The enhancement of the figure of merit for Thermoelectric Materials

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Outline

- Thermoelectric Effect
- Wiedemann-Franz **(WF)** Empirical Law
- Fermi Dirac Integrals and Polylogarithms
- Conclusions

The Thermoelectric effect

- Thermoelectric effect enables direct and reversible conversion between thermal and electrical energy, and provides a pathway for power generation from waste heat.

- Functional relationships between thermal and electrical properties are expressible in terms of the Lambert W functions and polylogarithms.

- Efficiency of thermoelectric material - measured by dimensionless figure of merit θ^2 (aka ZT) - ZT governs the Carnot efficiency for heat conversion.

$$ZT = (S^2\sigma/\kappa)\mathrm{T}$$

S: Seebeck coefficient, σ: electrical conductivity,

κ: Thermal conductivity, T: Absolute Temperature

- To be competitive with other conventional devices, ZT should be >3
- **Challenge:**
  - Achieve the maximum ZT in TE materials.
  - Improved analytic calculations and experiments - Better ways to enhance ZT.
- Can we make κ small and σ large?

WF Law;

$$\frac{\kappa_e(T)}{T\sigma(T)} = L_0 = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 = 2.44\times10^{-8} W\Omega K^{-2}$$

$$\kappa = \kappa_e + \kappa_l$$

κ_e: electronic component, κ_l: lattice component,

κ: total thermal conductivity

$$\kappa_e = \frac{16\pi m l_0 k^{r+3} T^{r+2}}{3h^3}\left[(r+3)F_{r+2} - \frac{(r+2)^2 {F_{r+1}}^2}{(r+1)F_r}\right]$$

$$\sigma = \frac{16\pi m e^2 l_0 (kT)^{r+1}(r+1)F_r}{3h^3}$$

***k*:** Boltzmann constant, **e:** electronic charge, **μ*:** reduced chemical potential = μ/kT, **m:** effective mass of the carriers, l_0 **:** Carrier mean free path constant.

L_0 = Lorenz # (Sommerfeld value) (More appropriately Lorenz function (L(T)).

Non polar materials: r=0; Polar Materials: r=1/2; Ionized impurity: r=2

Fermi-Dirac (FD) Integrals

$$F_i(\mu^*) = \int_0^\infty \frac{x^i dx}{e^{x-\mu^*} + 1}$$

FD Integrals are a subset of polylogarithm functions $Li_r(z)$

$$F_r(\mu^*) = -\Gamma(r+1) Li_{r+1}(-exp\mu^*)$$

$$\mu^* = \frac{\mu}{kT}$$

μ: Chemical potential, **T**: Temperature, **k**: Boltzmann constant

μ* can be less than or greater than zero

Exact FD Integral expressions can generalize WF Law

$$F_n(\mu^*) = \frac{(\mu^*)^{n+1}}{n+1} + (\mu^*)^n \ln\left(1+e^{-\mu^*}\right) + n \quad (\mu^*)^{n-1}\left(\frac{n^2}{6} - \mu^* \ln\left(1+e^{\beta\mu}\right) - Li_2\left(-e^{-\beta\mu}\right)\right)$$

$$+\frac{n(n-1)}{2}(\mu^*)^{n-2}\left\{\int_0^\infty \frac{x^2}{e^x+1}dx - \int_0^{\mu^*}\frac{x^2}{e^x+1}dx\right\} + \ldots$$

$$+\frac{n(n-1)(n-2)}{6}(\mu^*)^{n-3}\left\{\int_0^\infty \frac{x^3}{e^x+1}dx + \int_0^{\mu^*}\frac{x^3}{e^x+1}dx\right\} + \ldots$$

$$\mu^* = \frac{\mu}{kT} = \beta\mu$$

Highlighted terms are the fine tuned corrections to the empirical WF Law

$$L_e(T) = \frac{\kappa_e}{\sigma T}$$

$$= \left(\frac{k^{r+3}T^{r+2}}{3h^3}\left[(r+3)F_{r+2} - \frac{(r+2)^2F_{r+1}^2}{(r+1)F_r}\right]\right) / \left(\frac{e^2(kT)^{r+1}(r+1)F_r}{3h^3}\right)$$

$$= \left(\frac{k^2}{e^2}\right) A(r,\mu^*)$$

A(r,μ*) is a function of (r,μ*).
It can be expressed more concisely in terms of polylogarithms $Li_r(w)$.

$$A(r,\mu^*) = \frac{(r+3)(r+2)Li_{r+3}Li_{r+1} - (r+2)^2Li_{r+2}^2}{Li_{r+1}^2}$$

$Note: -w = e^{\mu^*}$

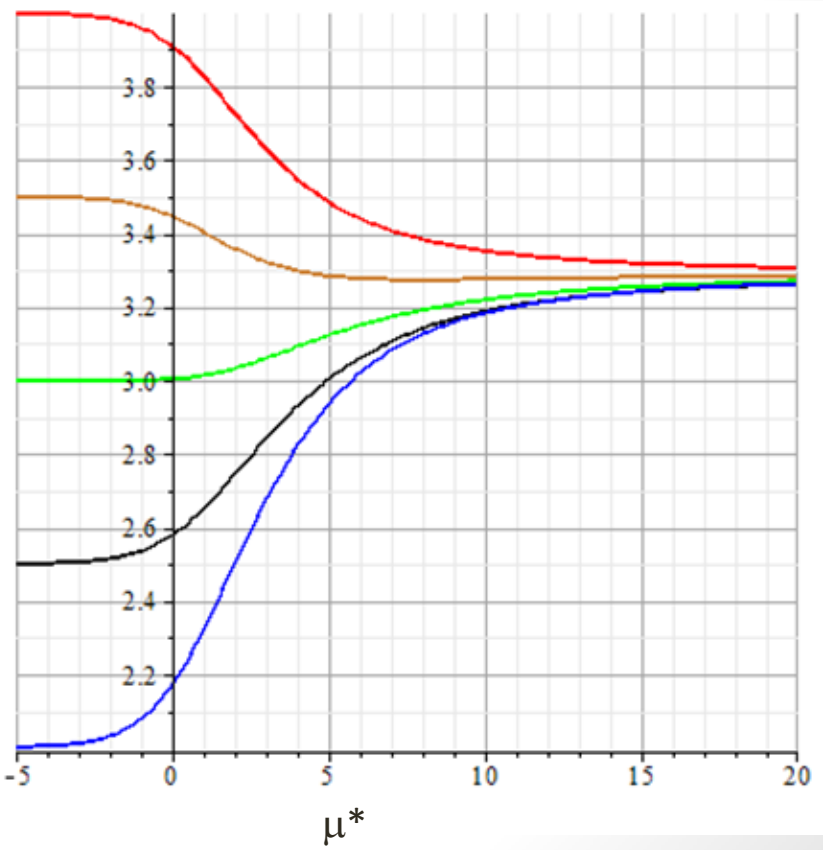
Scaling of the WF Law by A(r,μ*)

$$\frac{\kappa_e}{\sigma T} = \left(\frac{k}{e}\right)^2 A(r, \mu^*)$$

- WF Law is exact only if $A(r,\mu^*) = \pi^2/3$
- r is the scattering parameter.
- μ^* is the reduced chemical potential
- $A(r,\mu^*)$ is a function of μ^* and scales the WF law.

Graph of $A(r, \mu^*)$:

- r=-0.0 (blue)
- r=0.5(black)
- r=1.0 (green)
- r=1.5(gold)
- r=2.0(red)



Alternative strategies to nanostructuring- high thermoelectric performance SnSe single crystals and their ZT

Zhao, Kanatzidis et. al. , Nature; Volume 508, 2014

- Unprecedented ZT = 2.62 at 923K despite the lack of nanostructuring.
- Anomalously high Grüneisen parameters - reflect the anharmonic and anisotropic bonding
- These lead to low lattice thermal conductivity (0.23 ± 0.03 $Wm^{-1}K^{-1}$ at 973K)

Theoretically, calculated $\kappa_{l,min}$ are slightly larger than κ_m from experiments

Emphasizes the importance of κ_l

$\kappa_l(T)=\kappa_m(T) - L(T)T\sigma(T)$ (Generalization of WF Law)

$\kappa_l(T)=\kappa_m(T)-L_0T\sigma(T)$ (Assuming WF Law)

κ_l & $\kappa_{l,min}$: lattice and minimum lattice thermal conductivity
κ_m: measured thermal conductivity

Expression for the minimum lattice thermal conductivity (Cahill, et. al, PRB, 46, 1992, *Zhao, Kanatzidis et. al. , Nature; Volume 508, 2014)*

Grüneisen Parameters

$$\gamma_i = -\frac{V}{\omega_i}\frac{\partial \omega_i}{\partial V}$$

$$\kappa_{l,\min} = \left(\frac{\pi}{6}\right)^{1/3} k n^{2/3} \sum_i \nu_i \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2}\, dx = \frac{-x^3}{e^x - 1}\Bigg|_0^{\Theta_i/T} + \int_0^{\Theta_i/T} \frac{3x^2}{e^x - 1}\, dx$$

$$\int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2}\, dx = \frac{-x^3}{e^x - 1}\Bigg|_0^{\Theta_i/T} + \int_0^{\Theta_i/T} \frac{3x^2}{e^x - 1}\, dx$$

n= Number density of atoms

v_i= phonon longitudinal and transverse velocities

Θ= Debye or Einstein Temperature

The integral that occurs in $\kappa_{(l,min)}$ is given below

$$D_f\left(\frac{\theta_i}{T}\right) = \int_0^{\theta_i/T} \frac{x^3 e^x}{(e^x-1)^2} dx = \int_0^{\infty} \frac{x^3 e^x}{(e^x-1)^2} dx + \int_{\infty}^{\theta_i/T} \frac{x^3 e^x}{(e^x-1)^2} dx$$

$$= 6\zeta(3) - \int_0^{\theta_i/T} \frac{x^3 e^x}{(e^x-1)^2} dx$$

$$= 6\zeta(3) + \frac{x^3}{e^x-1}\Bigg|_{\theta_i/T}^{\infty} - \int_{\theta_i/T}^{\infty} \frac{3x^2}{e^x-1} dx$$

$$= 6\zeta(3) - \frac{\left(\frac{\theta_i}{T}\right)^2}{e^{\frac{\theta_i}{T}}-1} - 3.2\left[Z_3\left(\frac{\theta_i}{T}\right)\right]$$

where Z_n is the Debye Function .
Here we have $Z_3\left(\frac{\theta_i}{T}\right)$

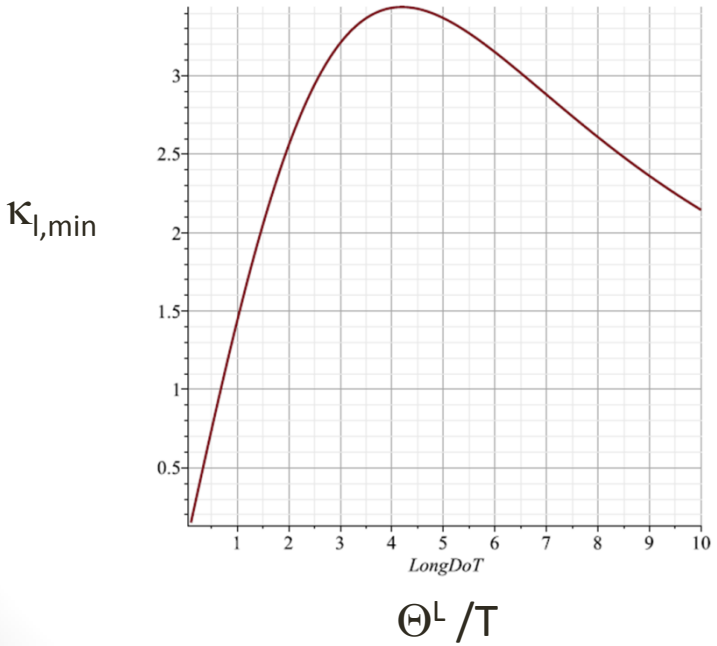
$$Z_3(\frac{\theta_i}{T}) = \sum_{k=0}^{2} Li_{3-k}(e^{-\frac{\theta_i}{T}}) \frac{(\frac{\theta_i}{T})^k}{k!}$$

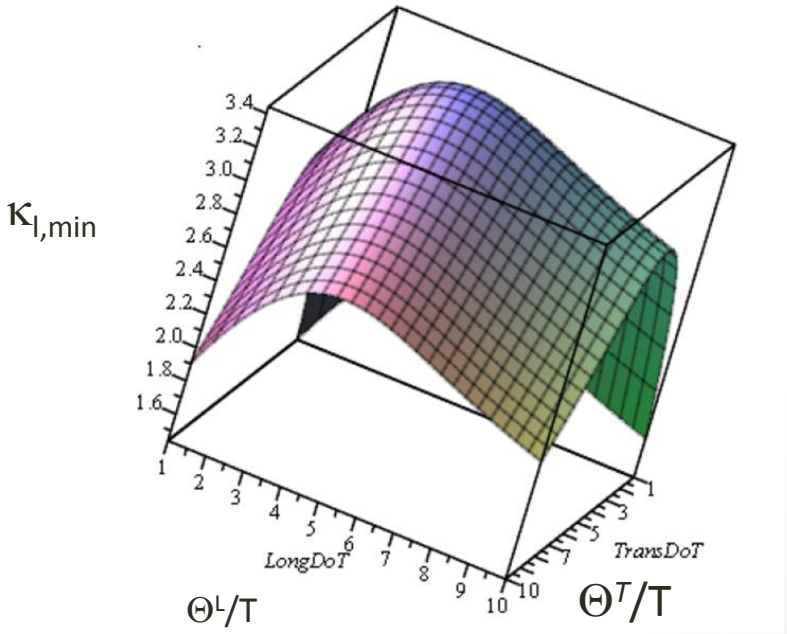
$$= Li_3(e^{-\frac{\theta\iota}{\tau}}) + Li_2(e^{-\frac{\theta\iota}{\tau}})(\frac{\theta\iota}{\tau}) + \frac{1}{2} Li(e^{-\frac{\theta\iota}{\tau}})(\frac{\theta\iota}{\tau})^2$$

$$\kappa_{l,\min} = (\frac{\pi}{6})^{1/3} kn^{2/3} \sum_{\iota=1,2,3} \upsilon_\iota (\frac{T}{\theta_\iota})^2 \cdot D_f(\frac{\theta_\iota}{T})$$

$K_{(l,min)}$: minimum thermal conductivity

- $\kappa_{(l,min)}$ plotted for Transverse (*T*) and Longitudinal (L) arguments both equal, going from 0.1 to 10.0. This gives a much sharper peak.
- Isotropic case, ie Θ_L , Θ_T are identical.
- $F_P(x,T) = x^3/(e^x-1)$ where $x = (\hbar\omega)/kT$.
- F_P = Plank black body radiation function
- Extremum of $F_P(\omega,T)$ gives the Wien's Displacement Law in terms of the Lambert W function.
- 3D plot of $\kappa_{l,min}$: Θ_T/T , Θ_L/T are the two independent variables.





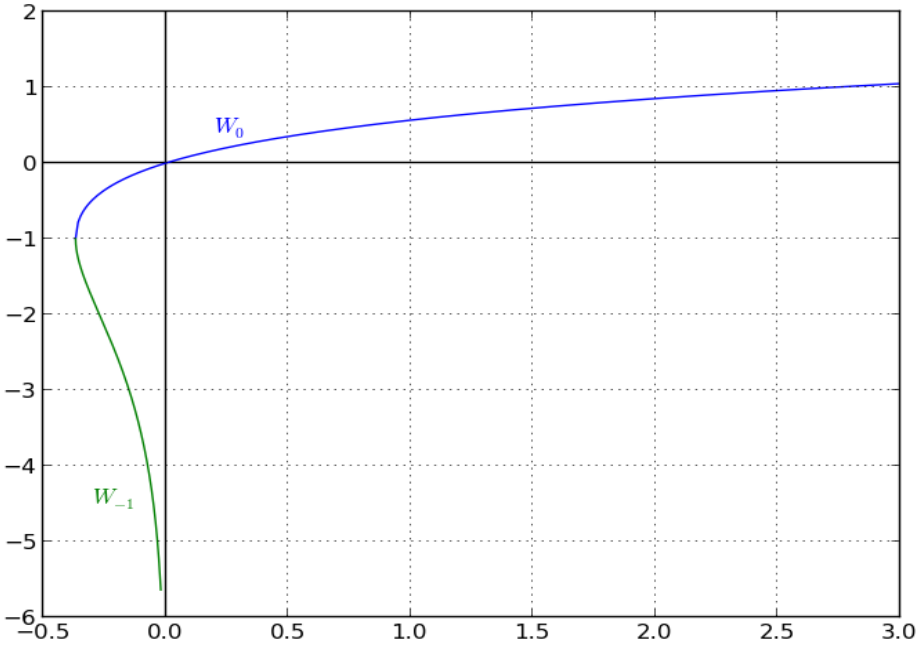
Conclusions

- Exact FD Integral expressions- generalize WF Law.
- Exact analytic expressions will assist material design.
- Electronic (κ_e) & Minimum lattice ($\kappa_{l,min}$) thermal conductivity have exact analytic expressions.
- More recent observations on the influence of anharmonicity on $\kappa_{l,min}$ suggest that the Polylogarithms and Lambert W can have more interesting applications.
- Goal: Enhance thermoelectric figure of merit (ZT).

Backup slides

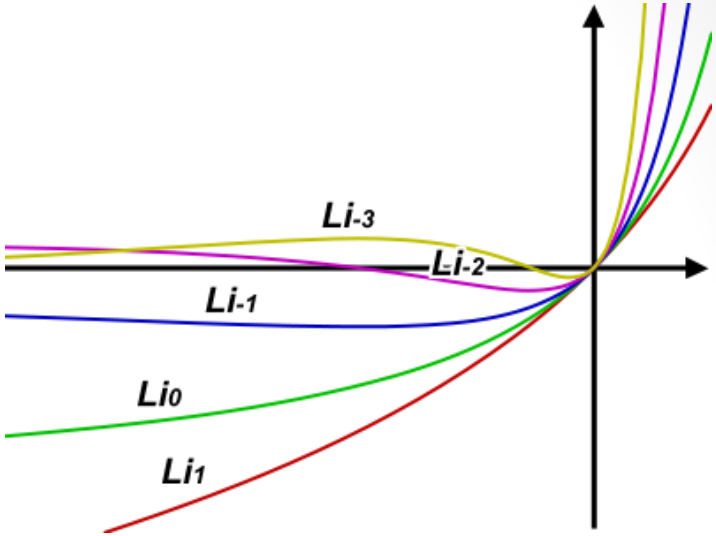
Lambert W function

$$we^{w}=z$$



Polylogarithms

$$Li_s(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^s} = z + \frac{z^2}{2^s} + \frac{z^3}{3^s} + \cdots$$

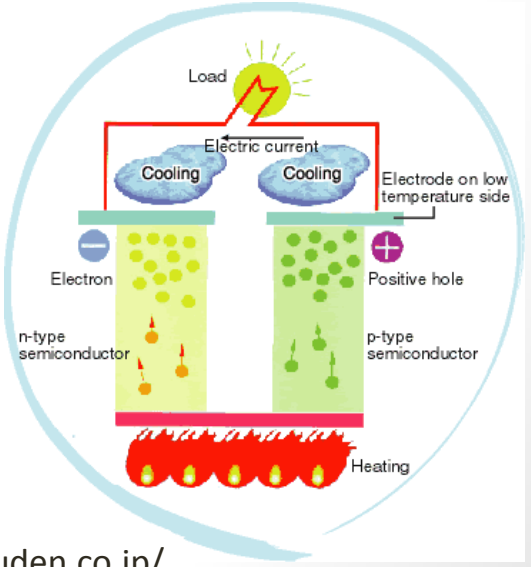


$$Li_{s+1}(z) = \int_0^z \frac{Li_s(t)}{t}\,dt$$

$$z\frac{\partial Li_s(z)}{\partial z} = Li_{s-1}(z)$$

Thermoelectric Energy (TE)

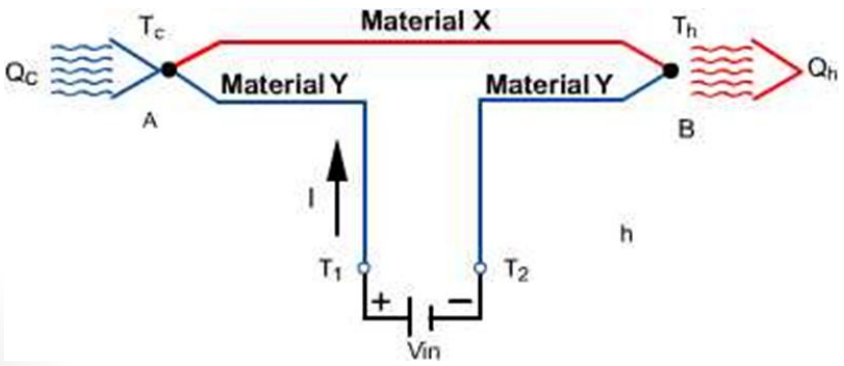
- TE used as an alternative energy source.
- Use temperature gradient in order to create a current.
- It has many uses, including:
  -heating/cooling,
  -generating electricity,
  -measuring temperature, and
  -controlling temperature



http://www.kyuden.co.jp/

TE contd.

- Includes 3 sub categories
  - The Seebeck effect (generate power)
  - The Peltier effect (refrigerate)
  - The Thomson effect (conductor with a temperature gradient : absorb or emit heat depending on the material)



https://www.ferrotec.com

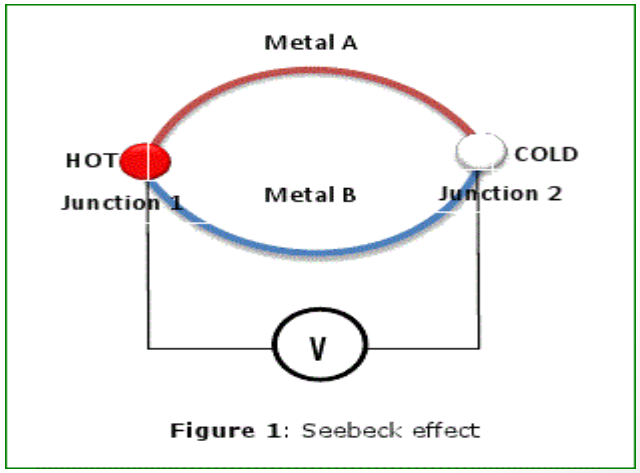


Figure 1: Seebeck effect

http://www.electrical4u.com/

Phonons

- Collective excitation in a periodic arrangement of atoms in condensed matter, such as solids and some liquids.
- Play a major role in many of the physical properties of condensed matter, such as thermal conductivity.
- Phonon density of states is able to determine the heat capacity of a crystal.
- Thermal phonons are created and destroyed through energy fluctuations – a phenomenon that is similar to the photon gas.

- Quasi crystals (Q_c : resemble more semiconductor like than metallic character)
- The empirical WF relation will not hold at intermediate T due to electron phonon scattering
- Lattice is not static!
- Wiedemann-Franz law assumes: $\kappa_e >> \kappa_l$; Only true when elastic processes dominate the transport coefficients.
- For $T << \Theta$, Lorenz number tends to decrease. Since, thermal and electrical relaxation times are not identical.

Theoretically, calculated κ_{min} are slightly larger than κ_{exp} measurements due to (Zhao et. Al, 508, Nature, (2014), 373) :

1. The variation in Lorenz values(1 $x10^{-8}$ -2.4 $x10^{-8}$)

$$L = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2$$

2. Thermal diffusivity values- depends on the details of a fit to time dependent reflectivity curves

- High Grüneisen parameters is a consequence of ‘soft’ bonding in SnSe
- High Grüneisen parameter of SnSe is reflection of its crystal structure.

Seebeck effect

- Produced in a circuit containing two or more different metals - junctions between the metals maintained at different temperatures
- Effect caused by thermal energy of valence electrons in the warmer part of the metal
  - kinetic energy (KE) of electrons (which are very free in metals) - migrate toward the colder part more readily than the colder electrons migrate to the warmer part.
  - colder part of the metal then more negatively charged than the warmer part causing an electric potential
- For every degree difference between the two metals - continuous flow of charge of several microvolts
- As difference in temperature increases, the thermoelectric effect increases

Peltier effect

- Thermodynamic effect occurs when current passes through a thermocouple circuit
- Produces heat at one junction - absorbs heat at the other junction - used in computers for cooling
- Heat produced is additional to heat arising from resistance of the wires
- Two metals must be dissimilar because one must be of a higher potential energy
- Typically requires temperature gradient of 70 degrees Celsius

Some important Fermi-Dirac integrals in the modified WF (Wiedemann- Franz Law) R

$$\int_0^\infty \frac{x^3}{e^x+1}dx = \frac{1}{4}(1-2^{1-4})\Gamma(4)\zeta(\upsilon) = \frac{7}{8}\Gamma(4)\frac{\pi^4}{90}$$

$$(\int_0^\infty \frac{x^{\upsilon-1}}{e^{\mu x}+1}dx = \frac{1}{\mu^\upsilon}(1-2^{1-\upsilon})\Gamma(4)\zeta(\upsilon)); \mathrm{Re}\,\mu > 0, \mathrm{Re}\,\upsilon > 0$$

$$\zeta(4) = \frac{\pi^4}{90}$$

$$For\ \left|e^{\mu^*}-1\right| \ll 1, higher\ order\ terms\ negligable$$

$$\int_0^{\mu^*} \frac{x^3}{e^x+1}$$

$$\frac{n(n-1)}{2}(\mu^*)^{n-2}\left\{\int_0^{\infty}\frac{x^2}{e^x+1}dx-\int_0^{\mu}\right.$$

$$=\frac{n(n-1)}{2}(\mu^*)^{n-2}\left\{\mu^{*2}e^{-\mu^*}-2\int_{\mu^*}^{\infty}xe^{-x}\,dx\right.$$

$$=\frac{n(n-1)}{2}\{(\mu^*)^n-2(\mu^*)^{n-1}+2(\mu^*)^{n-2}\}$$
$$+e^{-\mu^*}+higher\ order\ terms$$

Next correction is

$$\frac{n(n-1)(n-2)}{6}\left(\mu^*\right)^{n-3}\left\{\int_0^{\infty}\frac{x^3}{e^x+1}dx+\int_0^{\mu^*}\frac{x^3}{e^x+1}dx\right\}$$

$$-\frac{n(n-1)(n-2)}{6}\left(\mu^*\right)^{n-3}\left[\left\{-x^3e^{-x}\Big|_{\mu^*}^{\infty}+\int_{\mu^*}^{\infty}3x^2e^{-x}dx\right\}+\ldots\right]$$

$$=7\pi^4 n\frac{(n-1)(n-2)}{360}\left(\mu^*\right)^{n-3}-\frac{n(n-1)(n-2)}{6}\left(\mu^*\right)^{n}e^{-\mu^*}+\ldots$$

- The new expression now has a semi empirical basis and provides a modified version of the WF law.

- The modified WF Law includes the corrections that could show up for different ranges of values of μ^* - can occur in the synthesis of new doped TE materials and non TE materials.

- Lorenz number (L) will be accordingly not a constant, but will be a function of $\mu^* = \mu/kT$.
- μ^* is a better measure than just T.

Feynman calculations for the specific heat.

Note: We get extra terms which were not considered in Feynman (Lect 1 in Stat. Mechs). The analysis there assumes that $\beta\mu \to \infty$ $T \ll 1$

u = energy density (E/V)

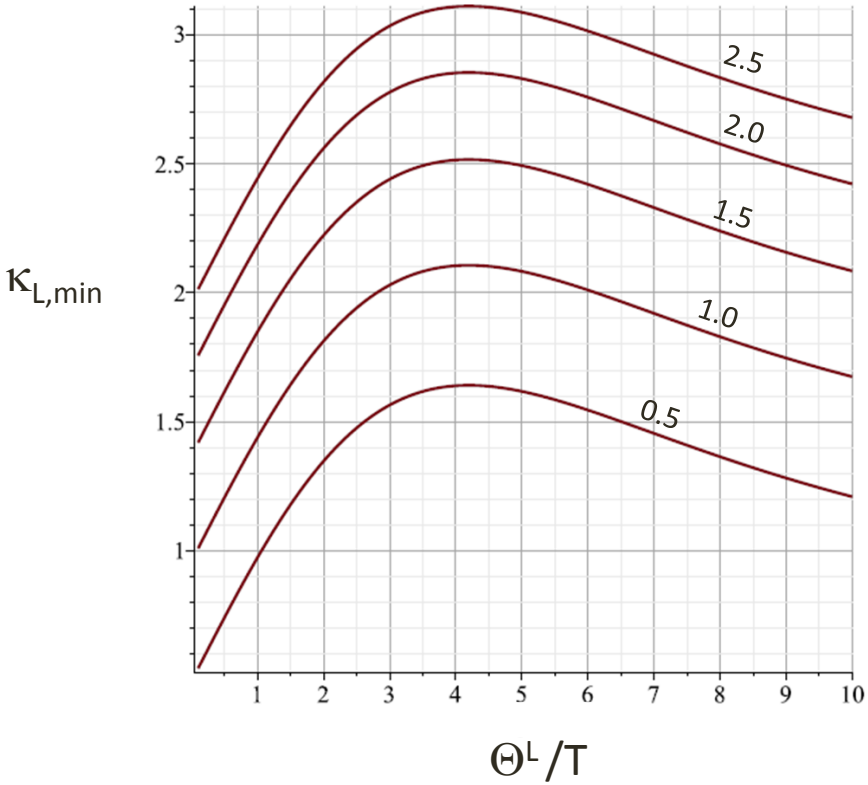
$$\frac{\partial u}{\partial \mu} = a\left[\frac{\frac{5}{2}(\mu^*)^{3/2}}{5/2} - \frac{(\mu^*)^{\frac{3}{2}} e^{-\mu^*}}{1+e^{-\mu^*}} + \frac{3}{2}\cdot\frac{1}{2}\cdot\frac{1}{(\mu^*)^{\frac{1}{2}}}\right.$$

$$\left\{\frac{\pi^2}{6} - \mu^* \ln\left(1+e^{-\mu^*}\right) - Li_2\left(-e^{-\mu^*}\right)\right\}$$

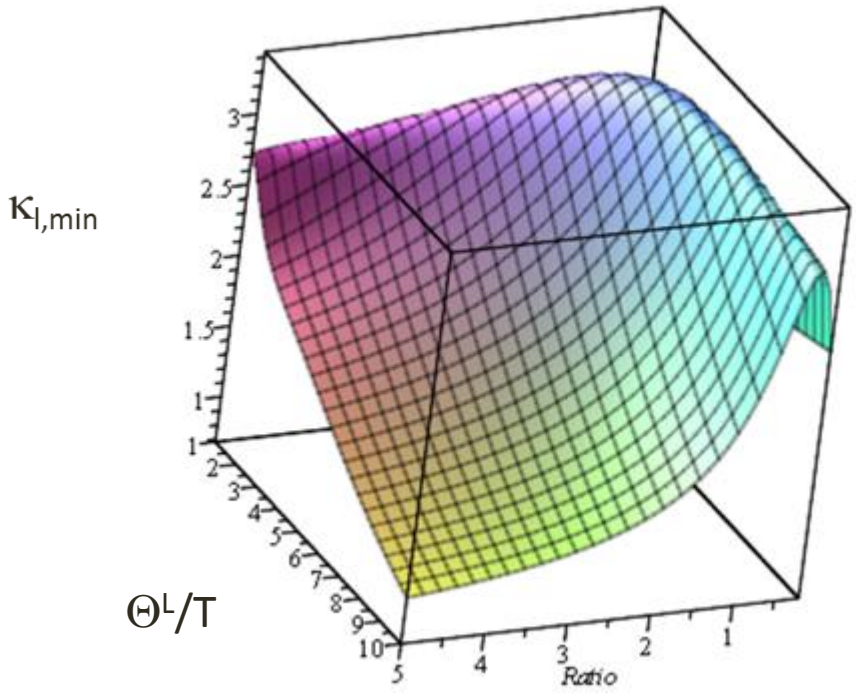
$$+\frac{3}{2}(\mu^*)^{\frac{1}{2}} + \frac{\mu^* - e^{-\mu^*}}{1+e^{-\mu^*}} + Li_1\left(-e^{-\mu^*}\right)$$

$$\left.+\frac{3}{8}\left\{-e^{-\mu^*}(\mu^{\cdot\frac{3}{2}} - 2\mu^{\cdot\frac{1}{2}} + 2\mu^{*-\frac{1}{2}}\right\} + \ldots\right]$$

- $\kappa_{(L,min)}$ plotted for five different values of Θ^L/T, from 0.5 (lowest on plot) to 2.5 (highest on plot).
- All the curves are similar, with peak at the same value of Θ^L/T. That is because the Transverse contribution to $\kappa_{(L,min)}$ is just a constant for each curve -- ie shifts the curve up or down
- $\kappa_{L,min}$ is the longitudinal minimum lattice thermal conductivity.
- The solution for the extrema in terms of the Lambert W function

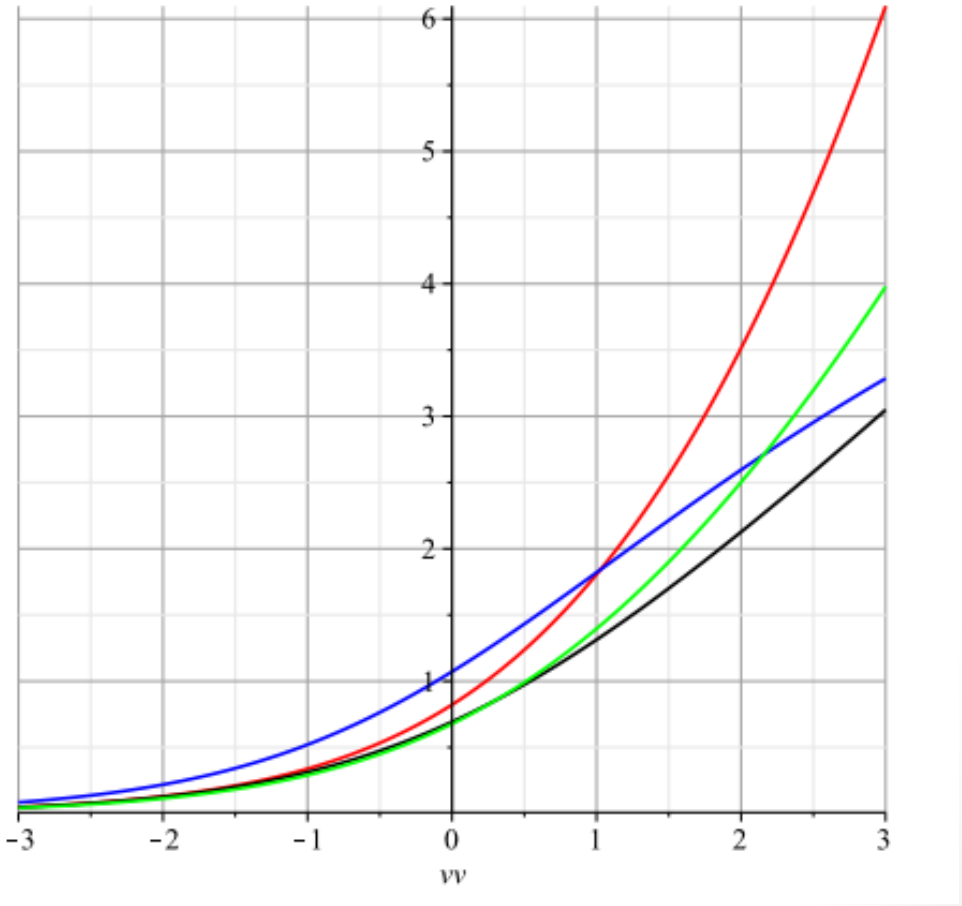


- Θ_L is one independent variable, and the Θ_T/Θ_L is the other independent variable.
- Sweeping peak: conditions for maxima.
- Not simply ratio = 1 for highest $\kappa_{l,min}$.
- Isotropy is not the highest $\kappa_{l,min}$ situation.
- Variation of lattice thermal conductivity is not uniform.



Graph of the FD integral $F_r(\mu^*)$:

- r=-0.5 (blue)
- r=0.0(black)
- r=0.5 (green)
- r=1.0(red)



Approximation used by Feynman was sufficient at the time he did his calculation for specific heat and chemical potential. In the context of current materials like nanostructures (which fynman himself predicted) and doped semi conductors, this more realistic approximation needs to be improvised.

$$\mu \approx \mu_0 \left(1 - \frac{\pi^2 k^2 T^2}{12\,(\mu_0{}^2)}\right)$$

$$u \approx a \int_0^{\mu} e^{\frac{3}{2}}\,\mathrm{d}\varepsilon + \frac{\pi^2}{6}(\kappa T)^2 \frac{3a}{2}\sqrt{u}$$

$$\frac{2}{5} a\mu_0{}^{5/2} + \frac{\pi^2}{6} - a\mu_0{}^{\frac{5}{2}} \frac{\pi^2}{12} \frac{(\kappa T)^2}{\mu_0{}^2} + \frac{a\pi^2}{4}(\kappa T)^2 \sqrt{\mu_0}$$

$$u = u_0 + \gamma T^2; \quad U = uV = U_0 + \gamma V T^2$$
$$= U_0 + \gamma' T^2$$

$$C_v \, of \, a \, metal \; = 2y'T + \propto T^3 at \; low \; T$$

More accurate formulation of the FD integral for the energy density ‘u’.

$$F_{3/2} = a\left[\frac{(\mu^*)^{\frac{5}{2}}}{\frac{5}{2}} + (\mu^*)^{\frac{3}{2}} ln\left(1+e^{-\mu^*}\right) + \frac{3}{2}(\mu^*)^{\frac{1}{2}}\left\{\frac{\pi^2}{6} - \mu^* \ln\left(1+e^{-\mu^*}\right) - Li_2(-e^{-\mu^*}\right\}\right.$$

$$+\frac{3}{2}\cdot\frac{1}{2}\cdot\frac{1}{2}(\mu^*)^{1/2}\left\{\mu^{*2} - 2\mu^* e^{-\mu^*} + 2e^{-\mu^*}\right\}$$

$$\left.+\frac{\frac{3}{2}\cdot\frac{1}{2}\left(-\frac{1}{2}\right)}{6}(\mu^*)^{-\frac{3}{2}}\left\{\frac{7\pi^4}{360} - (\mu^*)^{\frac{3}{2}} e^{-\mu^*} + \cdots\right\}\right]$$

The specific heat expression accordingly changes.

$$C_v = \frac{\partial U}{\partial T} = uV$$

Conditions for the extremum of the electronic thermal conductivity (κ_T)

$$D\left\{-\Gamma(r+4)Li_{r+2}-(r+2)\Gamma(r+3)\left[\frac{Li_{r+2}{}^{2}Li_{r}}{Li_{r+1}{}^{2}}-2Li_{r+2}\right]\right\}=0$$

$$\left[\Gamma(r+4)-2\Gamma(r+3)\right]Li_{r+1}{}^{2}Li_{r+2}-(r+2)\Gamma(r+3)Li_{r}Li_{r+2}{}^{2}=0$$

Solutions of this equation given in the following slides

This expression (MVV,CJP, 2011) occurs for the extremum for the electronic thermal conductivity.

Case 1

$$z = -\exp\ \mu^*, |z| << 1, |\mu^*| > 1, and \quad \mu^* < 0$$

$$-\left(\mu^* + \frac{3^s + 1}{2}\right) = W_j\left(-\frac{3^s}{2^{s+1}} e^{-\left(\frac{3^s+1}{2}\right)}\right)$$

or

$$\mu^* = -\left\{\frac{3^s + 1}{2} + W_j\left(-\frac{3^s}{2^{s+1}} e^{-\left(\frac{3^s+1}{2}\right)}\right)\right\}$$

where $W_j(.)$ is the multi-valued Lambert W function for branch j.

Case 2

$$z = -exp\,\mu^*, |z| << 1, |\mu^*| > 1, and\, \mu^* < 0$$

$$Li_s(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^s}$$

Case 3 & 4

$$z = -\exp\ \mu^*, |z| > 1, and\, \mu^* > 0$$

$$z = -\exp\ \mu^*, \mu^* >> 1, and\, |z| >> 1$$

Solutions for these equations are available on CJP manuscript

- Modification of the Debye Theory by Max Born
- Both longitudinal and transverse modes- Common minimum wavelength λ_m

$$\frac{\lambda_m \omega_{long}}{\lambda_m \omega_{trans}} = \frac{V_{long}}{V_{trans}}$$

- Work of Zhao, Kanatzidis et. al – anomalously high Gruneisen parameters which reflect strong anharmonicity and anisotropic bonding.
- Their work shows high ZT along certain axis.

Details of the Fermi-Dirac Integrals

All of the A(r,μ*) curves are seen to be asymptotic to value $3.29 \approx \pi^{\frac{2}{3}}$ = expected value for the Wiedemann Franz Lorenz ratio (WFL). The WFL relation may not to be accurate even for μ*>>1

$$\frac{1}{e^{u}+1} = 1 - \frac{1}{e^{-u}+1}$$

$$F_s(\mu^*) = G_1 + G_2 + G_3 = \int_0^{\mu^*} x^s\, dx - \int_0^{\mu^*} \frac{x^s}{e^{\mu^* - x}+1}\, dx + \int_{\mu^*}^{\infty} \frac{x^s}{e^{x-v}+1}\, dx$$

$$G_1 = \mu^{*s+1}/(s+1)$$

$$G_2 = -\int_0^{\mu^*} \frac{(\mu^* - y)^s}{e^{y}+1}\, dy$$

G_3 *is handled by making the substitution* $y = x - \mu^*$,

$$G_3 = \int_0^{\infty} \frac{(\mu^* + y)^s}{e^y + 1} dy$$

$as\ \mu^* \gg 1$

$$G_3 = \int_0^{\mu^*} \left[\mu^{*s} + sy\mu^{*s-1} + \frac{s(s-1)y^2}{2} \mu^{*s-2} + O\left(\mu^{*s-3}\right) \right] dy$$

$$= \mu^{*s} \int_0^{\mu^*} \frac{1}{e^y + 1} dy + s\mu^{*s-1} \int_0^{\mu^*} \frac{y}{e^y + 1} dy + \frac{s(s-1)\mu^{*s-2}}{2} \int_0^{\mu^*} \frac{y^2}{e^y + 1} dy + O(\mu^{*s-2})$$

$F_s(\mu^*)$ *can be calculated from* G_i

$$F_s(\mu^*) = G_1 + G_2 + G_3 = \frac{\mu^{*s+1}}{s+1} + 2s\mu^{*s-1}\int_0^\infty \frac{y}{e^y+1}dy + O\left(\mu^{*s-2}\right)$$

The limit of A_∞ *of* $A(r,\mu^*)$ *as* $\mu^* \to \infty$ *is*

$$= 2\zeta(2) = \frac{\pi^2}{3}$$

$$\approx \frac{\left(\mu^{*2r+4} + \zeta(2)\left(2\mathrm{r}^2 + 6r + 6\right)\mu^{*2r+2}\right) - \left(\mu^{*2r+4} + \zeta(2)\left(2r^2 + 6r + 4\right)\mu^{*2r+2}\right)}{\mu^{*2r+2}}$$

$$= \frac{\zeta(2)\left(\left(2r^2 + 6r + 6\right) - \left(2r^2 + 6r + 4\right)\right)\mu^{*2r+2}}{\mu^{*2r+2}}$$

$$A_\infty = \frac{(r+3)F_{r+2}(r+1)F_r - \left((r+2)F_{r+1}\right)^2}{\left((r+1)F_r\right)^2}$$

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