Phonon Engineering of Thermal Conductivity in Complex Materials

G. Jeffrey Snyder
Northwestern University
http://thermoelectrics.matsci.northwestern.edu/thermoelectrics/index.html#thermal

Toberer, Zevalkink, Snyder J. Mat. Chem., 21, 15843 (2011)
Hanus, Snyder et al, Applied Physics Reviews 8, 031311 (2021)
Mechanisms of Thermal Conductivity

Heat can be transported by:
- Convection = Mass Flow
- Radiation (Infra-red (IR) light)
- Conduction = heat diffusion (in solid)

\[ K = K_e + K_l \]

\[ K_e = L \sigma T \]

\[ \frac{L}{10^{-8} W \Omega K^{-2}} = 1.5 + \exp \left[ \frac{-|S|}{116 \mu V/K} \right] \]

Conduction of heat by electrons or lattice vibrations (phonons)

Conduction of heat by electrons
Proportional to Electrical Conductivity \( \sigma \)

Thermal Diffusivity

Thermal Conductivity from Thermal Diffusivity Measurements

less problem with radiative losses than direct measurement

\[ \kappa = \rho c_p D_T \]

\( \kappa = [\text{W/mK}] \)

\( D_T = [\text{m}^2/\text{s}] \)

\( \rho c_p = [\text{J/m}^3] \)

geometric density

not Archimedes

Specific Heat – Heat Capacity

Heat Capacity = Thermal Energy (Heat $Q \, [J]$) required to raise temperature
depends on size of sample

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

$$[c] = \frac{J}{kg \cdot K} \quad [c] = \frac{J}{m^3 \cdot K}$$

Specific Heat (capacity) = heat capacity per unit mass or volume
material property

High Temperature Specific Heat of solid

$$c = 3k_B / \text{atom}$$
Dulong-Petit Specific Heat

**Equipartition of Energy in Classical Systems**

In thermal equilibrium, energy is shared equally among all of its various forms: \( \frac{1}{2} k_B T \) for each dimension of KE and PE

**Monoatomic Gas**

\[
KE = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 = \frac{3}{2} k_B T \\
C = \frac{3}{2} k_B
\]

**Atoms in Solid**

\[
KE = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 = \frac{3}{2} k_B T \\
PE = \frac{1}{2} \beta \Delta x^2 + \frac{1}{2} \beta \Delta y^2 + \frac{1}{2} \beta \Delta z^2 = \frac{3}{2} k_B T \\
C = 3 k_B
\]

**Heat Capacity (per atom)**

\[
C = \frac{d(KE + PE)}{dT}
\]

---

Table 4.5  Debye temperatures \( T_D \), heat capacities, and thermal conductivities of selected elements

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Ag</th>
<th>Be</th>
<th>Cu</th>
<th>Diamond</th>
<th>Ge</th>
<th>Hg</th>
<th>Si</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_D )(K)</td>
<td>215</td>
<td>1000</td>
<td>315</td>
<td>1860</td>
<td>360</td>
<td>100</td>
<td>625</td>
<td>310</td>
</tr>
<tr>
<td>( C_m )(J K(^{-1}) mol(^{-1}))</td>
<td>25.6</td>
<td>16.46</td>
<td>24.5</td>
<td>6.48</td>
<td>23.38</td>
<td>27.68</td>
<td>19.74</td>
<td>24.45</td>
</tr>
<tr>
<td>( c_s )(J K(^{-1}) g(^{-1}))</td>
<td>0.237</td>
<td>1.825</td>
<td>0.385</td>
<td>0.540</td>
<td>0.322</td>
<td>0.138</td>
<td>0.703</td>
<td>0.133</td>
</tr>
<tr>
<td>( \kappa )(W m(^{-1}) K(^{-1}))</td>
<td>429</td>
<td>183</td>
<td>385</td>
<td>1000</td>
<td>60</td>
<td>8.65</td>
<td>148</td>
<td>173</td>
</tr>
</tbody>
</table>
General Heat Capacity Equation

\[
c_p [\text{J g}^{-1}\text{K}^{-1}] \approx \frac{3NR}{M_W} \left[ 1 + \frac{1}{10^4} \left( \frac{T}{\theta_D} \right) - \frac{1}{20} \left( \frac{T}{\theta_D} \right)^{-2} \right] + A \left( \frac{T}{\theta_D} \right)
\]

\[3NR = 124.7 \text{ Jmol}^{-1}\text{K}^{-1}\]
\[M_W \text{ is the molecular weight [g mol}^{-1}\text{]}\]
\[\theta_D \text{ is Debye Temperature}\]
\[\alpha_V \text{ is volumetric thermal expansion coefficient}\]
\[B \text{ is the isothermal bulk modulus}\]
\[\gamma \text{ is Gruneisen parameter}\]

\[A = BV_m \alpha_V^2 \theta_D / M_W\]

\[\gamma = B \alpha_V / C_V\]

Low Diffusivity near Phase Transformation

Thermal Diffusivity $D$ (mm$^2$s$^{-1}$) vs. $T$ (K)

Heat Capacity $\rho c_v$ ($10^6$ J m$^{-3}$K$^{-1}$) vs. $T$ (K)

Latent Heat vs. $T$ (K)

Dulong–Petit Behavior

Thermal Conductivity $\kappa$ (W m$^{-1}$K$^{-1}$) vs. $T$ (K)

$zT$ Figure-of-Merit vs. $T$ (K)

Thermal Conductivity Spectrum

phonon wave

Toberer, Zevalkink, Snyder *J. Mat. Chem.*, 21, 15843 (2011)
Phonon Heat Transport

\[ \kappa_L = \frac{1}{3} \int_0^{\omega_{\text{max}}} C(\omega) v_g^2(\omega) \tau(\omega) d\omega \]

- Spectral heat capacity:
- Phonon Velocity:
- Relaxation Time:
Near linear dispersion
like massless photons, unlike electrons

Debye Model
up to Debye Frequency
defines Debye Temperature

\[ E = \hbar \omega = \hbar v_p k \]

\[ v_p = v_g = v_s \]

\[ \hbar \omega_D = k_B \theta_D \]

\[ v_s - \text{average speed of sound} \]
\[ v_L - \text{longitudinal speed of sound} \]
\[ v_T - \text{transverse speed of sound} \]
\[ \theta_D - \text{Debye temperature} \]
\[ B - \text{bulk modulus} \]
\[ G - \text{shear modulus} \]
\[ \rho - \text{density} \]
\[ V - \text{volume/atom} \]

(all phonon Debye model)
\[ V - \text{volume of primitive cell} \]
(acoustic only Debye model)

\[ v_p = \frac{\omega}{k} \]
\[ v_g = \frac{d\omega}{dk} \]

\[ \hbar \omega_D = k_B \theta_D = \hbar \left( \frac{6\pi^2}{V} \right)^{1/3} v_s \]

\[ v_s = \left( \frac{1}{3} \left[ \frac{1}{v_L^3} + \frac{2}{v_T^3} \right] \right)^{-1/3} \]

\[ v_L = \sqrt{\frac{B + \frac{4}{3}G}{\rho}} \]
\[ v_T = \sqrt{\frac{G}{\rho}} \]
Debye Approximation

Acoustic Phonons in Copper

Debye density of states

\[
c_s/k_B = g(\omega) = \frac{3}{2\pi^2} \frac{\omega^2}{v_s^3}
\]

Debye dispersion

\[
\frac{d\omega}{dk} \approx v_s
\]
Phonon Heat Transport

\[ \kappa_l = \frac{1}{3} \int C_s(\omega) v_g^2(\omega) \tau(\omega) d\omega \]

\[ C_s = \frac{3k_B}{2\pi^2} \frac{\omega^2}{v_g v_p^2} \]

\[ v_g = \frac{d\omega}{dk} \]

Spectral Heat Capacity
Related to Phonon DOS

\[ C = \int C_s(\omega) d\omega = 3k_B \]
High Temperature Approx.

Phonon Group Velocity

Phonon Relaxation Time

\[ \tau^{-1} = \tau_{U}^{-1} + \tau_{PD}^{-1} + \tau_{PD}^{-1} + \ldots \]
Phonon Scattering Rate

\[ v_g \approx \text{Speed of Sound} \]
Phonon–Phonon Umklapp Scattering

\[ \tau_u^{-1} \propto g(\omega) \propto c_s(\omega) \]

\[ \kappa_s(\omega) = \frac{1}{3} c_s(\omega) v_g^2(\omega) \tau(\omega) \]

\[ \kappa_L = \int_0^{\omega_D} \kappa_s(\omega) d\omega \]

avg. speed of sound \( v_s \)
Grüneisen parameter \( \gamma \)
avg. atomic mass \( M \), volume \( V \)

\[ \kappa_U \sim 0.385 \frac{\overline{M}}{TV^{\frac{2}{3}}} \frac{v_s^3}{\gamma^2} \]

Toberer, Zevalkink, Snyder *J. Mat. Chem.*, 21, 15843 (2011)
Grüneisen and Thermal Expansion

Thermal Expansion due to anharmonicity of potential well

\[ \frac{\Delta l}{l} = \alpha_{cte} \Delta T \]
Linear CTE

\[ \gamma = \frac{3 \alpha_{cte} B}{c_V} \]

\( \alpha_{cte} \) linear Coeff. Thermal Expansion
3 x linear CTE = volume CTE
\( \gamma \) Grüneisen parameter
\( B \) Bulk Modulus
\( c_V \) specific heat (per volume)
Full Spectrum Phonon Scattering
Point Defect Scattering

Impurities and point defects scatter phonons with wavelengths similar in size to the defect.

$\omega^4$ like Raleigh Scattering due to strain (radius) $r$

and mass $m$ fluctuation

$\tau_{PD}^{-1} = \frac{V}{4\pi v_g v_p^2} \left( \sum f_i \left( \frac{\Delta m_i}{m} \right)^2 + \varepsilon \sum f_i \left( \frac{\Delta r_i}{r} \right)^2 \right)$

vacancy or interstitial

$\Delta m_i = m_i + 2m$

can be $10 \times$ stronger than impurity

Alloying affects Phonons and Electrons

Disorder reduces thermal conductivity

\[ \Delta M = \text{mass difference} \]
\[ \Delta r = \text{strain} \]

\[ \frac{\kappa_L}{\kappa_0} = \tan^{-1} \frac{u}{u_0} \]
\[ u^2 = \left( \frac{6\pi^5 V^2}{2k_B v_s} \right)^{1/3} \kappa_0 \Gamma \]
\[ \Gamma_M = \frac{\langle M^2 \rangle}{\langle M \rangle^2} \]

But also reduces electronic mobility

\[ zT \propto B \approx \frac{\mu}{\kappa_l} \]

Standard Boundary Scattering

Boundaries limit mean free path
nanowires, grain size

mean free path \( l = v_g \tau \)

Mean distance between boundaries
grain size or nanowire diameter
_not size of precipitates_
Characterized by Interface area/volume

Klemens & Callaway models

Spectral $\kappa$ and Matthiessen’s Rule

$$\kappa_1 = \frac{1}{3} \int C_s(\omega) v_g^2(\omega) \tau(\omega) d\omega$$

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{\tau_U} + \frac{1}{\tau_{PD}}$$

Boundary $\tau \sim \omega^0$

Umklapp $\tau \sim \omega^2$

Point defect $\tau \sim \omega^4$

Dislocation $\tau \sim \omega^{-1}$

Strain $\tau \sim \omega^{-3}$

Phonon relaxation time (ns)

Frequency (THz)

Effective $\tau$

Umklapp

Boundary

PD

$\kappa_\omega(\omega)$ (pW s m$^{-1}$ K$^{-1}$)

Frequency (THz)

Umklapp

Boundary

PD
Dislocation Strain Scattering

\[ \kappa = \int \kappa_s \, d\omega = \int \frac{1}{3} c_v(\omega) v^2_s(\omega) \tau(\omega) \, d\omega \]

\[ \tau = \frac{v}{d} + C_{DS} N_D B_D^2 \omega + C_U T \gamma^2 \omega^2 + C_{PD} \omega^4 \]


Husan, Snyder. et al. *Communications Physics*, 1, 78 (2018)
“Hierarchical Complexity”

Size ↔ Wavelength $\lambda$
Spacing ↔ Mean Free Path $l$

$$\tau^{-1} = \frac{v}{d} + C_{DS} N_D B_D^2 \omega + C_U T \gamma^2 \omega^2 + C_{PD} \omega^4$$

$\lambda \sim 3$ nm
long wavelengths for thermal transport

$\lambda \sim 0.3$ nm
interatomic distance

Thermal Conductivity of Complex Unit Cells
Complex Structures with low $\kappa_L$

Primitive unit cell volume is a good indicator for $\kappa_L$ (when constituent atoms are similar).

Acoustic vs. Optical Phonons

Acoustic Phonons
- Have high group velocity \( (v_g = d\omega/dk \sim \text{speed of sound}) \)
- only 3 modes per primitive cell
- Conduct most of the heat

Optical Phonons
- Have low group velocity \( (v_g = d\omega/dk \sim \text{small}) \)
- Large cells have many optic modes
  - \( (3N-3 \text{ per primitive cell}) \)
- Conduct little heat

\[
\kappa_L = \frac{1}{3} \int C_s(\omega) v_g^2(\omega) \tau(\omega) d\omega
\]

- \( C \) - heat capacity
- \( v \) - speed of sound
- \( \tau \) - phonon relaxation time
- \( N \) - atoms per cell
- \( V \) - volume of cell

Diamond Ge

Optical Phonon Modes
\( (3N-3 / \text{primitive cell}) \)

Acoustic Phonon Modes
\( (3 / \text{primitive cell}) \)

Large Cells = many optical phonons

\[ \kappa_l = \frac{1}{3} \int C_s(\omega) v_g^2(\omega) \tau(\omega) d\omega \]

Many atoms in unit cell (N) decreases average phonon \( v_g \) and \( \kappa \)

\[ v_g = \frac{d\omega}{dk} \]

Large Cells with low thermal cond.

Heat primarily carried by acoustic modes
But only 3 acoustic modes in a Large cell
Low lattice thermal conductivity
for large primitive unit cell volume ($V$)
should decrease with $V$

- for materials with same chemistry

$$\kappa_{\text{lattice}} = \frac{1}{3} CVl$$

Acoustic:
$$C = \frac{3k_B}{V}$$

$$K_l \approx \frac{k_Bvl}{V}$$

Antimonide Zintl Phases

Dashed line: $V^{-1} + \kappa_{\text{min}}$

Does $l$ change with $V$?!

Phonons in Large Unit Cell Crystals

Cu
1 atom per
primitive cell

PbTe
2 atoms per
primitive cell

Yb$_{14}$MnSb$_{11}$
104 atoms/primitive cell

Minimum Thermal Conductivity by Diffusive Heat Transport
Propagons vs Diffusons

Propagon Phonons
Ballistic Transport
heat pulse travels as $vt$

Diffusons
Diffusive Transport
heat pulse travels as $\sqrt{Dt}$

Generalized Atom Vibrations

Phonons = Eigenmodes of atom vibrations
Propagons = Classical wave-like phonon modes. Acoustic waves in anything transport energy linear with time $v_g t$

Diffusons = Eigenmodes with no apparent periodicity not localized transport energy square-root with time $\sqrt{t}$

Locons = localized vibrational modes – do not transport heat effectively

Diffusons in Complex Materials

Classical Phonons are good description in simple crystals
Diffusons dominate in Complex Materials
- amorphous, non crystalline materials
- disordered materials
- complex crystal structures
- high temperature
- strong phonon interactions

\[ \text{In}_{0.53}\text{Ga}_{0.47}\text{As} \]

Diffusive Thermal Conduction

\[ \kappa = \frac{1}{3} c v \ell = \frac{1}{3} c f a^2 \]

Minimum Phonon transport (Cahill)
min. mean free path \( l(\omega) = \frac{\lambda}{2} \) wavelength/2

\[ \kappa_{\text{Cahill}} = 1.21 \frac{n^{2/3} k_B}{3} (2v_T + v_L) \]

Diffusive Heat Transport (Diffuson)
Random walk of heat energy

step length \( a = l \) mean free path
attempt frequency \( f = v/l \)

\[ \kappa_{\text{Diff}} = 0.76 \frac{n^{2/3} k_B}{3} (2v_T + v_L) \]

\( c \) - heat capacity
\( v \) - speed of sound
\( \tau \) - phonon relaxation time
\( l = v \tau \) - mean free path
\( a \) = interatomic distance
\( n \) = number density of atoms
\( V = a^3 \) - volume per atom

Thermal Conductivity model

\[ \kappa_L = \kappa_U + \kappa_{optic} \]

\[ = \frac{A}{T} + B \]

Acoustic phonons
Umklapp Scattering

\[ \kappa_U \sim 0.385 \frac{\overline{M} v_s^3}{2TV^3\gamma^2} N^{-\frac{1}{3}} \]

Optical phonons at \( \kappa_{\text{min}} \)
Diffuson or Cahill model

\[ \kappa_{optic} \sim 1.2 \frac{k_B v_s}{2V^\frac{2}{3}} \left( 1 - N^{-\frac{2}{3}} \right) \]

Scanning Thermal Images

Spatially-resolved frequency domain thermoreflectance (FDTR)

Homogeneous Assumption

Homogeneous Models

Klemens-Callaway

\[ \kappa_l = \frac{1}{3} \int C_s(\omega) v_g^2(\omega) \tau(\omega) d\omega \]

Lattice or Phonon thermal conductivity

\[ \tau^{-1} = \frac{v}{d} + C_{DS} N_D B_D^2 \omega + C_U T \gamma^2 \omega^2 + C_{PD} \omega^4 \]

Grains

Grain Boundary

Series Circuit Model for Thermal Resistivity


Summary

Heat Capacity – Specific Heat

Dulong Petit $3k_B$/atom above $\Theta_D/2$

Thermal expansion adds a linear $T$ term

Watch out for phase transformations

Thermal Conductivity

$\kappa = A/T + B$

A from classical phonon transport

- Mostly Acoustic Phonons
- $v_s = v_g = v_p$ speed of sound
- Grüneisen $\gamma$ from thermal expansion
- $\tau_{PD}$ from mass (+strain) disorder

B from diffusion heat transport

$\kappa_{Diff} = 0.76 n^{2/3} k_B^1(2\nu_T + \nu_L)$

Excess Interface Resistance

- instead of boundary term
- adds $1/d\kappa_{GB}$ in series

\[ C_s = \frac{3k_B}{2\pi^2} \frac{\omega^2}{v_s v_p^2} \]

\[ \gamma = \frac{3\alpha_{cte}B}{c_v} \]

\[ \kappa_I = \frac{1}{3} \int C_s(\omega)v_g^2(\omega)\tau(\omega)d\omega \]

$\tau^{-1} = \frac{v}{d} + C_{DS}N_D B_D^2 \omega + C_U \gamma^2 \omega^2 + C_{PP} \omega^4$

\[ k = A/T + B \]

Excess Interface Resistance

- instead of boundary term
- adds $1/d\kappa_{GB}$ in series
Electronic Properties of Complex Semiconductors

G. Jeffrey Snyder
Northwestern University
http://thermoelectrics.matsci.northwestern.edu/thermoelectrics/index.html#electronic

Thermoelectric Quality Factor

\[ B \sim \frac{\mu W}{\kappa_L} \]

- Weighted Mobility
- Lattice Thermal Conductivity

**Thermoelectric Semiconductor**

**Bi$_2$Te$_3$**

- **n-type Thermoelectric**
  - $n$ electrons in conduction band
  - $m_e^*$ effective mass
  - $\mu_e$ mobility

- **p-type Thermoelectric**
  - $n$ holes in valence band
  - $m_h^*$ effective mass
  - $\mu_h$ mobility

**Doping from Charged Defects**


Degenerate Semiconductor Behavior

1. Linear Thermopower $|S|$ or $|\alpha|$  
2. Increasing, ~linear, Resistivity $\rho = 1/\sigma$  
3. $1/T + C + L\sigma T$ Thermal Conductivity
Goldsmid-Sharp Maximum Seebeck

Doping changes $S$ vs $T$

But peak $S$ is limited by $E_g$

$$E_g = 2eS_{\text{max}} T_{\text{max}}$$

Lightly doped semiconductors

Heavily doped semiconductors


Maximum $zT$ depends on Quality Factor

$$B = \frac{\mu m_{DOS}^{3/2}}{\kappa_L}$$

Density of States effective mass $m_{DOS}^*$

Weighted Mobility $\mu_w$

Optimized carrier concentration

$Lattice$ Thermal Conductivity $\kappa_L$

$\kappa$ Thermal Conductivity

$\sigma$ Electrical Conductivity

$S$ Seebeck Coefficient

$10^{19}$ $10^{20}$ $10^{21}$ $10^{22}$ $n \text{ (cm}^{-3}\text{)}$

Pei, Wang, Snyder  Advanced Materials 24, 6125 (2012)
Weighted Mobility

Single parameter for $S$ vs $\sigma$ curves

$$\mu_w = \mu_0 \left( \frac{m^*_{DOS}}{m_e} \right)^{3/2}$$

Define weighted mobility as simply a function of $|S|$ and $\sigma$

$$\mu_w \equiv \frac{331 \text{ cm}^2}{Vs} \left( \frac{m\Omega\text{cm}}{\rho} \right) \left( \frac{T}{300\text{K}} \right)^{-3/2} \frac{\exp \left[ \frac{|S|}{k_B/e} - 2 \right]}{1 + \exp \left[ -5 \left( \frac{|S|}{k_B/e} - 1 \right) \right]} + \frac{3|S|}{\pi^2 k_B/e} \frac{1}{1 + \exp \left[ 5 \left( \frac{|S|}{k_B/e} - 1 \right) \right]}$$

$$k_B/e = 86 \frac{\mu V}{K} \quad q = 1/\sigma$$

Snyder et. al. *Advanced Materials*, 32, 2001537 (2020)
Hall and Weighted Mobility

\[ \mu_H = \sigma R_H \]

\[ \mu_w = \mu_0 \left( \frac{m^*_\text{DOS}}{m_e} \right)^{3/2} \]

Hall Effect + Resistivity \Rightarrow \mu_H

Seebeck + Resistivity \Rightarrow \mu_w

Snyder et. al. *Advanced Materials*, 32, 2001537 (2020)
Weighed mobility for other materials

Typical Thermoelectric semiconductors

StarryData in *Advanced Materials*, **32**, 2001537 (2020)
**µ_W** for Conducting Polymers

- Model how properties change with doping
- Helps identify transport mechanism
- Quantify Localization
- Predicts peak S²σ

Effective Mass from Seebeck

**DOS Effective Mass**

\[ \text{DOS} \propto (m_{DOS}^*)^{3/2} \]

Historically from low temperature (1-10K) heat capacity \( C_P = \gamma T \)

From Seebeck and Hall (10K-1500K)

\[ \mu_w = \mu_0 \left( \frac{m_{DOS}^*}{m_e} \right)^{3/2} \]

Weighted Mobility

\[ \mu_H = \mu_d r_H \]

Hall Mobility

\[ m_{DOS}^* \equiv 0.924 \left( \frac{300K}{T} \right) \left( \frac{n_H}{10^{20} \text{cm}^{-3}} \right)^{2/3} \left[ \frac{3 \left( \exp \left[ \frac{|S|}{k_B/e} - 2 \right] - 0.17 \right)^{2/3}}{1 + \exp \left[ -5 \left( \frac{|S|}{k_B/e} - \frac{k_B/e}{|S|} \right) \right]} \right] + \left[ \frac{|S|}{k_B/e} \right] \]

Snyder et. al. *Advanced Functional Materials*, 202112772 (2022)
High DOS Complex Fermi Surfaces
DOS and Valley Degeneracy $N_V$

$N_V$ is number of carrier pockets (valleys)

Spherical Fermi Surface
- free-electron model

Multiple valley when:
- Symmetrically equivalent (not at $\Gamma$)
- Different bands at band gap (orbital degeneracy)

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Na
$N_V = 1$

Si
$N_V = 6$

PbTe
- $v: N_V = 4, 12$
- $c: N_V = 4$
Phonon Scattering of Electrons

**Atom Vibrations (phonons)**

- Scattering Cross-section
  \[ S = \pi a^2 \propto k_B T \]

- From equi-partition theorem, \( a^2 \) potential energy of atom is proportional to \( k_B T \)

**Metal**

- \( \nu_F = \text{constant} \)
- \( \frac{1}{2} m v_{th}^2 = k_B T \)
- \( \mu_L \propto \frac{1}{T} \)

**Semiconductor**

- \( \mu_L \propto \frac{1}{T^{3/2}} \)

- Resistivity \( \rho = \frac{1}{n e \mu} \sim T^p \)

  \( 1 < p < 1.5 \)

  *not just acoustic phonon scattering*

- \( \tau = \text{mean time between scattering} \), \( \nu = \text{mean speed of the electron} \), \( N_s = \text{concentration of scatterers} \), \( \mu = \text{mobility} \), \( n = \text{charge carrier concentration} \)
Grain Boundary Electrical Resistance

Thermally activated resistivity reduced by increasing the grain size

Seebeck unaffected by grain size

Bricklayer Model

Conducting Grains

Resistive Grain Boundaries

Grains Grain Boundary

\[ \rho_G \quad \rho_{GB}/d \]

Series Circuit Model For effective resistivity

Grain Boundary Resistance seen as thermally activated electron mobility