Thermoelectric Transport Calculation by DFT

SSLAB HPC Training Class, Songshan Lake, Dong Guan

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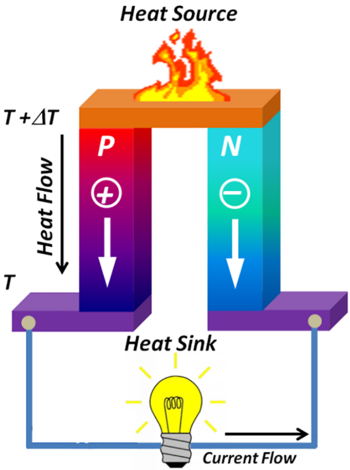
Contents

Introduction

Why the thermoelectric transport calculation?



Electron, Phonon, Scattering

Electron

- Kohn-Sham Hamiltonian

$$\widehat{\mathrm{H}}_{1\mathrm{el}} = -\frac{\hbar^2}{2\mathrm{m}}\nabla^2 + \mathrm{V}^{\mathrm{eff}}[\mathrm{n}](\mathrm{r}) \quad (1)$$

$$\mathrm{V}^{\mathrm{eff}}[\mathrm{n}](\mathrm{r}) = \mathrm{V}^{ee}[\mathrm{n}](\mathrm{r}) + \mathrm{V}^{en}(\mathrm{r}) + \mathrm{V}^{ext}(\mathrm{r}) \quad (2)$$

Electron, Phonon, Scattering

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- Single Electron Schrödinger Equation

$$\widehat{\mathrm{H}}_{1\mathrm{el}}\psi_\alpha(\mathrm{r}) = \epsilon_\alpha\psi_\alpha(\mathrm{r}) \quad (3)$$

$$\psi_\alpha(\mathrm{r}) = \sum_i \mathrm{c}_{\alpha i}\phi_i(\mathrm{r}) \quad (4)$$

$$\sum_j \mathrm{H}_{ij}\mathrm{c}_{\alpha j} = \epsilon_\alpha \sum_j \mathrm{S}_{ij}\mathrm{c}_{\alpha j} \quad (5)$$

$$\mathrm{H}_{ij} = \langle\phi_i \mid \widehat{\mathrm{H}}_{1\mathrm{el}} \mid \phi_j\rangle \quad (6)$$

$$\mathrm{S}_{ij} = \langle\phi_i \mid \phi_j\rangle \quad (7)$$

Electron, Phonon, Scattering

Electron

- Many Electron System

$$
\begin{aligned}
\mathrm{n}(\mathrm{r}) &= \sum_{\alpha} f_{\alpha} |\psi_{\alpha}(\mathrm{r})|^2 && (8) \\
&= \sum_{ij} \mathrm{D}_{ij} \phi_i(\mathrm{r}) \phi_j(\mathrm{r}) && (9) \\
\mathrm{D}_{ij} &= \sum_{\alpha} f_{\alpha} \mathrm{c}^{*}_{\alpha i} \mathrm{c}_{\alpha j} \quad \text{density matrix} && (10)
\end{aligned}
$$

Electron, Phonon, Scattering
Electron

- Many Electron System

$$n(r) = \sum_{\alpha} f_\alpha |\psi_\alpha(r)|^2 \quad (8)$$

$$= \sum_{ij} D_{ij}\phi_i(r)\phi_j(r) \quad (9)$$

$$D_{ij} = \sum_{\alpha} f_\alpha c^*_{\alpha i} c_{\alpha j} \quad \text{density matrix} \quad (10)$$

- Total Energy

$$V^{\mathrm{eff}}[n] = V^H[n] + V^{XC}[n] + V^{ext} \quad (11)$$

$$E[n] = T[n] + E^H[n] + E^{XC}[n] + E^{ext}[n] \quad (12)$$

$$T[n] = \sum_{\alpha} f_\alpha \langle\psi_\alpha \mid \frac{-\hbar^2}{2m}\nabla^2 \mid \psi_\alpha\rangle \quad (13)$$

$$f_\alpha = 1/[1 + e^{(\epsilon_\alpha - \epsilon_F)/k_B T}] \quad (14)$$

Electron, Phonon, Scattering
Phonon

- First-principles Forces

$$\mathbf{F}_i = -\frac{d\mathrm{E}[\mathrm{n}]}{d\mathbf{R}_i} \tag{15}$$

Electron, Phonon, Scattering

Phonon

- First-principles Forces

$$\mathbf{F}_i = -\frac{d\mathrm{E}[\mathrm{n}]}{d\mathbf{R}_i} \tag{15}$$

- Harmonic Approximation

$$\mathrm{H}_n = \frac{1}{2}\sum_m \dot{u}_m^\dagger \dot{u}_m + \frac{1}{2}\sum_{mn} u_m^\dagger \left.\frac{\partial^2 \mathrm{V}^n}{\partial u_m^\dagger \, \partial u_n}\right|_0 u_n \tag{16}$$

$$= \frac{1}{2}\sum_m^{\alpha=x,y,z} \dot{u}_{m\alpha}^2 + \frac{1}{2}\sum_{mn}^{\alpha\beta} u_{m\alpha}\, D_{m\alpha,n\beta}\, u_{n\beta} \tag{17}$$

$$D_{m\alpha,n\beta} = \left.\frac{\partial^2 \mathrm{V}^n}{\partial u_{m\alpha}\,\partial u_{n\beta}}\right|_0 \overset{q=0}{=} \frac{1}{\sqrt{M_m M_n}} \left.\frac{\partial^2 \mathrm{V}^n}{\partial \mathrm{R}_{m\alpha}\,\partial \mathrm{R}_{n\beta}}\right|_0 \tag{18}$$

$$\overset{q=0}{=} \frac{1}{\sqrt{M_m M_n}} \left.\frac{\partial \mathbf{F}_{m\alpha}}{\partial \mathbf{R}_{n\beta}}\right|_0 \tag{19}$$

Electron, Phonon, Scattering
Phonon

- Equation of Motion ⇒ Eigenvalue and Eigenvector

$$D(q)\,u = \omega_q^2\,u \tag{20}$$

Electron, Phonon, Scattering
Phonon

- Equation of Motion $\Rightarrow$ Eigenvalue and Eigenvector

$$D(q)\, u = \omega_q^2\, u \tag{20}$$

- Beyond Harmonic Approximation
  - Nonequilibrium Molecular Dynamics + Kubo-Greenwood Formula

    Huge System Size, Periodic Boundary
  - Relaxation Time Approximation + Boltzmann Transport Equation

    Limited Knowledge about Relaxation Time
  - Nonequilibrium Transport Theory + Green's Function

    Only Ballistic Transport Included

Electron, Phonon, Scattering
Scattering

- Carrier Scattering $\Rightarrow$
  Electron-Electron Scattering

Electron, Phonon, Scattering

Scattering

- Carrier Scattering $\Rightarrow$
  Electron-Electron Scattering
- Lattice Scattering $\Rightarrow$
  Electron-Phonon Scattering, Phonon-Phonon Scattering

Electron, Phonon, Scattering

Scattering

- Carrier Scattering ⇒
  Electron-Electron Scattering
- Lattice Scattering ⇒
  Electron-Phonon Scattering, Phonon-Phonon Scattering
- Defect Scattering ⇒
  0D, 1D, 2D, 3D Defects Scattering

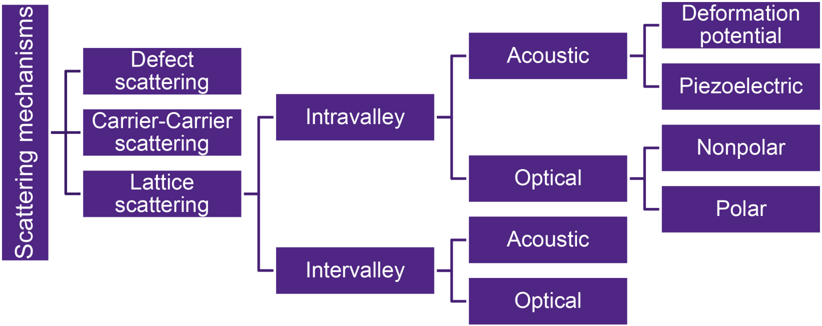
Electron, Phonon, Scattering

Scattering

- Carrier Scattering ⇒
  Electron-Electron Scattering
- Lattice Scattering ⇒
  Electron-Phonon Scattering, Phonon-Phonon Scattering
- Defect Scattering ⇒
  0D, 1D, 2D, 3D Defects Scattering
- Applied Field Scattering ⇒
  Laser, Visible light, Electrostatic Field, Alternating Electric Field, Stress Field, Press Field, Magnetic Field, Temperature Field, and so on.

Electron, Phonon, Scattering

Mechanism of Lattice Scattering

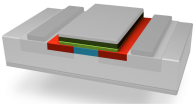


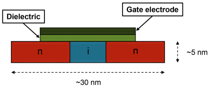
Open System

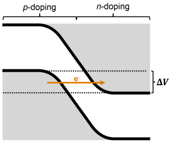
What does open mean?

The system has no boundary, and everything is changing.

1. The system is exchanging not only energy but matter with environment.
2. Time-reversal invariance does not exist.
3. The system is stochastic.
4. Real thermodynamics can happen $\Leftarrow$ the second law of thermodynamics.
5. Life is lived $\Rightarrow$ devices work.







6. Equilibrium $\rightleftharpoons$ Nonequilibrium

Dissipative Structure Theory (energy), Synergetics, Catastrophe Theory (self-assembly), Landauer-Büttiker Theory (electron&hole) ...

Open System

The Second Law of Thermodynamics

1. 熵增加原理：孤立系统的熵永不自动减少，熵在可逆过程中不变，在不可逆过程中增加。

Open System

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3. 第二定律指出在自然界中任何的过程都不可能自动地复原，要使系统从终态回到初态必需借助外界的作用。

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4. 第二定律在有限的宏观系统中使用时要保证：该系统是线性的；该系统全部是各向同性的。

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5. 热寂：宇宙的能量保持不变，宇宙的熵将趋于极大值，伴随着这一进程，宇宙进一步变化的能力越来越小，一切机械的、物理的、化学的、生命的等多种多样的运动逐渐全部转化为热运动，最终达到处处温度相等的热平衡状态，这时一切变化都不会发生，宇宙处于死寂的永恒状态。

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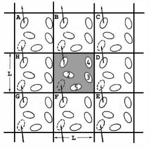
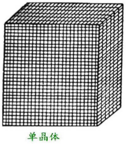
6. 解：宇宙是不稳定的热力学系统，并不像静态宇宙模型所设想的那样具有平衡态，因而其熵亦无最大值，即热寂并不存在。

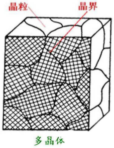
Open System
Boundary Condition

Boundary Condition 边界上的约束情况

1. Periodic Boundary Condition (PBC)







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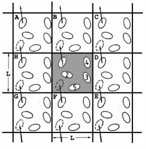
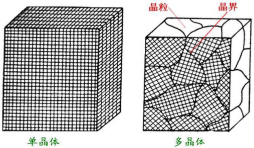
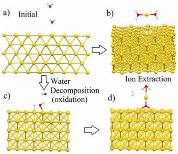
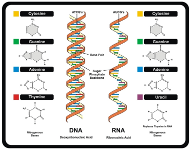




2. Rigid Boundary Condition (Slab Model)





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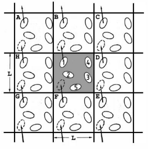

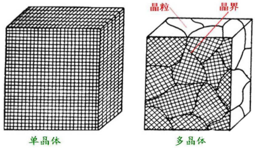

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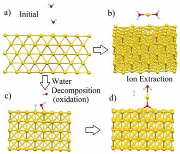
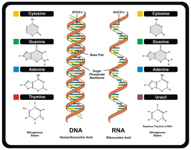


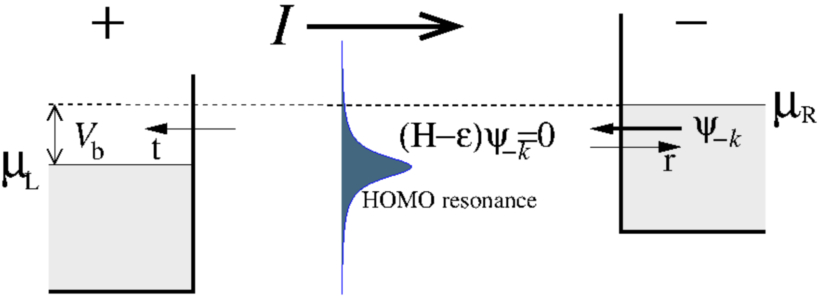


3. Open Boundary Condition (Cluster Model)

Nonequilibrium Green's Function

Green's Function of Schrödinger Equation

Non-equilibrium electron distribution



Nonequilibrium Green's Function

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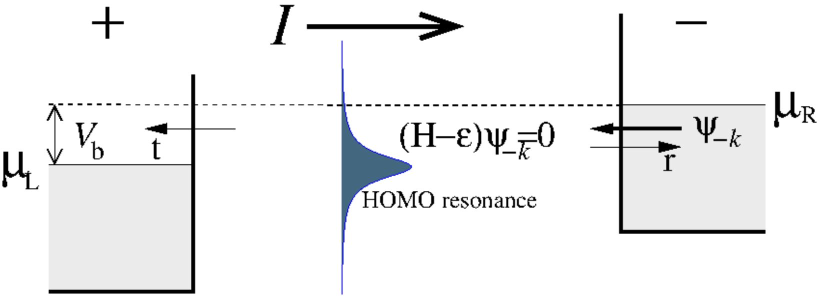

Retarded Green's function

$$G_C^r(\epsilon) = \frac{1}{(\epsilon + i\delta_+)\mathrm{S}_C - \mathrm{H}_C - \Sigma_L(\epsilon) - \Sigma_R(\epsilon)} \tag{21}$$

Nonequilibrium Green's Function

Green's Function of Schrödinger Equation

Broadening function

$$\Gamma_\alpha(\epsilon) = \frac{1}{i}[\Sigma_\alpha(\epsilon) - \Sigma_\alpha^\dagger(\epsilon)] \tag{22}$$

$$\alpha = L, R \tag{23}$$

Nonequilibrium Green's Function
Green's Function of Schrödinger Equation

Broadening function

$$\Gamma_\alpha(\epsilon) = \frac{1}{i}[\Sigma_\alpha(\epsilon) - \Sigma_\alpha^\dagger(\epsilon)] \tag{22}$$

$$\alpha = L, R \tag{23}$$

Transmission coefficient

$$T(\epsilon) = \mathrm{Tr}[G_C^r(\epsilon)\Gamma_L(\epsilon){G_C^r}^\dagger(\epsilon)\Gamma_R(\epsilon)] \tag{24}$$

Nonequilibrium Green's Function

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Transmission coefficient

$$T(\epsilon) = \mathrm{Tr}[G_C^r(\epsilon)\Gamma_L(\epsilon)G_C^{r\dagger}(\epsilon)\Gamma_R(\epsilon)] \tag{24}$$

Ballistic conductance

$$\mathrm{G}(\epsilon) = \frac{e^2}{h}T(\epsilon) \tag{25}$$

Nonequilibrium Green's Function

Green's Function of Schrödinger Equation

Ballistic current

$$\mathrm{I}(V_L, V_R, \mathrm{T}_L, \mathrm{T}_R) = \frac{e}{h}\sum_{\sigma}\int T_{\sigma}(\epsilon)\left[f\left(\frac{\epsilon - \epsilon_L^F + eV_R}{k_B \mathrm{T}_R}\right) - f\left(\frac{\epsilon - \epsilon_L^F + eV_L}{k_B \mathrm{T}_L}\right)\right] d\epsilon \quad (26)$$

Nonequilibrium Green's Function

Green's Function of Schrödinger Equation

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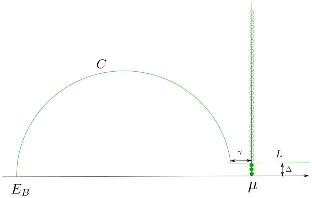
$$\mathrm{I}(V_L, V_R, \mathrm{T}_L, \mathrm{T}_R) = \frac{e}{h}\sum_{\sigma}\int T_{\sigma}(\epsilon)\left[f\left(\frac{\epsilon - \epsilon_L^F + eV_R}{k_B\mathrm{T}_R}\right) - f\left(\frac{\epsilon - \epsilon_L^F + eV_L}{k_B\mathrm{T}_L}\right)\right]d\epsilon \quad (26)$$

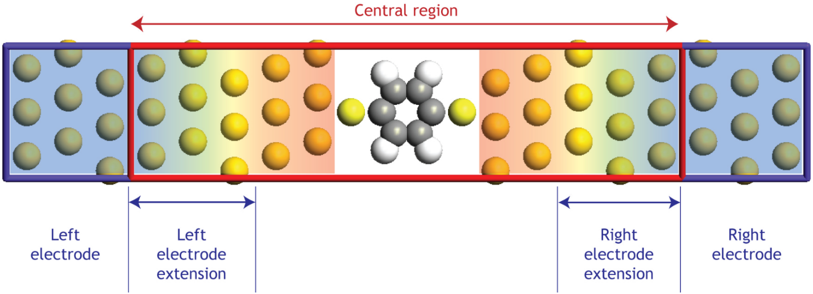
Complex contour integration



Nonequilibrium Green's Function
Transport Device

Device Model

A device system is an open system where charge can flow in and out of the central region from the left and right reservoirs.



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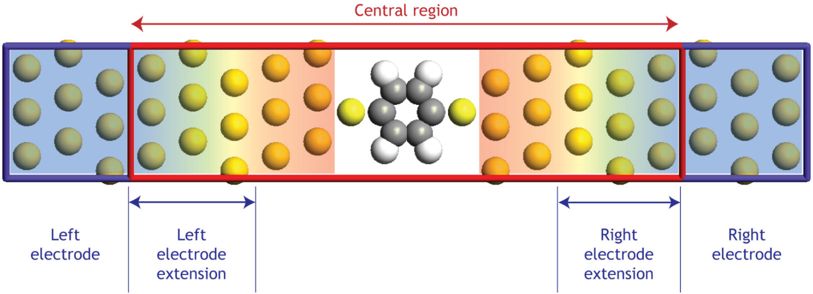

Three regions: left, central, right. The implementation relies on the screening approximation, which assumes that the properties of the left and right regions, the electrodes, can be described by solving a bulk problem for the fully periodic electrode cell.

Nonequilibrium Green's Function

NEGF of Electrons

PBC for electrodes, OBC for device

The left and right regions are equilibrium systems with periodic boundary conditions, and the properties of these systems are obtained using a conventional electronic structure calculation. The challenge in calculating the properties of a device system lies in the calculation of the non-equilibrium electron distribution in the central region.

Nonequilibrium Green's Function

NEGF of Electrons

PBC for electrodes, OBC for device

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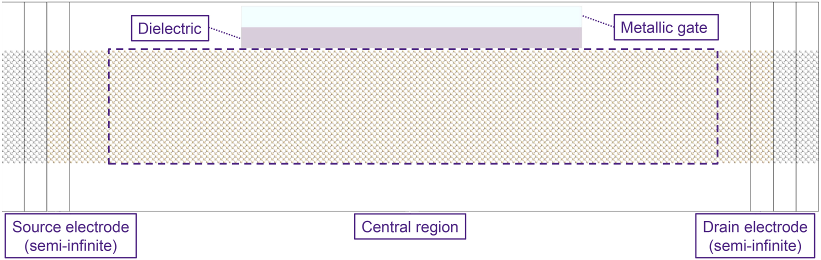
Electronic devices: transistor



Nonequilibrium Green's Function

NEGF of Phonons

Retarded green's function of phonons

$$G_C^r(\omega) = \frac{1}{(\omega + i\delta_+)^2 - D_C - \Sigma_L(\omega) - \Sigma_R(\omega)} \tag{27}$$

Nonequilibrium Green's Function

NEGF of Phonons

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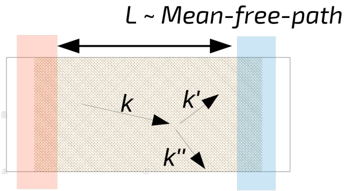
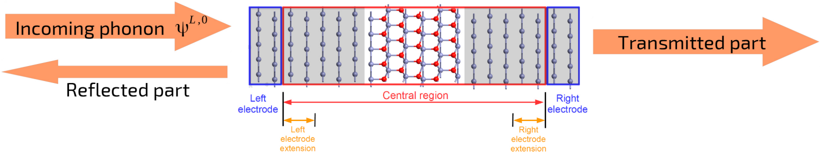
Phonon-phonon scattering





Nonequilibrium Green's Function

NEGF of Phonons

Transmission coefficient of phonons

$$T(\omega) = \mathrm{Tr}[G_C^r \Gamma_L G_C^{r\dagger} \Gamma_R] \quad (28)$$

Thermal current

$$\dot{\mathrm{Q}} = \int d\omega \frac{\hbar\omega}{2\pi} T(\omega)[n_L(\mathrm{T}_L) - n_R(\mathrm{T}_R)] \quad (29)$$

Nonequilibrium Green's Function

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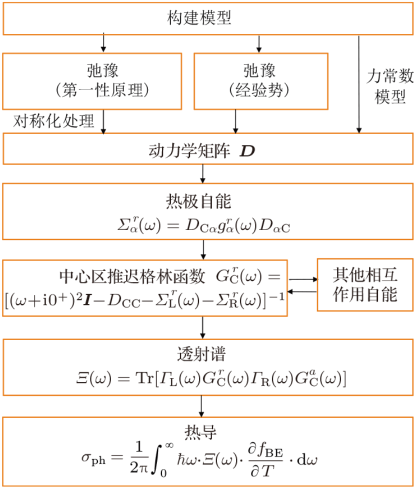
声子热导的 NEGF 计算流程



Thermoelectric Transport
Conductivity

- Electron conductivity

$$\sigma = \mathrm{G} \cdot \mathrm{L} \tag{30}$$

Thermoelectric Transport

Conductivity

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Thermoelectric Transport
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- Electron-phonon coupling (EPC)

$$\begin{aligned} P_{kk'}^{\lambda nn'} = \frac{2\pi}{\hbar} |g_{kk'}^{\lambda nn'}|^2 \times \Big[& n_q^\lambda \delta(\epsilon_{\mathrm{k'n'}} - \epsilon_{\mathrm{kn}} - \hbar\omega_{q\lambda}) \delta_{k',k+q} \\ & + (n_{-q}^\lambda + 1) \delta(\epsilon_{\mathrm{k'n'}} - \epsilon_{\mathrm{kn}} + \hbar\omega_{-q\lambda}) \delta_{k',k-q} \Big] \end{aligned} \tag{34}$$

Thermoelectric Transport
Thermal Conductivity

- Thermal conductivity: electron contribution, phonon contribution, ...

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Thermoelectric Transport

Thermal Conductivity

- Thermal conductivity: electron contribution, phonon contribution, ...

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- Electron contribution (Matthiessen's rule, Wiedemann-Franz law): EPC, impurity, ...

$$\kappa_{el} = [1/\kappa_{el}^{e-ph} + 1/\kappa_{el}^{imp}]^{-1} \tag{36}$$

$$\frac{1}{\kappa_{el}^{e-ph}} = \frac{1}{L_0 \mathrm{T}} \frac{2\pi Ad}{e^2 N_F v_F^2} \int_0^{\infty} d\omega \frac{x}{\sinh^2(x)} \times \left[\left(1 - \frac{2x^2}{\pi^2} \right) \alpha_{tr}^2 F(\omega) + \frac{6x^2}{\pi^2} \alpha^2 F(\omega) \right] \tag{37}$$

$$\kappa_{el}^{imp} = L_0 \mathrm{T} \sigma^{imp} \tag{38}$$

Thermoelectric Transport
Thermal Conductivity

- Electron contribution (continue)

$$\alpha^2_{tr}F(\omega) = \frac{1}{N_F}\sum_{m,m',\nu}\int\int\frac{dkdq}{A^2_{BZ}}|g^{\nu}_{m,m'}(k,q)|^2\left(1-\frac{v^{m'}_{k+q}\cdot v^{m}_{k}}{|v^{m}_{k}|^2}\right)\times \delta(\epsilon^{m'}_{k+q}-\epsilon_F)\delta(\epsilon^{m}_{k}-\epsilon_F)\delta(\hbar\omega^{\nu}_{q}-\hbar\omega) \quad (39)$$

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Thermal Conductivity

- Electron contribution (continue)

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- Phonon contribution

$$\kappa_{ph}(\mathrm{T}) = \int d\omega \frac{\hbar^2\omega^2}{2\pi k_B \mathrm{T}^2} T(\omega) \frac{e^{\hbar\omega/k_B\mathrm{T}}}{(e^{\hbar\omega/k_B\mathrm{T}} - 1)^2} \quad (41)$$

Thermoelectric Transport

Seebeck Coefficient

- Seebeck coefficient

$$S = -\frac{\Delta \mathrm{V}}{\Delta \mathrm{T}} \tag{42}$$

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- 热电效应是温度场驱动电荷移动做功和体积变化做功。

$$\mathrm{S}d\mathrm{T} = d(q\mathrm{V}) - \mathrm{P}d\mathrm{V} \tag{43}$$

$$\Rightarrow \quad d\mathrm{A} = -\mathrm{S}d\mathrm{T} - \mathrm{P}d\mathrm{V} + \mathrm{V}dq = -qd\mathrm{V} \tag{44}$$

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- A is Helmholtz free energy in thermodynamics or chmical potential in statistical mechanics.

$$S = \frac{1}{e}\frac{d\mathrm{A}}{d\mathrm{T}} \tag{45}$$

只要计算不同温度下的化学势就可以算出塞贝克系数。

Thermoelectric Transport
Figure of Merit (ZT)

Thermoelectric figure of merit (ZT)

$$ZT = \frac{\sigma S^2 \mathrm{T}}{\kappa} \tag{46}$$

Figure: 钚 238 的同位素温差发电机，能够在供热的同时，在黑暗中为探测器提供不低于 2.5 瓦的电能。

Question & Answer

Software and Suggestions

About software

There are or there have been probably hundreds even thousands of ab-initio packages!

They own different professional features and common basic functionalities, but none of them is perfect for everything and one need to study harder and harder for your own purpose!

No limit to the convergence-test for your parameter and model, because it is never enough!

Suggestions

Enjoy simulation, it's interesting!

Also, please contact me, if you have some exciting new ideas or just some simple interesting questions.

Zhang WenXing: Thank you for listening!

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室