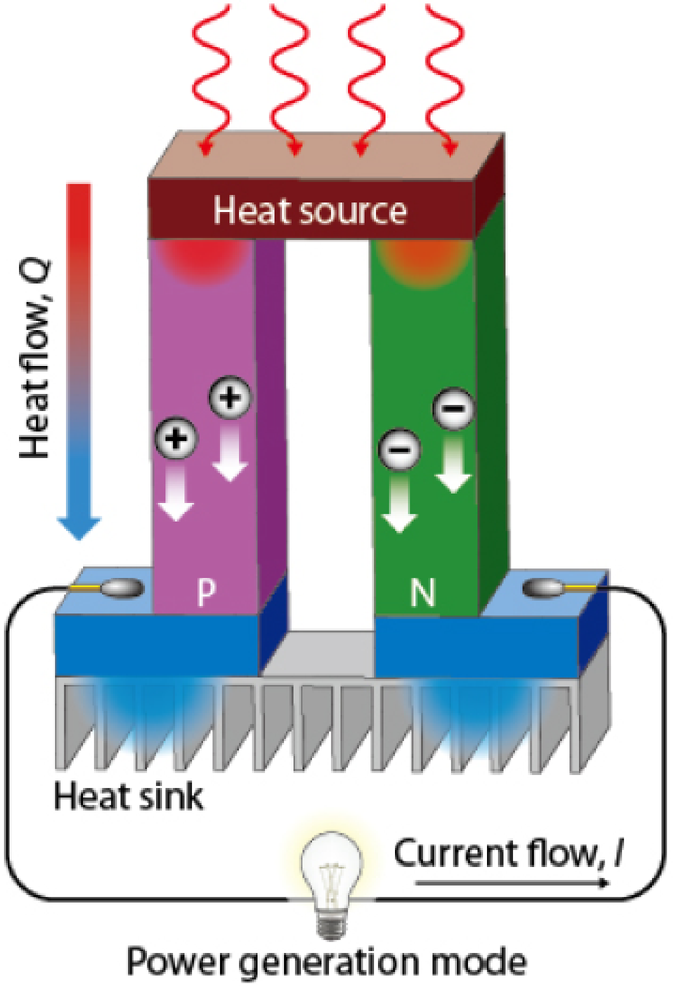

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Figure of merit of TE material:

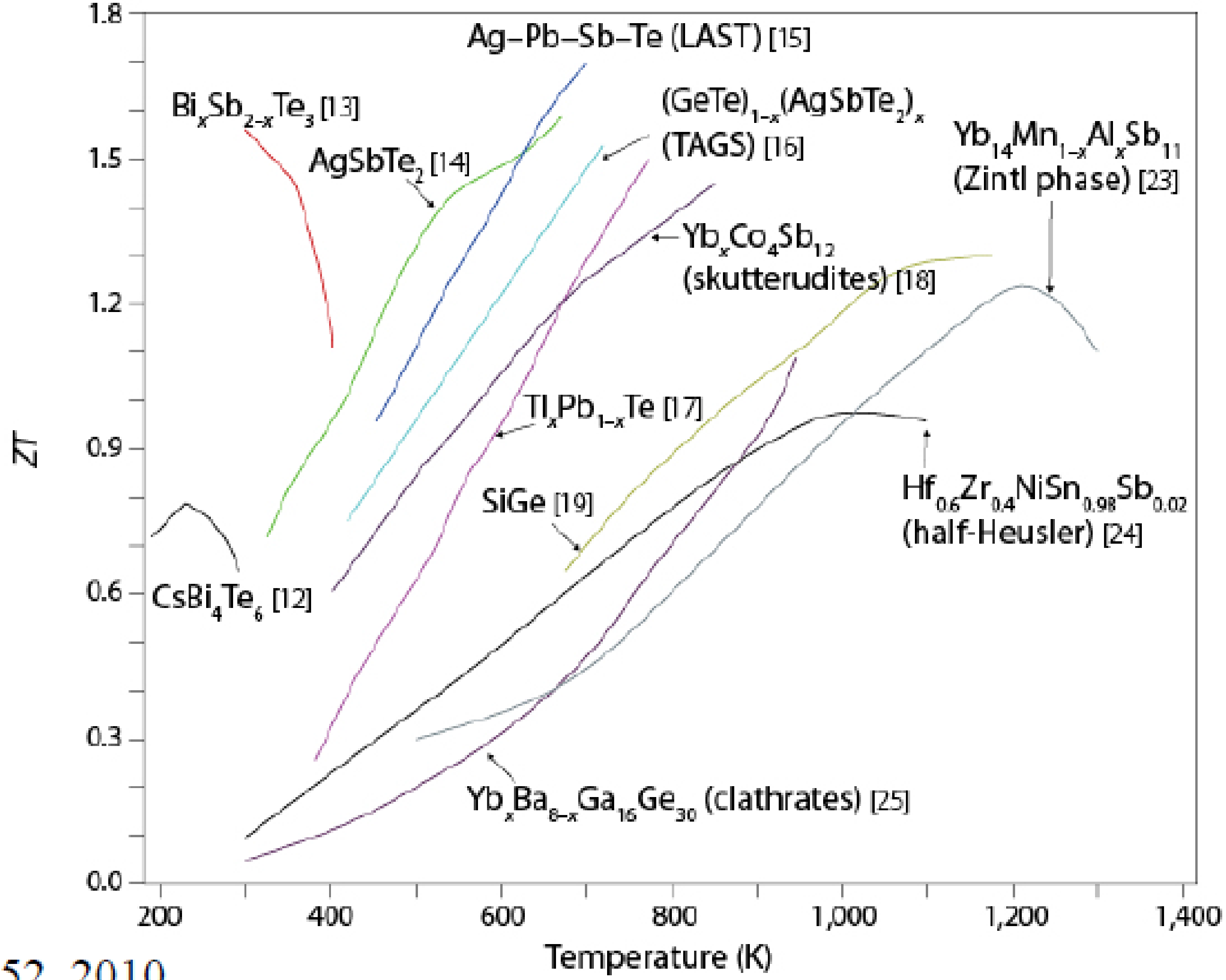
$$ZT = (\alpha^2\sigma/k)T$$

where σ, κ and α are the electrical conductivity, thermal conductivity, and Seebeck coefficient defined as $\alpha = \Delta V/\Delta T$.

Good TE material: High $\boldsymbol{\sigma}$ (low Joule heating), large Seebeck coefficient (large ΔV), low $\boldsymbol{k}$ (large ΔT) are necessary.

ZT ≈ 3 is needed for TE energy converters to compete with mechanical power generation and active refrigeration.

The high performance of these materials is related to nanostructure engineering



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9.6 Effective thermal conductivity of composite solids

- Effective thermal conductivity k_{eff} for spheres of thermal conductivity k_1 embedded in a continuous phase with thermal conductivity k_0 for small volume fraction ϕ

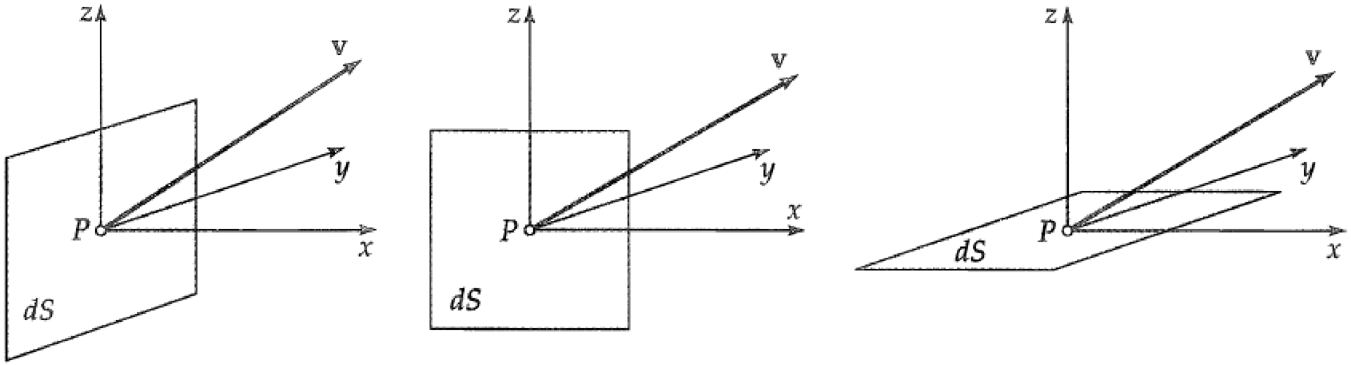
$$\frac{k_{\text{eff}}}{k_0} = 1 + \frac{3\phi}{\left(\dfrac{k_1 + 2k_0}{k_1 - k_0}\right) - \phi}$$

9.7 Convective transport of energy

- Energy is also transported by the bulk motion of the fluid
- Through a surface dS $(\frac{1}{2}\rho v^2 + \rho\hat{U})\overbrace{v_x dS}^{\text{Volumetric flow rate}}$
- Kinetic energy per unit volume $\frac{1}{2}\rho v^2$
- Internal energy per unit volume $\rho\hat{U}$

9.7 Convective transport of energy

- Energy transported by the bulk motion of the fluid



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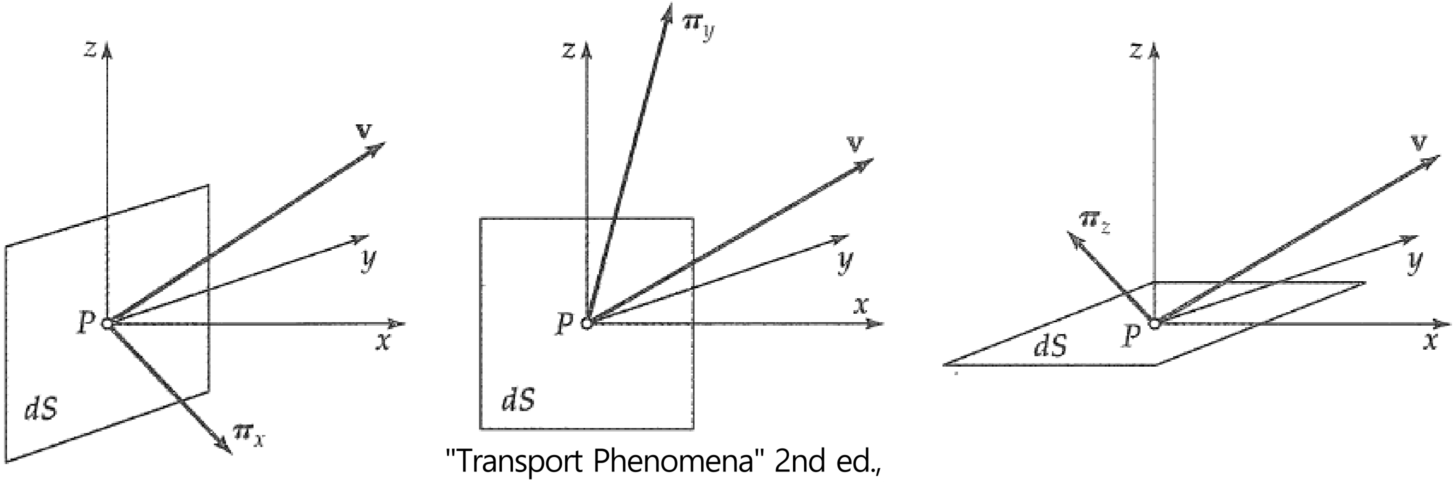
9.8 Work associated with molecular motions

- Work done per unit area

$$[\boldsymbol{\pi} \cdot \mathbf{v}]$$

$$[\boldsymbol{\pi} \cdot \mathbf{v}] = \boldsymbol{\delta}_x(\boldsymbol{\pi}_x \cdot \mathbf{v}) + \boldsymbol{\delta}_y(\boldsymbol{\pi}_y \cdot \mathbf{v}) + \boldsymbol{\delta}_z(\boldsymbol{\pi}_z \cdot \mathbf{v})$$



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Combined energy flux vector

- Combined energy flux vector

$$\mathbf{e} = (\tfrac{1}{2}\rho v^2 + \rho\hat{U})\mathbf{v} + [\boldsymbol{\pi} \cdot \mathbf{v}] + \mathbf{q}$$

  - Convective energy flux
  - Rate of doing work by molecular mechanisms
  - Heat transport by molecular mechanisms

- Stress tensor

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau}$$

- Then, using enthalpy

the rate of doing work

$$\mathbf{e} = (\tfrac{1}{2}\rho v^2 + \rho\hat{H})\mathbf{v} + [\boldsymbol{\tau} \cdot \mathbf{v}] + \mathbf{q}$$

the convective energy flux

the rate of transporting heat

by molecular mechanisms