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The thermoelectric variables are calculated in terms of spatially varying, band engineered conduction and valence band edges, and a spatially dependent electron-phonon relaxation time based on longitudinal acoustic dispersion; use is made of the spherical band approximation and a spatially dependent effective mass for conduction and valence band carriers to obtain explicit parametric results for the Seebeck coefficient and the figure of merit for a model slab of material of finite length.
The Seebeck coefficient is determined and is shown to be enhanced by the addition of a term which depends analytically upon a spatial average of the relative ``band engineered" energy band edge divided by k T(x), where T(x) is the spatially dependent temperature across the sample.
The figure of merit, Z T, is also estimated in terms of band-engineered variables and discussed in the light of a variational principle which allows for the optimization of Z T. Suggestions for more detailed and rigorous analysis of thermoelectric transport and optimization of Z T are discussed.

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# Modeling of enhanced thermoelectric processes based on asymmetrically-graded superlattices

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In this study, we explore the influence of spatially graded energy bands on the thermoelectric properties of thin film semiconductors. In the analysis, we utilize the semi-classical Boltzmann equation in the relaxation approximation, in a limit slightly displaced from equilibrium, to capture the salient features of the relevant "band-engineered" electronic transport properties of carrier current density and the carrier component of the heat flux density. Since emphasis is primarily focused on the "carrier" transport in this study, the lattice contribution to the heat flux density is assumed to be given by a constant lattice thermal conductivity times the external temperature gradient.

The thermoelectric variables of carrier current density and heat flux density are calculated in terms of spatially varying, band engineered conduction and valence band edges, and a spatially dependent electron-phonon relaxation time based on longitudinal acoustic dispersion; use is made of the spherical band approximation and a spatially dependent effective mass for conduction and valence band carriers to obtain explicit parametric results for the Seebeck coefficient and the figure of merit for a model slab of material of finite length. The temperature variation across the sample is assumed to have a linear spatial dependence during opened circuit conditions.

The Seebeck coefficient is determined and is shown to be enhanced by the addition of a term which depends analytically upon a spatial average of the relative "band engineered" energy band edge divided by $kT(x)$, where $T(x)$ is the spatially dependent temperature across the sample. Estimates of the enhanced Seebeck coefficient are calculated for various band edge models including a linear grade to offset the internal inhomogeneous temperature variation across the sample, and for a periodic symmetric as well as periodic asymmetric variation in gradation.

The figure of merit, $ZT$, is also estimated in terms of band-engineered variables and discussed in the light of a variational principle which allows for the optimization of $ZT$. Suggestions for more detailed and rigorous analysis of thermoelectric transport and optimization of $ZT$ are discussed.

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## I. POSITION-DEPENDENT BAND CONSIDERATION[1]

We consider a sample with a nonuniform band structure which is determined by the crystal potential, subject to an additional internal or external fields of force such as an electric field, stress, or temperature gradients. Let $\mathcal{E}_{\beta_0}(\vec{r},\vec{k})$ be the band structure of the unperturbed crystal, where $\beta$ is the band index. $\mathcal{E}_{\beta}(\vec{r},\vec{k}) = \mathcal{E}_{\beta_0}(\vec{r},\vec{k}) + \Delta\mathcal{E}_{\beta}(\vec{r})$ is the band structure in the presence of additional fields of force, and $\mathcal{E}_{\beta}(\vec{r}) = \mathcal{E}_{\beta}(\vec{r},\vec{k}_m)$ is the band edge, where $k_m$ are the wave vectores corresponding to the minima or maxima of the band. $\Psi(\vec{r}) = -e\Phi(\vec{r})$ is the potential energy for these forces. Thus the total energy of an electron for band $\beta$ is $E_{\beta}(\vec{r},\vec{k}) = \mathcal{E}_{\beta}(\vec{r},\vec{k}) + \Psi(\vec{r})$. We can introduce $E_{\beta}(\vec{r}) = \mathcal{E}_{\beta}(\vec{r}) + \Psi(\vec{r})$ to be the energy contours of the total energy.
For conduction band, we have,

$$E_c(\vec{r},\vec{k}) = \mathcal{E}_c(\vec{r},\vec{k}) + \Psi(\vec{r})$$
$$E_c(\vec{r}) = \mathcal{E}_c(\vec{r}) + \Psi(\vec{r})$$

and for valence band,

$$E_v(\vec{r},\vec{k}) = \mathcal{E}_v(\vec{r},\vec{k}) + \Psi(\vec{r})$$
$$E_v(\vec{r}) = \mathcal{E}_v(\vec{r}) + \Psi(\vec{r})$$

## II. WANNIER EQUIVALENT HAMILTONIAN[1,2]

For a single band, for example, the conduction band, the total Hamiltonian operator can be replaced by the equivalent Hamiltonian operator,

$$H_c(\vec{r},-i\vec{\nabla}) = \mathcal{E}_c(\vec{r},-i\vec{\nabla}) + \Psi(\vec{r}) \tag{1}$$

where $\mathcal{E}_c(\vec{r},\vec{k})$ is the band energy.
The classical equivalent Hamiltonian is introduced by the correspondence $-i\vec{\nabla} \rightarrow \vec{k}$,

$$H_c(\vec{r},\vec{k}) = \mathcal{E}_c(\vec{r},\vec{k}) + \Psi(\vec{r}) = E_c(\vec{r},\vec{k}) \tag{2}$$

and which gives us the Hamiltonian equation, with momentum $\vec{p} = \hbar\vec{k}$, as

$$\frac{d\vec{r}}{dt} = \vec{v}_n(\vec{r},\vec{k}) = \frac{\partial H_c}{\partial \vec{p}} = \frac{1}{\hbar}\vec{\nabla}_{\vec{k}}E_c(\vec{r},\vec{k}) \tag{3}$$

$$\vec{F}_n = \hbar\frac{d\vec{k}}{dt} = -\frac{\partial H_c}{\partial \vec{r}} = -\vec{\nabla}E_c(\vec{r},\vec{k}) \tag{4}$$

$\vec{F}_n$ is the total force act on an electron in the conduction band.
The same is true for holes in valence band, by noticing that the force act on holes has opposite signs as on electrons,

$$\vec{v}_p(\vec{r},\vec{k}) = \frac{\partial H_v}{\partial \vec{p}} = \frac{1}{\hbar}\vec{\nabla}_{\vec{k}}E_v(\vec{r},\vec{k}) \tag{5}$$

$$\vec{F}_p = -\hbar\frac{d\vec{k}}{dt} = -\left[-\frac{\partial H_v}{\partial \vec{r}}\right] = \vec{\nabla}E_v(\vec{r},\vec{k}) \tag{6}$$

## III. BOLTZMANN TRANSPORT EQUATION[3]

Let $f_n(\vec{r},\vec{k},t)$ to be distribution function of electrons in the conduction band. The Boltzman Transport Equation (BTE) states,

$$\frac{\partial f_n(\vec{r},\vec{k},t)}{\partial t} + \vec{v}_n(\vec{r},\vec{k})\cdot\vec{\nabla}f_n(\vec{r},\vec{k},t) + \frac{\vec{F}_n}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f_n(\vec{r},\vec{k},t) = C[f_n(\vec{r},\vec{k},t)] \tag{7}$$

$C[f_n(\vec{r},\vec{k},t)]$ is the collision integral. Under relaxation time approximation, we let

$$C[f_n(\vec{r},\vec{k},t)] = -\frac{f_n(\vec{r},\vec{k},t) - f_n^0(\vec{r},\vec{k},t)}{\tau_n(\vec{r},\vec{k})} \tag{8}$$

where $f_n^0(\vec{r},\vec{k},t)$ is the local equilibrium distribution. Thus for the stationary situation, we have,

$$\vec{v}_n(\vec{r},\vec{k})\cdot\vec{\nabla}f_n(\vec{r},\vec{k}) + \frac{\vec{F}_n}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f_n(\vec{r},\vec{k}) = -\frac{f_n(\vec{r},\vec{k}) - f_n^0(\vec{r},\vec{k})}{\tau_n(\vec{r},\vec{k})} \tag{9}$$

Writing $f_n(\vec{r},\vec{k}) = f_n^0(\vec{r},\vec{k}) + f_n^1(\vec{r},\vec{k})$, we find the perturbation solution for $f_n^1(\vec{r},\vec{k})$ as

$$f_n^1(\vec{r},\vec{k}) = -\tau_n(\vec{r},\vec{k})\left[\vec{v}_n(\vec{r},\vec{k})\cdot\vec{\nabla}f_n^0(\vec{r},\vec{k}) - \frac{\vec{\nabla}E_c(\vec{r},\vec{k})}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f_n^0(\vec{r},\vec{k})\right] \tag{10}$$

For holes in valence band, the Boltzman Transport Equation (BTE) has the form,

$$\frac{\partial f_p(\vec{r},\vec{k},t)}{\partial t} + \vec{v}_p(\vec{r},\vec{k})\cdot\vec{\nabla}f_p(\vec{r},\vec{k},t) + \frac{\vec{F}_p}{\hbar}\cdot\left[-\vec{\nabla}_{\vec{k}}f_n(\vec{r},\vec{k},t)\right] = C[f_p(\vec{r},\vec{k},t)] \tag{11}$$

Writing $f_p(\vec{r},\vec{k}) = f_p^0(\vec{r},\vec{k}) + f_p^1(\vec{r},\vec{k})$,

$$f_p^1(\vec{r},\vec{k}) = -\tau_p(\vec{r},\vec{k})\left[\vec{v}_p(\vec{r},\vec{k})\cdot\vec{\nabla}f_p^0(\vec{r},\vec{k}) - \frac{\vec{\nabla}E_v(\vec{r},\vec{k})}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f_p^0(\vec{r},\vec{k})\right] \tag{12}$$

## IV. LOCAL EQUILIBRIUM DISTRIBUTION, ELECTRIC AND HEAT CURRENT

The local equilibrium distribution for electrons is given as the local Fermi-Dirac distribution,

$$f_n^0(\vec{r},\vec{k}) = \left[e^{\frac{E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})}{k_BT}}+1\right]^{-1} \tag{13}$$

where $\zeta_n(\vec{r})$ is the Fermi level, or the electrochemical potential, for electrons.
The electric current and heat current induced by electrons can be found as, respectively,

$$\vec{J}_n = -\frac{e}{4\pi^3}\int d^3\vec{k}\vec{v}_n(\vec{r},\vec{k})f_n^1(\vec{r},\vec{k}) \tag{14}$$

$$\vec{J}_{nQ} = \frac{1}{4\pi^3}\int d^3\vec{k}\vec{v}_n(\vec{r},\vec{k})\left[E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right]f_n^1(\vec{r},\vec{k}) \tag{15}$$

or,

$$\vec{J}_n = \frac{e}{4\pi^3}\int d^3\vec{k}\tau_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\left[\vec{v}_n(\vec{r},\vec{k})\cdot\vec{\nabla}f_n^0(\vec{r},\vec{k})-\frac{\vec{\nabla}E_c(\vec{r},\vec{k})}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f_n^0(\vec{r},\vec{k})\right] \tag{16}$$

$$\vec{J}_{nQ} = -\frac{1}{4\pi^3}\int d^3\vec{k}\tau_n(\vec{r},\vec{k})\left[E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right]\vec{v}_n(\vec{r},\vec{k})\left[\vec{v}_n(\vec{r},\vec{k})\cdot\vec{\nabla}f_n^0(\vec{r},\vec{k})-\frac{\vec{\nabla}E_c(\vec{r},\vec{k})}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f_n^0(\vec{r},\vec{k})\right] \tag{17}$$

From Eq. (13) we have,

$$\vec{\nabla}f_n^0(\vec{r},\vec{k}) = \frac{\partial f_n^0}{\partial E_c}\left[\vec{\nabla}E_c(\vec{r},\vec{k})-\vec{\nabla}\zeta_n(\vec{r})-\left(E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right)\frac{\vec{\nabla}T}{T}\right] \tag{18}$$

$$\vec{\nabla}_{\vec{k}}f_n^0(\vec{r},\vec{k}) = \frac{\partial f_n^0}{\partial E_c}\vec{\nabla}_{\vec{k}}E_c(\vec{r},\vec{k}) = \frac{\partial f_n^0}{\partial E_c}\hbar\vec{v}_n(\vec{r},\vec{k}) \tag{19}$$

$$\vec{J}_n = -\frac{e}{4\pi^3}\int d^3\vec{k}\frac{\partial f_n^0}{\partial E_c}\tau_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\cdot\left[\vec{\nabla}\zeta_n(\vec{r})+\left(E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right)\frac{\vec{\nabla}T}{T}\right] \tag{20}$$

$$\vec{J}_{nQ} = \frac{1}{4\pi^3}\int d^3\vec{k}\frac{\partial f_n^0}{\partial E_c}\tau_n(\vec{r},\vec{k})\left[E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right]\vec{v}_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\cdot\left[\vec{\nabla}\zeta_n(\vec{r})+\left(E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right)\frac{\vec{\nabla}T}{T}\right] \tag{21}$$

Rewrite it as,

$$\vec{J}_n = \sigma_{\mathbf{n}}\cdot\vec{\nabla}\frac{\zeta_n}{e}-\mathbf{L}_{\mathbf{n}}^{\mathbf{12}}\cdot\frac{\vec{\nabla}T}{T} \tag{22}$$

$$\vec{J}_{nQ} = \mathbf{L}_{\mathbf{n}}^{\mathbf{21}}\cdot\vec{\nabla}\frac{\zeta_n}{e}-\mathbf{L}_{\mathbf{n}}^{\mathbf{22}}\cdot\frac{\vec{\nabla}T}{T} \tag{23}$$

with

$$\sigma_{\mathbf{n}} = -\frac{e^2}{4\pi^3}\int d^3\vec{k}\frac{\partial f_n^0}{\partial E_c}\tau_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k}) \tag{24}$$

$$\mathbf{L}_{\mathbf{n}}^{\mathbf{12}} = \frac{e}{4\pi^3}\int d^3\vec{k}\frac{\partial f_n^0}{\partial E_c}\tau_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\left[E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right] \tag{25}$$

$$\mathbf{L}_{\mathbf{n}}^{\mathbf{21}} = \mathbf{L}_{\mathbf{n}}^{\mathbf{12}} = \frac{e}{4\pi^3}\int d^3\vec{k}\frac{\partial f_n^0}{\partial E_c}\tau_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\left[E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right] \tag{26}$$

$$\mathbf{L}_{\mathbf{n}}^{\mathbf{22}} = -\frac{1}{4\pi^3}\int d^3\vec{k}\frac{\partial f_n^0}{\partial E_c}\tau_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\vec{v}_n(\vec{r},\vec{k})\left[E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})\right]^2 \tag{27}$$

$\sigma_{\mathbf{n}}$ is the electric conductivity for electrons in the conduction band. We can also find the thermal conductivity as,

$$\left.\vec{J}_{nQ}\right|_{\vec{J}_n=0} = -\kappa_{\mathbf{n}}\vec{\nabla}T \tag{28}$$

$$\kappa_{\mathbf{n}} = \frac{1}{T}\left[\mathbf{L}_{\mathbf{n}}^{\mathbf{22}}-\mathbf{L}_{\mathbf{n}}^{\mathbf{21}}\cdot\sigma_{\mathbf{n}}{}^{-1}\cdot\mathbf{L}_{\mathbf{n}}^{\mathbf{12}}\right] \tag{29}$$

We can also define,

$$\vec{\nabla}\frac{\zeta_n}{e}\bigg|_{\vec{J}_n=0} = \mathbf{S_n}\vec{\nabla}T \tag{30}$$

$$\mathbf{S_n} = \sigma_{\mathbf{n}}{}^{-1}\frac{\mathbf{L_n^{12}}}{T} \tag{31}$$

For holes,

$$f_p^0(\vec{r},\vec{k}) = 1 - f_n^0(\vec{r},\vec{k}) = 1 - \left[e^{\frac{E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})}{k_BT}}+1\right]^{-1} = \left[e^{-\frac{E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})}{k_BT}}+1\right]^{-1} \tag{32}$$

where $\zeta_p(\vec{r})$ is the Fermi level, or the electrochemical potential, for holes.
The electric current and heat current induced by electrons can be found as, respectively,

$$\vec{J}_p = \frac{e}{4\pi^3}\int d^3\vec{k}\vec{v}_p(\vec{r},\vec{k})f_p^1(\vec{r},\vec{k}) \tag{33}$$

$$\vec{J}_{pQ} = \frac{1}{4\pi^3}\int d^3\vec{k}\vec{v}_p(\vec{r},\vec{k})\left[E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right]f_p^1(\vec{r},\vec{k}) \tag{34}$$

or,

$$\vec{J}_p = -\frac{e}{4\pi^3}\int d^3\vec{k}\tau_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\left[\vec{v}_p(\vec{r},\vec{k})\cdot\vec{\nabla}f_p^0(\vec{r},\vec{k}) - \frac{\vec{\nabla}E_v(\vec{r},\vec{k})}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f_p^0(\vec{r},\vec{k})\right] \tag{35}$$

$$\vec{J}_{pQ} = -\frac{1}{4\pi^3}\int d^3\vec{k}\tau_p(\vec{r},\vec{k})\left[E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right]\vec{v}_p(\vec{r},\vec{k})\left[\vec{v}_p(\vec{r},\vec{k})\cdot\vec{\nabla}f_p^0(\vec{r},\vec{k}) - \frac{\vec{\nabla}E_v(\vec{r},\vec{k})}{\hbar}\cdot\vec{\nabla}_{\vec{k}}f_p^0(\vec{r},\vec{k})\right] \tag{36}$$

From Eq. (32) we have,

$$\vec{\nabla}f_p^0(\vec{r},\vec{k}) = \frac{\partial f_p^0}{\partial E_v}\left[\vec{\nabla}E_v(\vec{r},\vec{k}) - \vec{\nabla}\zeta_p(\vec{r}) - \left(E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right)\frac{\vec{\nabla}T}{T}\right] \tag{37}$$

$$\vec{\nabla}_{\vec{k}}f_p^0(\vec{r},\vec{k}) = \frac{\partial f_p^0}{\partial E_v}\vec{\nabla}_{\vec{k}}E_v(\vec{r},\vec{k}) = \frac{\partial f_p^0}{\partial E_v}\hbar\vec{v}_p(\vec{r},\vec{k}) \tag{38}$$

$$\vec{J}_p = \frac{e}{4\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\cdot\left[\vec{\nabla}\zeta_p(\vec{r}) + \left(E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right)\frac{\vec{\nabla}T}{T}\right] \tag{39}$$

$$\vec{J}_{pQ} = \frac{1}{4\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},\vec{k})\left[E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right]\vec{v}_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\cdot\left[\vec{\nabla}\zeta_p(\vec{r}) + \left(E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right)\frac{\vec{\nabla}T}{T}\right] \tag{40}$$

Rewrite it as,

$$\vec{J}_p = \sigma_{\mathbf{p}}\cdot\vec{\nabla}\frac{\zeta_p}{e} - \mathbf{L_p^{12}}\cdot\frac{\vec{\nabla}T}{T} \tag{41}$$

$$\vec{J}_{pQ} = \mathbf{L_p^{21}}\cdot\vec{\nabla}\frac{\zeta_p}{e} - \mathbf{L_p^{22}}\cdot\frac{\vec{\nabla}T}{T} \tag{42}$$

with

$$\sigma_{\mathbf{p}} = \frac{e^2}{4\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k}) \tag{43}$$

$$\mathbf{L_p^{12}} = -\frac{e}{4\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\left[E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right] \tag{44}$$

$$\mathbf{L_p^{21}} = -\mathbf{L_p^{12}} = \frac{e}{4\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\left[E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right] \tag{45}$$

$$\mathbf{L_p^{22}} = -\frac{1}{4\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\vec{v}_p(\vec{r},\vec{k})\left[E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})\right]^2 \tag{46}$$

$\sigma_{\mathbf{p}}$ is the electric conductivity for holes in the valence band. We can also find the thermal conductivity as,

$$\vec{J}_{pQ}\Big|_{\vec{J}_p=0} = -\kappa_{\mathbf{p}}\vec{\nabla}T \quad (47)$$

$$\kappa_{\mathbf{p}} = \frac{1}{T}\left[\mathbf{L}^{22}_{\mathbf{p}} - \mathbf{L}^{21}_{\mathbf{p}}\cdot{\sigma_{\mathbf{p}}}^{-1}\cdot\mathbf{L}^{12}_{\mathbf{p}}\right] \quad (48)$$

We can also define,

$$\vec{\nabla}\frac{\zeta_p}{e}\Big|_{\vec{J}_p=0} = \mathbf{S}_{\mathbf{p}}\vec{\nabla}T \quad (49)$$

$$\mathbf{S}_{\mathbf{p}} = {\sigma_{\mathbf{p}}}^{-1}\frac{\mathbf{L}^{12}_{\mathbf{p}}}{T} \quad (50)$$

For lattice heat flux density, we assume that

$$\vec{J}_{L_Q} = -K_L\,\vec{\nabla}T, \quad (51)$$

where $K_L$ is the lattice thermal conductivity assumed to be known from other experimental considerations.

## V. SPHERICAL BAND, LONGITUDINAL ACOUSTIC WAVE

Assume we have spherical parabolic, effective mass band structures centered at $\vec{k} = (0,0,0)$. For electrons in conduction band,

$$\mathcal{E}_c(\vec{r},\vec{k}) = \mathcal{E}_c(\vec{r}) + \frac{\hbar^2k^2}{2m^*_n(\vec{r})} \quad (52)$$

$m^*_n(\vec{r})$ is the coordinate dependent effective mass. Thus we have,

$$\vec{v}_n(\vec{r},\vec{k}) = \frac{\hbar\vec{k}}{m^*_n(\vec{r})} \quad (53)$$

We further assume[3] the longitudinal acoustic dispersion relations for phonons, $\omega_{ql} = v_0q$, so that,

$$\tau_n(\vec{r},\vec{k}) = \tau_n(\vec{r},k) = \frac{\tau_{n0k}(\vec{r})}{k} = \frac{\tau_{n0}(\vec{r})}{\sqrt{\mathcal{E}_c(\vec{r},\vec{k}) - \mathcal{E}_c(\vec{r})}} \quad (54)$$

where $\tau_{n0k}(\vec{r}) = \frac{9\pi}{4}\frac{Mv_0^2\hbar^3}{\Omega_0c^2m^*_nk_0T}$, and $\tau_{n0}(\vec{r}) = \frac{\hbar}{\sqrt{2m^*_n}}\tau_{n0k}(\vec{r})$.
Component of the electric conductivity has the form,

$$(\sigma_{\mathbf{n}})_{\alpha\beta} = -\frac{e^2}{4\pi^3}\int d^3\vec{k}\frac{\partial f^0_n}{\partial E_c}\tau_n(\vec{r},k)\left(\frac{\hbar}{m^*_n}\right)^2k_\alpha k_\beta \quad (55)$$

All the components in the above integral, except for $k_\alpha$ and $k_\beta$, are spherically symmetric, thus $\sigma_{\mathbf{n}}$ is a scalar instead of a tensor and we have,

$$(\sigma_{\mathbf{n}})_{\alpha\beta} = 0, \qquad (\alpha\neq\beta) \quad (56)$$

$$\begin{aligned}\sigma_n &= (\sigma_{\mathbf{n}})_{11} = (\sigma_{\mathbf{n}})_{22} = (\sigma_{\mathbf{n}})_{33} = \frac{(\sigma_{\mathbf{n}})_{11} + (\sigma_{\mathbf{n}})_{22} + (\sigma_{\mathbf{n}})_{33}}{3}\\ &= -\frac{e^2}{12\pi^3}\int d^3\vec{k}\frac{\partial f^0_n}{\partial E_c}\tau_n(\vec{r},k)\frac{\hbar^2k^2}{m^{*2}_n}\end{aligned} \quad (57)$$

For the same reason, $\mathbf{L}^{12}_{\mathbf{n}}$, $\mathbf{L}^{21}_{\mathbf{n}}$ and $\mathbf{L}^{22}_{\mathbf{n}}$ are all scalars,

$$L^{12}_n = \frac{e}{12\pi^3}\int d^3\vec{k}\frac{\partial f^0_n}{\partial E_c}\tau_n(\vec{r},k)\frac{\hbar^2k^2}{m^{*2}_n}\left[E_c(\vec{r},k) - \zeta_n(\vec{r})\right] \quad (58)$$

$$L^{21}_n = L^{12}_n = \frac{e}{12\pi^3}\int d^3\vec{k}\frac{\partial f^0_n}{\partial E_c}\tau_n(\vec{r},k)\frac{\hbar^2k^2}{m^{*2}_n}\left[E_c(\vec{r},k) - \zeta_n(\vec{r})\right] \quad (59)$$

$$L^{22}_n = -\frac{1}{12\pi^3}\int d^3\vec{k}\frac{\partial f^0_n}{\partial E_c}\tau_n(\vec{r},k)\frac{\hbar^2k^2}{m^{*2}_n}\left[E_c(\vec{r},k) - \zeta_n(\vec{r})\right]^2 \quad (60)$$

Let

$$\mathcal{E}_n = \frac{\mathcal{E}_c(\vec{r},k) - \mathcal{E}_c(\vec{r})}{k_B T} = \frac{E_c(\vec{r},k) - E_c(\vec{r})}{k_B T} \tag{61}$$

$$\eta_n(\vec{r}) = -\frac{E_c(\vec{r}) - \zeta_n(\vec{r})}{k_B T} \tag{62}$$

then,

$$f_n^0(\mathcal{E}_n, \vec{r}) = \frac{1}{e^{\mathcal{E}_n - \eta_n} + 1} \tag{63}$$

$$\frac{\partial f_n^0}{\partial E_c} = \frac{1}{k_B T}\frac{\partial f_n^0}{\partial \mathcal{E}_n} \tag{64}$$

Let $\int d\vec{k}^3 = \int dk k^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi$ and integrate over $\theta$ and $\phi$, noticing that $k = \sqrt{\frac{2m_p^*}{\hbar^2}}\sqrt{k_B T}\sqrt{\mathcal{E}_n}$ and Eq. (54),

$$\sigma_n = -\frac{e^2}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)\int_0^\infty d\mathcal{E}_n \mathcal{E}_n \frac{\partial f_n^0}{\partial \mathcal{E}_n} \tag{65}$$

$$L_n^{12} = \frac{e}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_n \mathcal{E}_n \left(\mathcal{E}_n - \eta_n\right)\frac{\partial f_n^0}{\partial \mathcal{E}_n} \tag{66}$$

$$L_n^{21} = L_n^{12} = \frac{e}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_n \mathcal{E}_n \left(\mathcal{E}_n - \eta_n\right)\frac{\partial f_n^0}{\partial \mathcal{E}_n} \tag{67}$$

$$L_n^{22} = -\frac{1}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^3\int_0^\infty d\mathcal{E}_n \mathcal{E}_n \left(\mathcal{E}_n - \eta_n\right)^2\frac{\partial f_n^0}{\partial \mathcal{E}_n} \tag{68}$$

Consider integral, where $g(\mathcal{E}_n)$ is an arbitrary function with $g(0) = 0$,

$$\int_0^\infty d\mathcal{E}_n g(\mathcal{E}_n)\frac{\partial f_n^0}{\partial \mathcal{E}_n} = \left[f_n^0(\mathcal{E}_n)g(\mathcal{E}_n)\right]\Big|_0^\infty - \int_0^\infty d\mathcal{E}_n \frac{\partial g(\mathcal{E}_n)}{\partial \mathcal{E}_n} f_n^0 = -\int_0^\infty d\mathcal{E}_n \frac{\partial g(\mathcal{E}_n)}{\partial \mathcal{E}_n} f_n^0 \tag{69}$$

Then we have

$$\sigma_n = \frac{e^2}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)\int_0^\infty d\mathcal{E}_n f_n^0(\mathcal{E}_n, \vec{r}) \tag{70}$$

$$L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_n f_n^0(\mathcal{E}_n, \vec{r})\left[2\mathcal{E}_n - \eta_n\right] \tag{71}$$

$$L_n^{21} = L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_n f_n^0(\mathcal{E}_n, \vec{r})\left[2\mathcal{E}_n - \eta_n\right] \tag{72}$$

$$L_n^{22} = \frac{1}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^3\int_0^\infty d\mathcal{E}_n f_n^0(\mathcal{E}_n, \vec{r})\left[3\mathcal{E}_n^2 - 4\eta_n\mathcal{E}_n + \eta_n^2\right] \tag{73}$$

Introduce Fermi-Dirac function $F_i(\eta)$, which is defined as $F_i(\eta) = \int_0^\infty \frac{\mathcal{E}^i d\mathcal{E}}{e^{(\mathcal{E}-\eta)}+1}$. Thus,

$$\sigma_n = \frac{e^2}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)F_0(\eta_n) \tag{74}$$

$$L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^2\left[2F_1(\eta_n) - \eta_n F_0(\eta_n)\right] \tag{75}$$

$$L_n^{21} = L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^2\left[2F_1(\eta_n) - \eta_n F_0(\eta_n)\right] \tag{76}$$

$$L_n^{22} = \frac{1}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_B T)^3\left[3F_2(\eta_n) - 4\eta_n F_1(\eta_n) + \eta_n^2 F_0(\eta_n)\right] \tag{77}$$

and then,

$$S_n(\vec{r}) = \frac{L_n^{12}}{\sigma_n T} = -\frac{k_B}{e}\frac{2F_1(\eta_n) - \eta_n F_0(\eta_n)}{F_0(\eta_n)} \tag{78}$$

$$\frac{\sigma_n(\vec{r})}{\kappa_n(\vec{r})} = \frac{\sigma_n T}{L_n^{22} - \frac{L_n^{12}L_n^{21}}{\sigma_n}} = \left(\frac{e}{k_B}\right)^2 \frac{1}{T}\frac{F_0^2(\eta_n)}{3F_0(\eta_n)F_2(\eta_n) - 4F_1^2(\eta_n)} \tag{79}$$

For holes in valence band,

$$\mathcal{E}_v(\vec{r},\vec{k}) = \mathcal{E}_v(\vec{r}) - \frac{\hbar^2 k^2}{2m_p^*(\vec{r})} \tag{80}$$

$m_p^*(\vec{r})$ is absolute value of the coordinate dependent effective mass. Thus we have,

$$\vec{v}_p(\vec{r},\vec{k}) = -\frac{\hbar\vec{k}}{m_p^*(\vec{r})} \tag{81}$$

We again assume the longitudinal acoustic dispersion relations for phonons, $\omega_{ql} = v_0 q$, so that,

$$\tau_p(\vec{r},\vec{k}) = \tau_p(\vec{r},k) = \frac{\tau_{p0k}(\vec{r})}{k} = \frac{\tau_{p0}(\vec{r})}{\sqrt{\mathcal{E}_v(\vec{r}) - \mathcal{E}_v(\vec{r},\vec{k})}} \tag{82}$$

where $\tau_{n0p}(\vec{r}) = \frac{9\pi}{4}\frac{M v_0^2 \hbar^3}{\Omega_0 c^2 m_p^* k_0 T}$, and $\tau_{p0}(\vec{r}) = \frac{\hbar}{\sqrt{2m_p^*}}\tau_{p0k}(\vec{r})$.
For the same reason as for electrons in conduction band, $\sigma_\mathbf{p}$, $\mathbf{L_p^{12}}$, $\mathbf{L_p^{21}}$ and $\mathbf{L_p^{22}}$ are all scalars,

$$\sigma_p = \frac{e^2}{12\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},k)\frac{\hbar^2 k^2}{m_p^{*2}} \tag{83}$$

$$L_p^{12} = -\frac{e}{12\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},k)\frac{\hbar^2 k^2}{m_p^{*2}}\left[E_v(\vec{r},\vec{k}) - \zeta_p(\vec{r})\right] \tag{84}$$

$$L_p^{21} = -L_p^{12} = \frac{e}{12\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},k)\frac{\hbar^2 k^2}{m_p^{*2}}\left[E_v(\vec{r},\vec{k}) - \zeta_p(\vec{r})\right] \tag{85}$$

$$L_p^{22} = -\frac{1}{12\pi^3}\int d^3\vec{k}\frac{\partial f_p^0}{\partial E_v}\tau_p(\vec{r},k)\frac{\hbar^2 k^2}{m_p^{*2}}\left[E_v(\vec{r},\vec{k}) - \zeta_p(\vec{r})\right]^2 \tag{86}$$

Let

$$\mathcal{E}_p = \frac{\mathcal{E}_v(\vec{r}) - \mathcal{E}_v(\vec{r},k)}{k_B T} = \frac{E_v(\vec{r}) - E_v(\vec{r},k)}{k_B T} \tag{87}$$

$$\eta_p(\vec{r}) = \frac{E_v(\vec{r}) - \zeta_p(\vec{r})}{k_B T} \tag{88}$$

then we have,

$$f_p^0(\mathcal{E}_p,\vec{r}) = \frac{1}{e^{\mathcal{E}_p - \eta_p} + 1} \tag{89}$$

$$\frac{\partial f_p^0}{\partial E_v} = -\frac{1}{k_B T}\frac{\partial f_p^0}{\partial \mathcal{E}_p} \tag{90}$$

Let $\int d\vec{k}^3 = \int dk k^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi$ and integrate over $\theta$ and $\phi$, noticing that $k = \sqrt{\frac{2m_p^*}{\hbar^2}}\sqrt{k_B T}\sqrt{\mathcal{E}_p}$ and Eq. (82),

$$\sigma_p = -\frac{e^2}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)\int_0^\infty d\mathcal{E}_p \mathcal{E}_p \frac{\partial f_p^0}{\partial \mathcal{E}_p} \tag{91}$$

$$L_p^{12} = \frac{e}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_p \mathcal{E}_p(\eta_p - \mathcal{E}_p) \frac{\partial f_p^0}{\partial \mathcal{E}_p} \tag{92}$$

$$L_p^{21} = -L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_p \mathcal{E}_p(\eta_p - \mathcal{E}_p) \frac{\partial f_p^0}{\partial \mathcal{E}_p} \tag{93}$$

$$L_p^{22} = \frac{1}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_p \mathcal{E}_p(\eta_p - \mathcal{E}_p)^2 \frac{\partial f_p^0}{\partial \mathcal{E}_p} \tag{94}$$

Consider integral, where $g(\mathcal{E}_p)$ is an arbitrary function with $g(0) = 0$,

$$\int_0^\infty d\mathcal{E}_p g(\mathcal{E}_p)\frac{\partial f_p^0}{\partial \mathcal{E}_p} = \left[f_p^0(\mathcal{E}_p)g(\mathcal{E}_p)\right]\Big|_0^\infty - \int_0^\infty d\mathcal{E}_p \frac{\partial g(\mathcal{E}_p)}{\partial \mathcal{E}_p} f_p^0 = -\int_0^\infty d\mathcal{E}_p \frac{\partial g(\mathcal{E}_p)}{\partial \mathcal{E}_p} f_p^0 \tag{95}$$

Thus,

$$\sigma_p = \frac{e^2}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)\int_0^\infty d\mathcal{E}_p f_p^0(\mathcal{E}_p, \vec{r}) \tag{96}$$

$$L_p^{12} = -\frac{e}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_p (\eta_p - 2\mathcal{E}_p) f_p^0(\mathcal{E}_p, \vec{r}) \tag{97}$$

$$L_p^{21} = -L_n^{12} = \frac{e}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_p (\eta_p - 2\mathcal{E}_p) f_p^0(\mathcal{E}_p, \vec{r}) \tag{98}$$

$$L_p^{22} = -\frac{1}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^2\int_0^\infty d\mathcal{E}_p \left[3\mathcal{E}_p^2 - 4\eta_p\mathcal{E}_p + \eta_p^2\right] f_p^0(\mathcal{E}_p, \vec{r}) \tag{99}$$

Thus,

$$\sigma_p = \frac{e^2}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)F_0(\eta_p) \tag{100}$$

$$L_p^{12} = \frac{e}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^2\left[2F_1(\eta_p) - \eta_p F_0(\eta)\right] \tag{101}$$

$$L_p^{21} = -L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^2\left[2F_1(\eta_p) - \eta_p F_0(\eta)\right] \tag{102}$$

$$L_p^{22} = -\frac{1}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_B T)^3\left[3F_2(\eta_p) - 4\eta_p F_1(\eta_p) + \eta_p^2 F_0(\eta_p)\right] \tag{103}$$

and then,

$$S_p(\vec{r}) = \frac{L_p^{12}}{\sigma_p T} = \frac{k_B}{e}\frac{2F_1(\eta_p) - \eta_p F_0(\eta_p)}{F_0(\eta_p)} \tag{104}$$

$$\frac{\sigma_p(\vec{r})}{\kappa_p(\vec{r})} = \frac{\sigma_p T}{L_p^{22} - \frac{L_p^{12}L_p^{21}}{\sigma_p}} = -\left(\frac{e}{k_B}\right)^2 \frac{1}{T}\frac{F_0^2(\eta_p)}{3F_0(\eta_p)F_2(\eta_p) - 4F_1^2(\eta_p)} \tag{105}$$

## VI. NONDEGENERATE BOLTZMANN APPROXIMATION

In the nondegenerate approximation, $E_c(\vec{r},k)-\zeta_n(\vec{r}) > E_c(\vec{r})-\zeta_n(\vec{r}) \gg k_BT$, and $\zeta_p(\vec{r})-E_v(\vec{r},k) > \zeta_p(\vec{r})-E_v(\vec{r}) \gg k_BT$,the Fermi-Dirac distribution function goes to classical Boltzman distribution,

$$f_n^0(\vec{r},\vec{k}) \to e^{-\frac{E_c(\vec{r},\vec{k})-\zeta_n(\vec{r})}{k_BT}}$$
$$f_p^0(\vec{r},\vec{k}) \to e^{\frac{E_v(\vec{r},\vec{k})-\zeta_p(\vec{r})}{k_BT}} \tag{106}$$

and

$$F_i(\eta) \to \int_0^\infty \mathcal{E}^i e^{-(\mathcal{E}-\eta)} d\mathcal{E} \tag{107}$$

That is,

$$F_0(\eta) \to \int_0^\infty e^{-(\mathcal{E}-\eta)} d\mathcal{E} = e^\eta$$
$$F_1(\eta) \to \int_0^\infty \mathcal{E} e^{-(\mathcal{E}-\eta)} d\mathcal{E} = e^\eta$$
$$F_2(\eta) \to \int_0^\infty \mathcal{E}^2 e^{-(\mathcal{E}-\eta)} d\mathcal{E} = 2e^\eta \tag{108}$$

Thus,

$$\sigma_n = \frac{e^2}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_BT)e^{\eta_n} \tag{109}$$

$$L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_BT)^2e^{\eta_n}\left[2-\eta_n\right] \tag{110}$$

$$L_n^{21} = L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_BT)^2e^{\eta_n}\left[2-\eta_n\right] \tag{111}$$

$$L_n^{22} = \frac{1}{3\pi^2}\frac{1}{m_n^*}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{3}{2}} \tau_{n0}(\vec{r})(k_BT)^3e^{\eta_n}\left[6-4\eta_n+\eta_n^2\right] \tag{112}$$

$$\sigma_p = \frac{e^2}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_BT)e^{\eta_p} \tag{113}$$

$$L_p^{12} = \frac{e}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_BT)^2e^{\eta_p}\left[2-\eta_p\right] \tag{114}$$

$$L_p^{21} = -L_n^{12} = -\frac{e}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_BT)^2e^{\eta_p}\left[2-\eta_p\right] \tag{115}$$

$$L_p^{22} = -\frac{1}{3\pi^2}\frac{1}{m_p^*}\left(\frac{2m_p^*}{\hbar}\right)^{\frac{3}{2}} \tau_{p0}(\vec{r})(k_BT)^3e^{\eta_p}\left[6-4\eta_p+\eta_p^2\right] \tag{116}$$

and then,

$$S_n(\vec{r}) = \frac{L_n^{12}}{\sigma_nT} = -\frac{2k_B}{e}\left(1-\frac{\eta_n}{2}\right) = -\frac{2k_B}{e}\left(1+\frac{E_c(\vec{r})-\zeta_n(\vec{r})}{2k_BT(\vec{r})}\right) \tag{117}$$

$$\frac{\sigma_n(\vec{r})}{\kappa_n(\vec{r})} = \frac{\sigma_nT}{L_n^{22}-\frac{L_n^{12}L_n^{21}}{\sigma_n}} = \frac{1}{2}\left(\frac{e}{k_B}\right)^2\frac{1}{T} \tag{118}$$

$$S_p(\vec{r}) = \frac{L_p^{12}}{\sigma_pT} = \frac{k_B}{e}\left(2+\frac{\zeta_p(\vec{r})-E_v(\vec{r})}{k_BT}\right) \tag{119}$$

$$\frac{\sigma_p(\vec{r})}{\kappa_p(\vec{r})} = \frac{\sigma_pT}{L_p^{22}-\frac{L_p^{12}L_p^{21}}{\sigma_p}} = -\frac{1}{2}\left(\frac{e}{k_B}\right)^2\frac{1}{T} \tag{120}$$

## VII. TWO BAND - CONDUCTION BAND AND VALENCE BAND - MODEL

Letting $\zeta_n = \zeta_p = \zeta$, it follows in a straightforward fashion that the two-band dynamical variables become

$$\begin{aligned} \vec{J} = \vec{J}_n + \vec{J}_p &= (\sigma_n + \sigma_p)\frac{\vec{\nabla}\zeta}{e} - \left\{L_n^{(12)} + L_p^{(12)}\right\}\frac{\vec{\nabla}T}{T} \\ &= \sigma\frac{\vec{\nabla}\zeta}{e} - L^{(12)}\frac{\vec{\nabla}T}{T}, \end{aligned} \tag{121}$$

where $\sigma \equiv \sigma_n + \sigma_p$, and $L^{(12)} \equiv L_n^{(12)} + L_p^{(12)}$. From this, we obtain

$$S = \frac{L^{(12)}}{\sigma T} = \frac{L_n^{(12)} + L_p^{(12)}}{(\sigma_n+\sigma_p)T} = \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n+\sigma_p}. \tag{122}$$

$$\vec{J}_Q = \vec{J}_{nQ} + \vec{J}_{pQ} = \left\{L_n^{(21)} + L_p^{(21)}\right\}\frac{\vec{\nabla}\zeta}{e} - \left\{L_n^{(22)} + L_p^{(22)}\right\}\frac{\vec{\nabla}T}{T} = L^{(21)}\frac{\vec{\nabla}\zeta}{e} - L^{(22)}\frac{\vec{\nabla}T}{T}, \tag{123}$$

where $L^{(21)} \equiv L_n^{(21)} + L_p^{(21)}$, and $L^{(22)} \equiv L_n^{(22)} + L_p^{(22)}$. Also, we acquire

$$\begin{aligned} \kappa &= \frac{1}{T}\left(L^{(22)} - \frac{L^{(12)}L^{(21)}}{\sigma}\right) = \frac{1}{T}\left(L_n^{(22)} + L_p^{(22)} - \frac{\{L_n^{(21)}+L_p^{(21)}\}\{L_n^{(12)}+L_p^{(12)}\}}{\sigma_n+\sigma_p}\right) \\ &= \frac{1}{T}\left(Tk_n + \frac{L_n^{(12)}L_n^{(21)}}{\sigma_n} + Tk_p + \frac{L_p^{(12)}L_p^{(21)}}{\sigma_p} - \frac{\{L_n^{(21)}+L_p^{(21)}\}\{L_n^{(12)}+L_p^{(12)}\}}{\sigma_n+\sigma_p}\right) \\ &= k_n + k_p + \frac{1}{T}\left\{TS_nL_n^{(21)} + TS_pL_p^{(21)} - TS(L_n^{(21)} + L_p^{(21)})\right\}. \end{aligned} \tag{124}$$

Or

$$\kappa = k_n + k_p + (S_n - S)\,L_n^{(21)} + (S_p - S)\,L_p^{(21)}. \tag{125}$$

## VIII. SEEBECK COEFFICIENT; FIGURE OF MERIT[4]

For a given carrier band, the current is given by $\vec{J}_n$ in eq. (22) and $\vec{J}_p$ in eq. (41), respectively. Then, since the Seebeck coefficient is determined from the open circuit condition that $\vec{J}_n$ or $\vec{J}_p = 0$, it follows that

$$\frac{\vec{\nabla}\zeta_m(\vec{r})}{e} - \frac{L_m^{(12)}}{\sigma_m}\frac{\vec{\nabla}T}{T} = 0, \tag{126}$$

where $m$ represents $n$ or $p$ from eqs. (22), (41), respectively. Here, $\zeta_m(\vec{r})$ is the electro-chemical potential, given by

$$\zeta_m(\vec{r}) = E_{F_m} + q\phi(\vec{r}), \tag{127}$$

where $\phi(\vec{r})$ is the external potential across the sample and $q$ is the charge of the carrier. Therefore, after integrating across the sample of length $L$, one obtains

$$\phi(L) - \phi(0) = \{E_{F_m}(0) - E_{F_m}(L)\} + \int_0^L S_m\,\vec{\nabla}T\,dx, \tag{128}$$

where $S_m = L_m^{(12)}/(\sigma_m T)$ is defined in eqs. (31),(50) for $m = n, p$, respectively. For a slab in which $E_{F_m}(0) = E_{F_m}(L)$, we see that eq. (128) simplifies so that in one dimensional case, we get

$$\Delta\phi \equiv \phi(L) - \phi(0) = q\int_0^L S_m\frac{dT}{dx}\,dx. \tag{129}$$

Therefore, from eq. (129) we can see that the voltage developed across the slab depends upon the quantities $S_m(x) = L_m^{(12)}(x)/(\sigma_m(x)\,T(x))$ and $\frac{dT}{dx}$. $L_m^{(12)}$ and $\sigma_m$ have already been calculated for conduction and valence band cases, and for degenerate and non-degenerate Boltzmann approximations. As for $T(x)$, given that the temperature at the ends of the slab are fixed at hot and cold values to provide a temperature gradient across the sample, the value of the temperature within the sample will vary with position since $T(x)$ will classically depend upon the solution of a boundary value problem for thermal diffusion. The classical solution has been well documented, and in fact, in the open circuit condition, it is well known that $T(x)$ varies linearly across the slab as

$$T(x) = T(0) + \frac{\Delta T}{L}\,x\,, \tag{130}$$

where $T(0)$ is the cold temperature and $T(L)$ is the hot temperature, and $\Delta T = T(L) - T(0)$, Using $T(x)$ of eq. (130) in eq. (129) therefore gives the simple result that

$$\frac{\Delta\phi}{\Delta T} \equiv \bar{S} = \frac{1}{L}\int_0^L S_m\,dx\,. \tag{131}$$

That is, the Seebeck coefficient is the spatial average of $S_m(x)$ over the slab.

We have evaluated $S_m = L_m^{(12)}(x)/(\sigma_m(x)\,T(x))$ for the spherical band model with spatially varying band edge and longitudinal acoustic wave phonon approximation in Section V. $S_m$ has been evaluated as a function of position for both degenerate Fermi-Dirac [eqs. (78), (104) for $n, p$, respectively] and non-degenerate Boltzmann thermodynamic limits (eqs. (117), (119) for $n, p$, respectively). For simplicity of discussion, we present the result for the non-degenerate case for electrons so that eq. (131) becomes

$$\bar{S} = -\frac{1}{L}\int_0^L \frac{2k_B}{e}\left(1 + \frac{E_c(x) - \zeta_n(x)}{2\,k_B\,T(x)}\right)dx \tag{132}$$

or

$$\bar{S} = -\frac{k_B}{e}\left(2 + \frac{1}{L}\int_0^L\left(\frac{E_c(x) - \zeta_n(x)}{2\,k_B\,T(x)}\right)dx\right). \tag{133}$$

Thus, the Seebeck coefficient is enhanced by the addition of the spatial average of spatially dependent Boltzmann energy ratio $(E_c - \zeta_n)/(k_B\,T)$ directly in the Boltzmann limit. If we were to evaluate $\bar{S}_n$ for electrons in the Fermi-Dirac limit, we would have to use $S_n$ in eq. (78) which would then require an integral over Fermi-Dirac integral functionals of $(E_c - \zeta_n)/(k_B\,T)$ in a much more non-linear dependence on the spatially varying Boltzmann energy ratio.

For simplicity in discussing the estimate of the enhancement factor, we assume that $\zeta_n(x) = \zeta_n(0)$ a constant. We note that if the Boltzmann factor were a simple constant in total, the enhancement would simply result in an increase in the Seebeck coefficient from the free electron value to the semiconductor value. In fact, in enhancing the Seebeck coefficient, we simply want to maximize the area under the curve of the Boltzmann energy ratio in eq. (133). However, this dependence upon the Seebeck coefficient needs to be balanced with the other transport parameters that enter into the well-known figure merit, $Z_m(x)$ which is given, for a given carrier type, as

$$Z_m(x) = \frac{S_m^2\,\sigma_m}{k_m + k_L} \equiv \frac{S_m^2\,\sigma_m}{\frac{\sigma_m\,L_m^{(22)} - L_m^{(12)}\,L_m^{(21)}}{\sigma_m\,T} + k_L}\,. \tag{134}$$

Here, there dependence of $S_m^2, \sigma_m, L_m^{(22)}, L_m^{(12)}$, and $L_m^{(12)}$ upon the spatially dependent Boltzmann factor has been calculated for degenerate and non-degenerate statistics in Section V, VI, respectively; also $k_L$ is the lattice thermal conductivity. For the case of non-degenerate statistical analysis, we see from eqs. (109)-(112) for electrons that $L_m^{(22)}, L_m^{(12)} = L_m^{(21)}$ can be expressed in terms of $\sigma_n$ so that $Z_n$ in eq. (134) can be greatly simplified as

$$Z_m(x)\,T(x) = \frac{S_n^2\,\sigma_n(x)\,T(x)}{2\,(k_B/e)^2\,\sigma_n(x)\,T(x) + k_L} \equiv \frac{S_n^2}{2\,(k_B/e)^2 + k_L/(\sigma_n(x)\,T(x))}\,, \tag{135}$$

where, from eq. (109), $\sigma_n$ is given by

$$\sigma_n = \frac{e^2}{3\pi^2}\frac{1}{m_n^*}\left(\frac{3\,m_n^*}{\hbar}\right)^{3/2}\tau_{n_0}(x)\,(k_B\,T(x))\,e^{-(E_c - \zeta_0)/(k_b\,T(x))}\,. \tag{136}$$

The dependence of all the thermodynamic variables on the spatially dependent Boltzmann factor, even though introduced explicitly here through the approximate form of the relaxation approximation, is resonant with Landauer's original concept of "motion out of noisy states"[5] where non-uniform temperature effects drive the system dynamics - in this analysis, it is a non-uniform Boltzmann factor which drives the system, where the energy band edge is tailored and fixed, and the non-uniform temperature, apart from the fixed hot and cold ends, is transferring energy dynamically. Therefore, even though $(E_c - \zeta_0)/(k_b\,T(x))$ can be chosen to enhance $S_n(x)$ over the slab of material, the spatial dependence of the figure of merit will depend upon the term $k_L/(\sigma_n\,T(x))$ in eq. (135) in a very sensitive way; in fact, the model dependence of $\sigma_n$ in eq. (136) shows that the conductivity will depend exponentially on the spatial Boltzmann factor.

As a few illustrative examples of $E_c(x)$ to estimate $\bar{S}$ in eq. (132), we consider the following simple cases, always assuming that $T(x) = T(0) + \frac{\Delta T}{L}\,x$, with $\Delta T = T(L) - T(0)$, and $\zeta = \zeta(0) \equiv \zeta_0$ .

Case 1: $E_c(x) = E_c(0)$, a constant band edge.

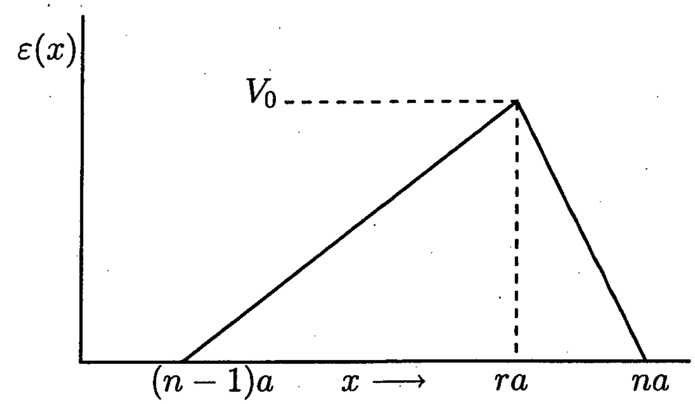
$$I_1 \;=\; \frac{1}{L}\int_0^L \left(\frac{E_c(x)-\zeta_0}{k\,T(x)}\right) dx \;\equiv\; \left(\frac{E_c(0)-\zeta_0}{k\,\Delta T}\right) \ln\frac{T(L)}{T(0)}\,. \tag{137}$$

Case 2: $E_c(x) = E_c(0) + \frac{\Delta\mathcal{E}}{L}\,x$, a linear spatial band edge.

$$I_2 \;=\; \frac{1}{L}\int_0^L \left(\frac{E_c(x)-\zeta_0}{k\,T(x)}\right) dx \;\equiv\; \left(\frac{E_c(0)-\zeta_0}{k\,\Delta T}\right) \ln\frac{T(L)}{T(0)} \;+\; \frac{\Delta\mathcal{E}}{k\Delta T}\left(1 \;-\; \frac{T(0)}{\Delta T}\,\ln\frac{T(L)}{T(0)}\right). \tag{138}$$

Case 3: $E_c(x) = E_c(0) + \sum_{n=0}^{N-1} \mathcal{E}(x-na)$, aperiodic but asymmetrical spatial saw tooth band edge; here, $\mathcal{E}(x-na)$ defines a unit cell (see sketch) of the periodic band edge, where

$$\mathcal{E}(x \;-\; n\,a) \;=\; \begin{cases} \frac{V_0}{r}\,\left\{\frac{x}{a} \;-\; (n-1)\right\} & \text{for} \quad (n-1)a \le x \le (n-1)a + ra \\ \frac{V_0}{1-r}\,\left(-\frac{x}{a} \;+\; n\right) & \text{for} \quad (n-1)a + ra \le x \le na \end{cases}\,. \tag{139}$$




In $\mathcal{E}(x \;-\; n\,a)$, the parameter $r$, where $0 < r < 1$, measures the degree of asymmetry; of course, for $r = 1/2$, one achieves total symmetry; when $r = 1$, one achieves a perfect saw tooth. For this case,

$$I_3 \;=\; \frac{1}{L}\int_0^L \left(\frac{E_c(x)-\zeta_0}{k\,T(x)}\right) dx \;\equiv\; \left(\frac{E_c(0)-\zeta_0}{k\,\Delta T}\right) \ln\frac{T(L)}{T(0)} \;+\; \Delta I_3(r)\,, \tag{140}$$

where

$$\Delta I_3(r) \;=\; \frac{1}{L}\int_0^L \sum_{n=0}^{N-1} \mathcal{E}(x-na)\,dx \;\equiv\; \frac{V_0}{k\Delta T}\left[ y\frac{1}{r}\sum_{l=0}^{N-1}\ln\frac{y+l}{y+l+r} + \frac{1}{r}\sum_{l=0}^{N-1} l\cdot\ln\frac{y+l}{y+l+r} + (y+1)\frac{1}{1-r}\sum_{l=0}^{N-1}\ln\frac{y+l+1}{y+l+r} + \frac{1}{1-r}\sum_{l=0}^{N-1} l\cdot\ln\frac{y+l+1}{y+l+r}\right]. \tag{141}$$

Here, $y = L\,T(0)/(a\Delta T)$. In particular, when $r = 1/2$, we see that eq. (141) reduces to

$$\Delta I_3\left(\tfrac{1}{2}\right) \;=\; \frac{2V_0}{k\Delta T}\left[\sum_{l=0}^{N-1}(y+l)\,\ln\frac{y+l}{y+l+\frac{1}{2}} + \sum_{l=0}^{N-1}(y+l+1)\,\ln\frac{y+l+1}{y+l+\frac{1}{2}}\right], \tag{142}$$

whereas for $r = 1$ (the perfect sawtooth case), we see that eq.(141) becomes

$$\Delta I_3\,(1) \;=\; \frac{V_0}{k\Delta T}\left[\sum_{l=0}^{N-1}(y+l)\;\ln\frac{y+l}{y+l+1}\right]. \tag{143}$$

Comparative inspection of eqs. (142), (143) indicates that $\Delta I_3(1) < \Delta I_3(1/2)$ so that for all other equal parameters, the symmetric periodic band edge produces a larger area under the curve of eq. (140) than the asymmetric band edge; thus the enhancement to the spatially averaged open-circuit Seebeck coefficient would be larger for the symmetrical ($r = 1/2$) band edge case. However, it should be noted that even though a given choice of spatial energy band configuration may give rise to a relatively large Seebeck coefficient, the more significant consideration is to choose an energy band configuration which optimizes the figure of merit $ZT$. In this case, the physics is not determined by open circuit conditions, as is done in evaluating the Seebeck coefficient, but is determined generally under non-equilibrium, current driven conditions. Thus, an effort should be pursued to examine the role of band engineering on the relevant thermoelectric transport properties, and to properly address the ability to enhance and optimize the thermoelectric figure of merit based on a basic variational principle for $ZT$.

## IX. VARIATIONAL PRINCIPLE FOR $ZT$, THE FIGURE OF MERIT

As noted in eqs. (134), (135), the well-known figure of merit for a given carrier type is generally given by

$$Z_m T = \frac{S_m^2 \sigma_m T}{K_m + K_L}. \tag{144}$$

In a very nice variational analysis developed by Nishio and Hirano,[6] they treated $S_m$ and $K_m$ as functionals of differential conductivity, $\sigma_D(\epsilon)$, where $\sigma_D(\epsilon)$ is known and is defined as the integrand of total conductivity

$$\sigma_m = \int \sigma_D(\epsilon)\, d\epsilon. \tag{145}$$

The transport variables $S_m$ and $K_m$ can be expressed in terms of $\sigma_D(\epsilon)$ as

$$S_m = -\frac{1}{e\sigma_m T} \int d\epsilon\, (\epsilon - \zeta)\, \sigma_D(\epsilon) \tag{146}$$

and

$$K_m = \frac{1}{e^2 T} \int d\epsilon\, (\epsilon - \zeta)^2\, \sigma_D(\epsilon) - T\sigma_m S_m^2, \tag{147}$$

where $\zeta$ is the chemical potential, and $K_L$ the lattice thermal conductivity, is considered constant. Thus, $Z_m T$ in eq. (144) can be viewed as a functional of $\sigma_D$ alone, provided $K_L$ is a constant. Thus, a small change in $\sigma_D(\epsilon)$ functionally gives rise to a change in $Z$ through the functional derivative expression

$$\delta Z_m \equiv Z[\sigma_m + \delta\sigma_m] - Z[\sigma_m] = \int d\epsilon\, \frac{\delta Z_m}{\delta \sigma_D(\epsilon)}\, \delta\epsilon_D(\epsilon). \tag{148}$$

Nishio and Hirano[6] have shown that this functional derivative in eq. (148) yields a maximum for eq. (144) in an energy range given by

$$\frac{\epsilon_\pm - \zeta}{kT} = -\frac{eS_m}{k}\left(1 + \frac{1}{Z_m}\right)\left(1 \pm \frac{1}{\sqrt{1+Z_m}}\right). \tag{149}$$

This suggests that it is possible to improve the figure of merit of thermoelectrics by tailoring the transport energetics by band engineering the carriers so that they transport across the thermoelectric device in an energetically favorable range.

The variational principle developed by Nishio and Hirano is very illuminating, but it only applies to situations where the lattice thermal conductivity is constant. A more useful form of the variational principle would allow the lattice thermal conductivity to vary as a subsidiary condition through a functional dependence on the conductivity. It is interesting to note that the expression for $Z_m T$ in eq. (135) can be written in terms of a calculated function of transport variables $L_m^{(22)}, L_m^{(12)}, L_m^{(21)}$, which can all be expressed in terms of the conductivity $\sigma_m$. Therefore, $Z_m T$ would be a function of $(E_c - \zeta_0)/kT(x)$, the spatially dependent relaxation time $\tau_{n_0}(x)$, and the spatially dependent effective mass $m_n^*(x)$. In plotting $Z_m T$ as a function of $(E_c - \zeta)/kT$, one would find that $Z_m T$ peaks for a given $K_L$,[7] thus indicating that $Z_m T$ is amenable to optimization with respect to the Boltzmann ratio parameter in $\sigma(x)$. This optimization scheme is given physical meaning based on the variational principle discussed herein.

## X. DISCUSSION FOR FOLLOW-ON AND CONCLUSION

In this study, we have explored the influence of spatially graded energy bands on the thermoelectric properties of thin film semiconductors. For an assumed linear spatial temperature variation across the sample during open circuit conditions, the Seebeck coefficient was determined and was shown to be enhanced by the addition of a term which depended analytically upon the Boltzmann factor comprised of the "band-engineered" energy band edge divided by the spatially dependent temperature across the sample. Estimates of the enhanced Seebeck coefficient for a symmetric versus asymmetric periodic band edge indicate that the symmetric band edge gave rise to a larger Seebeck correction; however we noted that the more significant consideration for ultimate thermoelectric optimization is the figure of merit, which is determined under current-driven conditions - here we feel that the asymmetric, periodic band edge will have a dominant role in driving the non-equilibrium carrier dynamics due to its non-linear influence upon the conductivity.[8]

Overall, the study revealed the potential for optimizing the thermoelectric figure of merit through band-gap engineering. A more detailed and rigorous analysis of thermoelectric transport under graded band-gap conditions are required, and a more comprehensive approach to the variational optimization of $ZT$, including the integration of thermal lattice dynamics, is necessary to explore the physical frame work for uncovering the potential of enhanced thermoelectricity in thin film semiconductors. This more detailed and rigorous analysis moves along the following road map.

- formulate the transport equations with a careful analysis of the spatial dependence of the energy bands; this means developing a Wannier-equivalent theorem for spatially varying band edges from the Wigner-Boltzmann picture, and deriving the correct equation of motion for the Boltzmann drift term.

- develop the full Boltzmann formulation for carriers in bands subject to electron-phonon interactions, and electron-mediated phonon dynamics. One needs the electron Boltzmann equation with electron-phonon scattering; in addition, one needs the phonon Boltzmann equation with electron-phonon scattering. Both equations are solved simultaneously with inhomogeneous energy band edges and doping, and then calculates the Seebeck coefficient and $ZT$ using appropriate boundary conditions.

- explore the variational principle for $ZT$ optimization including both fixed and varying lattice thermal conductivity as a subsidiary condition.

- overall objective - fully explore the role of band-gap engineering in enhancing the thermoelectric properties of semiconductors

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