Phonons, Electron-Phonon Coupling and Transport in Solids

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CRystalline SOLIDS

Idealized Crystal Structure

Infinite grid of immobile atoms with perfect periodicity

cf. Sergey Levchenko, Wednesday August 2

Real Materials

Everything moves!

cf. Mariana Rossi, & Yair Litman,
Friday August 4

Perfect periodicity disturbed!
FAILURES OF THE STATIC LATTICE MODEL


• **Inaccuracies** in the **equilibrium** properties at **0K**: 
  Lattice Constants, Cohesive Energies, Elastic Constants,…

• **Failure** to describe **thermodynamic equilibrium properties**: 
  Specific Heat, Thermal Lattice Expansion, Phase Transformations, …

• **Failure** to describe **thermodynamic non-equilibrium properties**:
  ✦ **Charge Transport:**
    Electrical AC/DC Conductivity, Superconductivity,…
  ✦ **Heat Transport:**
    Thermal Conductivity, Transmission of Sound,…
  ✦ **Coupling of Charge & Heat Transport:**
    Seebeck and Peltier Effect,…
  ✦ **Interaction with Radiation:**
    X-Ray, Infrared, Neutron, …
Semiconductor Technology

Miniaturization has lead to enormous transistor densities.


Miniaturization has lead to local hot spots at the nanoscale.

Understanding heat transport on the nanoscale and increasing its efficiency essential for next-generation CPUs.
Suppressing heat transport in **thermal barrier coatings** has driven the fuel-efficiency increase over the last 30 years.

TECHNOLOGICAL EDGE CASES

\( \text{ZrO}_2: \) Thermal conductivity

**minute** (~3 W/mK)

Suppress heat transport even further!
TECHNOLOGICAL EDGE CASES

**ZrO$_2$:** Thermal conductivity **minute** (~3 W/mK)

*Suppress* heat transport even further!

**Si:** Thermal conductivity **huge** (~250 W/mK)

*Boost* heat transport even further!
TECHNOLOGICAL EDGE CASES

ZrO$_2$: Thermal conductivity minute ($\sim$3 W/mK)

Suppress heat transport even further!

Si: Thermal conductivity huge ($\sim$250 W/mK)

Boost heat transport even further!

First Principles Theory

A quantitative theory of thermal transport is required to achieve a qualitative understanding of the underlying mechanisms!
I. THE HARMONIC CRYSTAL
The total energy $E$ is a **3N-dimensional surface**:

$$ E = V (R_1, R_2, \cdots, R_N) $$

Approximate by Taylor Expansion around the Static Equilibrium $R_i^0$

$$ E (\{R_0 + \Delta R\}) \approx E (\{R_0\}) + \cdots $$

Static Equilibrium Energy
THE HARMONIC APPROXIMATION

The total energy $E$ is a 3N-dimensional surface:

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$$E (\{R_0 + \Delta R\}) \approx E (\{R_0\}) + \sum_i \left. \frac{\partial E}{\partial R_i} \right|_{R_0} \Delta R_i + \cdots$$

Forces vanish at $R_0$
The total energy $E$ is a $3N$-dimensional surface:

$$E = V(R_1, R_2, \cdots, R_N)$$

Approximate by Taylor Expansion around the Static Equilibrium $R_i^0$

$$E(\{R_0 + \Delta R\}) \approx E(\{R_0\}) + \sum_i \frac{\partial E}{\partial R_i} \bigg|_{R_0} \Delta R_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 E}{\partial R_i \partial R_j} \bigg|_{R_0} \Delta R_i \Delta R_j$$

Hessian $\Phi_{ij}$
The total energy $E$ is a 3N-dimensional surface:

$$E = V \left( R_1, R_2, \cdots, R_N \right)$$

**Warning:**
Harmonic Approximation is only valid for small displacements from $R^0$!
THE HARMONIC APPROXIMATION

\[ E(\{R_0 + \Delta R\}) \approx E(\{R_0\}) + \sum_i \frac{\partial E}{\partial R_i} \Delta R_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 E}{\partial R_i \partial R_j} \Delta R_i \Delta R_j \]

Static Equilibrium Energy from DFT

Determine Hessian aka the Harmonic Force Constants \( \Phi_{ij} \):

Why is this theoretically challenging?
HELLMAN-FEYNMAN THEOREM

Born-Oppenheimer Approximation:

Ground State Electrons determine the Potential Energy

\[ U(R) = \langle \Psi_R(r) | H_R | \Psi_R(r) \rangle \]

Forces:

\[ F_i = - \frac{\partial U(R)}{\partial R_i} \]

\[ = - \langle \Psi_R(r) | \frac{\partial H_R}{\partial R_i} | \Psi_R(r) \rangle - 2 \langle \Psi_R(r) | H_R | \frac{\partial \Psi_R(r)}{\partial R_i} \rangle \]

Forces are an expectation value of the wave function and do not depend on changes in the wave function itself.
HIGHER ORDER DERIVATIVES

\( \Phi_{ij} = -\frac{\partial F_i}{\partial R_j} \)

Hessian:

\[
= \langle \Psi_R(r) | \frac{\partial^2 H_R}{\partial R_i \partial R_j} | \Psi_R(r) \rangle - 2 \langle \Psi_R(r) | \frac{\partial H_R}{\partial R_i} \frac{\partial}{\partial R_j} \Psi_R(r) / \partial R_j \rangle
\]

**Hessian** depends explicitly on the response of the wave function to a nuclear displacement.

\( \Rightarrow \) Adiabatic Electron-Phonon Coupling

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**2n+1 Theorem:**

\((2n+1)^{th}\) derivative of the energy requires the \(n^{th}\) derivative of the wave function / electron density.

THE HARMONIC APPROXIMATION

\[ E(\{\mathbf{R}_0 + \Delta \mathbf{R}\}) \approx E(\{\mathbf{R}_0\}) + \sum_i \left. \frac{\partial E}{\partial \mathbf{R}_i} \right|_{\mathbf{R}_0} \Delta \mathbf{R}_i + \frac{1}{2} \sum_{i,j} \left. \frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j} \right|_{\mathbf{R}_0} \Delta \mathbf{R}_i \Delta \mathbf{R}_j \]

Static Equilibrium Energy from DFT

Determine **Hessian** aka the **Harmonic Force Constants** \( \Phi_{ij} \):

- **from Density-Functional Perturbation Theory**

- **from Finite Differences**
Density Functional Theory:

density \( n(r) \)
Density Functional Theory: 

\[ n(r) \]

Density Functional Perturbation Theory: 

\[ d n(r) / dR_i \]
Density Functional Theory:

- Density $n(r)$

Density Functional Perturbation Theory:

- Density response $dn(r)/dR_I$

All phonon properties!
Density Functional Theory:

Density response is localized in real space.

Accelerating DFPT

Response computed in **reciprocal-space** on a finite **q-grid**.

**Truncated** Fourier-Transform to **real-space**.

**Localization** enables **real-space interpolation**
(e.g. **Wannier**: Vanderbilt, Marzari, Giustino, etc.)

**Truncated** Fourier-Transform back to **reciprocal-space**.

Accelerating DFPT

Response computed in *reciprocal-space* on a finite *q*-grid.

Can we find a more straightforward approach?

Localization enables real-space interpolation (e.g. Wannier).

Truncated Fourier-Transform back to *reciprocal-space*. 
Periodic Boundary Conditions in Real-Space

original design and implementation by Paula Havu, Ville Havu, Volker Blum

Atoms in **unit cell** interact with their periodic images.

**Orbitals → Bloch Orbitals**

\[ \varphi_i \rightarrow \sum_{M} \exp(i \mathbf{k} \cdot \mathbf{T}(M)) \varphi_{i,M}(\mathbf{r}). \]
Atoms in **unit cell** interact with their periodic images.

Orbitals $\rightarrow$ Bloch Orbitals

$$\varphi_i \rightarrow \sum_M \exp \left( i k \cdot T(M) \right) \varphi_{i,M}(r) .$$

All **periodic images** that have overlap with the orbitals of the primitive atoms needed:

$$h_{ij}(k) = \sum_M \exp \left( i k T(M) \right) \int_{-\infty}^{\infty} \varphi_{i,M}(r) h_{KS} \varphi_j(r) \, dr$$
Periodic Boundary Conditions in Real-Space

original design and implementation by Paula Havu, Ville Havu, Volker Blum

In practice:

<table>
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<tr>
<th>Material</th>
<th>Atoms in unit cell</th>
<th>Atoms in DFT supercluster</th>
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<tbody>
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<td>Polyethylene</td>
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\[ h_{ij}(k) = \sum_M \exp(ikT(M)) \int \varphi_{i,M}(r) h_{KS} \varphi_j(r) dr \]
Periodic Boundary Conditions in Real-Space

original design and implementation by Paula Havu, Ville Havu, Volker Blum

\[ h_{ij}(k) = \sum_{M} \exp(i k \cdot T(M)) \]

\[ \int_{-\infty}^{\infty} \phi_{i,M}(r) h_{KS} \phi_{j}(r) dr \]

Unbound integral numerically not desirable.
Restrict integration to unit cell:

→ **Double** sum over a **reduced** set of **periodic images**:

\[
\begin{align*}
    h_{ij}(k) & = \sum_{M,N} \exp\left(ik[T(M) - T(N)]\right) \int_{\text{unit cell}} \varphi_{i,M}(\mathbf{r}) h_{KS} \varphi_{j,N}(\mathbf{r})d\mathbf{r} \\
\end{align*}
\]

**Unbound integral** numerically not desirable.
Restricted integration to unit cell: 
→ Double sum over a reduced set of periodic images: 

\[ h_{ij}(k) = \sum_{M,N} \exp(i k [T(M) - T(N)]) \int_{\text{unit cell}} \varphi_{i,M}(r) h_{KS} \varphi_{j,N}(r) \, dr \]
Periodic Boundary Conditions in Real-Space
original design and implementation by Paula Havu, Ville Havu, Volker Blum

Example: Overlap Matrix

\[ h_{ij}(k) = \sum_{M,N} \exp(\mathbf{i} k [T(M) - T(N)]) \int_{\text{unit cell}} \varphi_{i,M}(\mathbf{r}) h_{KS} \varphi_{j,N}(\mathbf{r}) d\mathbf{r} \]
Periodic Boundary Conditions in Real-Space
original design and implementation by Paula Havu, Ville Havu, Volker Blum

Nota bene:
DFT supercluster is not a Born-von Kármán supercell.
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Translational symmetry restored in DFPT by using an extended Born-von Kármán DFPT supercell.

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Nota bene: DFT supercluster is not a Born-von Kármán supercell.

Translational symmetry restored in DFPT by using an extended Born-von Kármán DFPT supercell.

No interpolation required: All non-vanishing Hessian elements computed in real space. ➣

Fourier transform yields all properties in reciprocal space.
Validation:
Comparison DFPT and finite differences for vibrational properties
Periodic Boundary Conditions in FHI-aims

**Nota bene:**
DFT supercluster is not a Born-von Kármán supercell.

Translational symmetry restored in DFPT by using an extended Born-von Kármán DFPT supercell.

No interpolation required: All non-vanishing Hessian elements computed in real space.

These calculations yield all response properties, i.e., the full electron-phonon couplings in the complete Brillouin zone:

Gives access to all electronic response properties!
THE HARMONIC APPROXIMATION

\[ E(\{R_0 + \Delta R\}) \approx E(\{R_0\}) + \sum_i \left. \frac{\partial E}{\partial R_i} \right|_{R_0} \Delta R_i + \frac{1}{2} \sum_{i,j} \left. \frac{\partial^2 E}{\partial R_i \partial R_j} \right|_{R_0} \Delta R_i \Delta R_j \]

Static Equilibrium Energy from DFT

Determine Hessian aka the Harmonic Force Constants \( \Phi_{ij} \):

- from Density-Functional Perturbation Theory

- from Finite Differences

**phonopy-FHI-aims**

Finite differences using normalized displacements $d$:

$$
\Phi_{ij} = \left. \frac{\partial^2 E}{\partial R_i \partial R_j} \right|_{R_0} = - \left. \frac{\partial}{\partial R_i} F_j \right|_{R_0} \approx - \frac{F_j (R_i^0 + \varepsilon d_i)}{\varepsilon}
$$

**Example:** Diamond Si (2 atoms in the basis):

$$
\begin{pmatrix}
\Phi_{xx}^{11} & \Phi_{xy}^{11} & \Phi_{xz}^{11} & \Phi_{xx}^{12} & \Phi_{xy}^{12} & \Phi_{xz}^{12} \\
\Phi_{yx}^{11} & \Phi_{yy}^{11} & \Phi_{yz}^{11} & \Phi_{yx}^{12} & \Phi_{yy}^{12} & \Phi_{yz}^{12} \\
\Phi_{zx}^{11} & \Phi_{zy}^{11} & \Phi_{zz}^{11} & \Phi_{zx}^{12} & \Phi_{zy}^{12} & \Phi_{zz}^{12} \\
\Phi_{zx}^{21} & \Phi_{zy}^{21} & \Phi_{zz}^{21} & \Phi_{zx}^{22} & \Phi_{zy}^{22} & \Phi_{zz}^{22} \\
\Phi_{zx}^{21} & \Phi_{zy}^{21} & \Phi_{zz}^{21} & \Phi_{zx}^{22} & \Phi_{zy}^{22} & \Phi_{zz}^{22}
\end{pmatrix}
$$

Hessian has **36** entries:  
⇒ 6 displacements $d$ required
Finite differences using normalized displacements \( d \):

\[
\Phi_{ij} = \left. \frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j} \right|_{\mathbf{R}_0} = -\left. \frac{\partial}{\partial \mathbf{R}_i} \mathbf{F}_j \right|_{\mathbf{R}_0} \approx -\left. \frac{\mathbf{F}_j (\mathbf{R}_i^0 + \varepsilon \mathbf{d}_i)}{\varepsilon} \right|_{\mathbf{R}_0}
\]

**Example:** Diamond Si (2 atoms in the basis):

**Space Group Analysis**

Hessian has **5 unique, non-zero** entries:

\[\Rightarrow\text{ Only 1 displacement } \mathbf{d} \text{ required}\]
THE HARMONIC APPROXIMATION

...in Molecules:

N ... Number of atoms
↓
Degrees of Freedom: 3N
Dimension of Hessian: 9N²

...in Crystalline Solids:

N ... Number of atoms
↓
Degrees of Freedom: 3N
Dimension of Hessian: 9N²

BUT:

N → ∞
PERIODIC BOUNDARY CONDITIONS

cf. Sergey Levchenko, “Periodic Structures”, Wednesday August 2
PERIODIC BOUNDARY CONDITIONS

cf. Sergey Levchenko, “Periodic Structures”, Wednesday August 2

Periodic Images

Unit Cell with \( N_p \) atoms

Periodic Images

Lattice vector: \( \mathbf{E}_0 \)

Real Space:

Hessian \( \Phi_{ij} \)

with \( i,j \to \infty \)

Fourier Transform

\[
D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i(\mathbf{q} \cdot (\mathbf{R}_j^0 - \mathbf{R}_{j'}^0))}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}
\]

Reciprocal Space:

Dynamical Matrix \( D_{i'j'}(\mathbf{q}) \)

with \( i',j' \leq N_p \)
**Vibrations in a Crystal 101**


---

**Real Space:**

Hessian $\Phi_{ij}$ with $i, j \to \infty$

---

**Fourier Transform**

$$D_{i'j'}(q) = \sum_j \frac{e^{i(q \cdot (R_j^0 - R_{j'}^0))}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}$$

---

**Reciprocal Space:**

Dynamical Matrix $D_{ij'}(q)$ with $i', j' \leq N_p$

---

**Fourier Transform** can be truncated since $\Phi_{ij} = 0$ for large $|R_j^0 - R_{j'}^0|$

---

Hessian $\Phi_{ij}$ with **finite** number of non-zero entries

---

Dynamical Matrix $D_{ij'}(q)$ known for the whole reciprocal space
VIBRATIONS IN A CRYSTAL 101

e.g. N.W Ashcroft and N. D. Mermin, “Solid State Physics” (1976)
also see Sergey Levchenko, Wednesday August 2

Dynamical matrix:

\[ D_{i'j'}(q) = \sum_j e^{i(q \cdot (R_j^0 - R_{j'}^0))} \frac{\Phi_{i'j}}{\sqrt{M_{i'}M_{j'}}} \]

Equation of Motion becomes an Eigenvalue Problem:

\[ D(q) [\nu(q)] = \omega^2(q) [\nu(q)] \]

Analytical Solution in Real Space:

Superposition of Harmonic Oscillations

\[ R_j(t) = R_j^0 + \Re \left( \sum_s \frac{A_s}{\sqrt{M_i}} e^{i(q \cdot (R_j^0 - R_{j'}^0) - \omega_s(q)t)} \cdot [\nu_s(q)]_{j'} \right) \]
VIBRATIONS IN A CRYSTAL 101

e.g. N. W. Ashcroft and N. D. Mermin, "Solid State Physics" (1976)
also see Sergey Levchenko, Wednesday August 2

Eigenvalue problem:
$$D(q) \left[ \nu(q) \right] = \omega^2(q) \left[ \nu(q) \right]$$

Dynamical matrix:
$$D_{i'j'}(\Gamma) = \sum_j \frac{e^{i(q \cdot (R_{j'} - R_j))}}{\sqrt{M_{i'}M_{j'}}} \Phi_{i'j}$$
VIBRATIONS IN A CRYSTAL 101

e.g. N.W. Ashcroft and N. D. Mermin, "Solid State Physics" (1976)
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Dynamical matrix:

\[ D_{i'j'}(\mathbf{\Gamma}) = \sum_j \frac{e^{i(q \cdot (\mathbf{R}_{j'} - \mathbf{R}_j))}}{\sqrt{M_{i'}M_{j'}}} \Phi_{i'j} \]

Eigenvalue problem:

\[ D(\mathbf{\Gamma}) [\nu(\mathbf{\Gamma})] = \omega^2(\mathbf{\Gamma}) [\nu(\mathbf{\Gamma})] \]
Eigenvalue problem:
\[ D(q)\left[\nu(q)\right] = \omega^2(q)\left[\nu(q)\right] \]

Dynamical matrix:
\[ D_{i'j'}(X) = \sum_j \frac{e^{i(q \cdot (R_j - R_{j'}))}}{\sqrt{M_{i'}M_j'}} \Phi_{i'j} \]

VIBRATIONS IN A CRYSTAL 101

e.g. N.W. Ashcroft and N. D. Mermin, “Solid State Physics” (1976)
also see Sergey Levchenko, Wednesday August 2
For \( N_p \) atoms in the unit cell there are:

**3 Acoustic modes:**
- Atoms in unit cell in-phase
- Acoustic modes vanish at \( \Gamma \)
- Strong (typically linear) dispersion close to \( \Gamma \)

**\((3N_p - 3)\) Optical modes:**
- Atoms in unit cell out-of-phase
- \( \omega > 0 \) at \( \Gamma \) (and everywhere else)
- Weak dispersion
VIBRATIONAL BAND STRUCTURE

Silicon, diamond structure
VIBRATIONAL DENSITY OF STATES

\[ g(\omega) = \sum_s \int \frac{dq}{(2\pi)^3} \delta(\omega - \omega(q)) = \sum_s \int \frac{dS}{(2\pi)^3} \frac{1}{|\nabla \omega(q)|} \]

\[ g(\omega) \text{ (a.u.)} \]

\[ \omega \text{ (cm}^{-1}) \]
THE HARMONIC FREE ENERGY

\[ F^{\text{ha}}(T) = E(\{R_0\}) + \int d\omega \ g(\omega) \frac{\hbar \omega}{2} + \int d\omega \ g(\omega) \ k_B T \ln \left( 1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \]

- Static Equilibrium Energy
- Zero-point vibration
- Thermally induced vibrations
FREE ENERGY AND HEAT CAPACITY

\[ C_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F(T)}{\partial T^2} \right)_V \]
II. APPLICATION AND LIMITS OF THE HARMONIC APPROXIMATION
PHASE DIAGRAM OF ZrO$_2$

- **Monoclinic**
  - Baddeleyite Structure
  - $T < 1200^\circ C$

- **Tetragonal**

- **Cubic**
PHASE DIAGRAM OF ZrO$_2$

1200°C < $T$ < 2400°C

„Tetragonal“
P4$_2$/nmc Structure
\[ \Delta F(T) = -F_{m}^{ha}(T) + F_{t}^{ha}(T) \]
\[ \Delta F(T) = -F_{m}^{ha}(T) + F_{t}^{ha}(T) \]

T = 1544 K
The Harmonic Approximation

**Warning:**
Harmonic Approximation is only valid for small displacements from \( R_0 \)!

At elevated temperatures the harmonic approximation becomes increasingly **inaccurate** – and often **terribly misleading**!
PHASE DIAGRAM OF ZrO$_2$

Monoclinic  Tetragonal  Cubic

0 K  500 K  1000 K  1500 K  2000 K  2500 K  3000 K

T > 2400°C

„Cubic“
Fluorite Structure
Cubic Zirconia exhibits a soft mode (imaginary mode):

$$D(X) [\nu(X)] = \omega^2(X) [\nu(X)] \Rightarrow \omega_1^2(X) < 0$$
The Tetragonal-Cubic Phase Transition

- $dz < 0$
- $dz = 0$
- $dz > 0$

Tetragonal

\( dy > 0 \)
\( dz, dx = 0 \)

\( dz < 0 \)
\( dx, dy = 0 \)

\( dy < 0 \)
\( dz, dx = 0 \)

Tetragonal
Distance from cubic geometry  \( dr = \sqrt{dx^2 + dy^2 + dz^2} \) always conserved!

Cubic Structure is **never** realised at a **microscopic** level!
ZrO$_2$ exhibits **not one, but six degenerate** equilibrium configurations.

Switches between these configurations occur quite **frequently**.

**Severe violation of the harmonic approximation.**
II. THE QUASI-HARMONIC APPROXIMATION
THE HARMONIC APPROXIMATION

\[
\mathcal{H} = \sum_i T_i + \frac{1}{2} \sum_{i,j} \Phi_{i,j} \Delta R_i \Delta R_j \quad \Rightarrow \quad \frac{\partial \mathcal{H}}{\partial V} = 0
\]

*Lattice expansion* vanishes in the *harmonic* approximation.

THE QUASI-HARMONIC APPROACH

\[
\mathcal{H} = \sum_i T_i + \frac{1}{2} \sum_{i,j} \Phi_{i,j}(V) \Delta R_i \Delta R_j \quad \Rightarrow \quad \frac{\partial \mathcal{H}}{\partial V} \neq 0
\]

Assess *lattice expansion* by explicitly accounting for the *volume dependence* of the *Hessian*.
Lattice constant $a_0$ can be determined from a Birch-Murnaghan fit of $E(a_0)$

cf. William Huhn, Practical Session 2
Lattice constant $a_0$ can be determined from Birch-Murnaghan fit of $E(a_0)$

Add vibrational free energy for each individual value of $a_0$
THE QUASI-HARMONIC APPROACH

Lattice constant $a_0$ can be determined from Birch-Murnaghan fit of $E(a_0)$

Add vibrational free energy for each individual value of $a_0$

Repeat for each temperature $0K < T_1 < T_2$

Birch-Murnaghan fits for each individual temperature allow to determine temperature dependence of lattice constant $a_0(T)$. 

Birch-Murnaghan fits
EXERCISE 3 – LATTICE EXPANSION

\[ \alpha(T) = \frac{1}{a} \left( \frac{\partial a}{\partial T} \right)_p \]
\[ \alpha(T) = \frac{1}{a} \left( \frac{\partial a}{\partial T} \right)_p \]

EXERCISE 3 – LATTICE EXPANSION

\[ \alpha < 0 ? \]
We have introduced the harmonic approximation under periodic boundary conditions.

The harmonic approximation can be very useful to approximatively assess dynamic and thermodynamic effects at low temperatures.

The harmonic approximation becomes increasingly inaccurate at elevated temperatures and must be handled with care under such thermodynamic conditions.
III. HEAT TRANSPORT
HEAT TRANSPORT

Macroscopic Effect:

Fourier's Law:

\[ \mathbf{J} = -\kappa \nabla T = -\alpha \rho c_V \nabla T \]
HEAT TRANSPORT

Macroscopic Effect:

Fourier's Law:

\[ J = -\kappa \nabla T = -\alpha \rho c_v \nabla T \]

\[ \kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}} \]
HEAT TRANSPORT

Macroscopic Effect:

Fourier's Law:

\[ J = -\kappa \nabla T = -\alpha \rho c_V \nabla T \]

Microscopic Mechanisms:

\[ \kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}} \]
Heat Transport Theory 101

Real Space Representation

Harmonic Approximation:
Second order Taylor expansion of the potential energy surface around equilibrium

Decoupled Normal Modes

Reciprocal Space Representation

Phonon ($\omega, q$)

Infinite Phonon Lifetime
**Heat Transport Theory 101**

**Real Space Representation**

- Decoupled Normal Modes

**Reciprocal Space Representation**

- Phonon ($\omega, q$)
- Infinite Phonon Lifetime

**Infinite thermal conductivity!**
Heat Transport Theory 101

Real Space Representation

- Anharmonic dynamics

Reciprocal Space Representation

- Phonon \((\omega,q)\)

**Key Concepts**

- Anharmonicity
- Electron-Phonon Coupling
- Phonon Scattering
Heat Transport Theory 101

Real Space Representation

Reciprocal Space Representation

Anharmonic dynamics

Phonon $(\omega, q)$

Anharmonicity

Electron-Phonon Coupling

Phonon Scattering

Theory Toolbox

Molecular Dynamics

Electronic Structure Theory

Perturbation Theory
Heat Transport Mechanisms
TIME AND LENGTH SCALES

Heat Transport Mechanisms

Semi-empirical potentials

+ vast experience
+ established methodologies
– accuracy is a question
TIME AND LENGTH SCALES

Heat Transport Mechanisms

Semi-empirical potentials:
+ vast experience
+ established methodologies
– accuracy is a question

First-principles approaches:
+ more accurate interactions
– limited time and length scales
BOLTZMANN TRANSPORT EQUATION


Boltzmann-Peierls-Transport-Equation describes the evolution of the phonon phase space distribution \( f(\omega, q, t) \).
Boltzmann-Peierls-Transport-Equation describes the evolution of the phonon phase space distribution $f(\omega, q, t)$.

Single-mode relaxation time approximation

$$\kappa \sim \sum_s \nu_s^2 \omega_s^2 n_s (n_s + 1) \tau_s$$

- **Group velocity**
- **Frequency**
- **Equilibrium population**
- **phonon lifetime**

**Harmonic phonon theory**

Phonon Lifetimes from First Principles

• from Density Functional Perturbation Theory

• from fitting the forces in ab initio MD

• from fitting the phonon line width determined via ab initio MD

All these approaches give very accurate results for good thermal conductors at low temperatures.

Results are questionable at high levels of anharmonicity!
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Boltzmann-Transport-Eq. gives very accurate results for perfect crystals at low temperatures.
Thermal conductivity can be calculated by applying Fourier’s Law.

\[ J = -\kappa \nabla T \]
FINITE SIZE EFFECTS

Finite Size Corrections

\[ \frac{1}{\kappa} \sim \left( \frac{1}{l_\infty} + \frac{4}{L_z} \right) \]

mean free path

supercell length

Finite Size Effects

Non-equilibrium MD exhibits strong finite-size artifacts in supercells typically accessible within DFT/AIMD.

Non-equilibrium MD can suffer from non-linear artifacts in supercells typically accessible within DFT/AIMD.
Non-Equilibrium MD approaches are in principle exact, in DFT however prohibitively costly to converge accurately.
The fluctuations of the forces in thermodynamic equilibrium is related to the generalized resistance in non-equilibrium for linear dissipative systems.


Brownian Motion:

The erratic motion of the particles is closely related to frictional force under perturbation.

Random walk in 2D
GREEN-KUBO METHOD

Fluctuation-Dissipation Theorem

Simulations of the thermodynamic equilibrium

Information about non-equilibrium processes

\[ \kappa \sim \int_{0}^{\infty} d\tau \left\langle J(0) J(\tau) \right\rangle_{eq} \]

The thermal conductivity is related to the autocorrelation function of the heat flux

Graph showing heat flux autocorrelation as a function of time (ps).
$$T(r, t) = \frac{1}{(4\pi \kappa t)^{3/2}} \exp\left(-\frac{r^2}{4\kappa t}\right) \rightarrow \int \langle J(t), J(t + \tau) \rangle \, d\tau \sim \kappa$$
Heat Flux Autocorr. $<J(t) J(t+\tau)>$ (a.u.)

Heat Flux (eVÅ/ps)

Temperature (K)
THE ATOMICHE METHE FLUX


Continuity Equation:

\[
\frac{\partial E(r)}{\partial t} + \nabla \cdot j(r) = 0 \quad \text{J}(t) = \int j(r) \, dr
\]

Energy decomposition

\[
E(r) = \sum_I E_I \delta(r - R_I) \quad \Rightarrow \quad J(t) = \frac{d}{dt} \left( \sum_I R_I E_I \right)
\]

Correct heat flux definition requires a decomposition of the energy, which is not unique by definition.
**THE ATOMISTIC HEAT FLUX**


---

*Same problem in first-principles formulation:*

\[
E(r) = \int \varepsilon(r') \delta(r - r') \, dr' \quad \Rightarrow \quad J(t) = \frac{d}{dt} \left( \int r \, \varepsilon(r) \, dr \right)
\]

First-principles **energy densities** are **not** gauge-independent.


THE VIRIAL HEAT FLUX


\[ J(t) = \frac{d}{dt} \left( \sum_I R_I E_I \right) = \sum_I V_I E_I + \sum_I R_I \dot{E}_I \]

**Helfands’ Heat Flux**

**Hardys’ Heat Flux**

**Convective Heat Flux**

**Liquids & Gases:**

⇒ use energy density


**Virial Heat Flux:**

- **Unique:** Does not depend on partitioning
- **Describes** phonon transports
- **Well-defined** for classical potentials
- **Well-defined** in first-principles frameworks
WHAT ABOUT FIRST-PRINCIPLES?

\[ J(t) = \sum_I R_I \dot{E}_I \]

This is the \textit{virial} of atom \( I \), i.e., its contribution to the \textit{internal stress} \( \sigma_I \) of the system.

\[ J(t) = \frac{1}{V} \sum_I Z_I \left( \sum_J Z_J \frac{(R_I - R_J)(R_I - R_J)}{|R_I - R_J|^3} - \int n(r) \frac{(r - R_I)(r - R_I)}{|r - R_I|^3} \, dr \right) \dot{R}_I \]

\( \Rightarrow \text{Unique and well-defined!} \)
Formulas for analytical stress

\[ \sigma_{ij} = \sigma_{ij}^{\text{HF}} + \sigma_{ij}^{\text{MP}} + \sigma_{ij}^{\text{Pulay}} + \sigma_{ij}^{\text{kin}} + \sigma_{ij}^{\text{Jac}}. \]

\[ \sigma_{ij}^{\text{HF}} = \frac{1}{2V} \sum_{\alpha, \beta \neq \alpha} \left[ \frac{\partial v^{\text{es,tot}}_\beta}{\partial R_i^\alpha} (R_\alpha - R_\beta)_j \right] \]

\[ \sigma_{ij}^{\text{MP}} = \frac{1}{V} \sum_{\alpha} \int dr \left[ n(r) - \frac{1}{2} n_{\text{MP}}(r) \right] \frac{\partial v^{\text{es,tot}}_\alpha}{\partial r_i} (r - R_\alpha)_j \]

\[ - \frac{1}{2V} \sum_{\alpha} \int dr \frac{\partial n_{\alpha}^{\text{MP}}}{\partial r_i} (r - R_\alpha)_j v_{\text{es,tot}}(r) \]

\[ \sigma_{ij}^{\text{Pulay}} = \frac{2}{V} \sum_k \sum_{\alpha, l(\alpha)} \sum_{\beta, m(\beta)} f_k c_{kl} c_{km} \int_{\text{UC}} dr \frac{\partial \varphi_l(r - R_\alpha)}{\partial r_i} (r - R_\alpha)_j \left[ \hat{h}_{\text{KS}} - \varepsilon_k \right] \varphi_m(r - R_\beta) \]

\[ \sigma_{ij}^{\text{kin}} = \frac{1}{V} \sum_k \sum_{\alpha, l(\alpha)} \sum_{\beta, m(\beta)} f_k c_{kl} c_{km} \int_{\text{UC}} dr \varphi_l(r - R_\alpha)(r - R_\alpha)_j \left[ \frac{\partial}{\partial r_i} \frac{\partial}{\partial r_j} \varphi_m(r - R_\beta) \right] \]

\[ \sigma_{ij}^{\text{Jac}} = \frac{1}{V} \delta_{ij} \left[ E_{\text{xc}}[n] - \int dr n(r) v_{\text{xc}}(r) - \frac{1}{2} \int dr n_{\text{MP}}(r) v_{\text{es,tot}}(r) \right] \]
APPLICATION TO ZIRCONIA

Experiment:

Semi-empirical MD:

2x2x2 Supercell, > 200ps AIMD / data point

Temperature (K)

\( \kappa \) (W/mK)

Semi-empirical potential

ZrO\(_2\) - PBEsol

Experiment
APPLICATION TO ZIRCONIA

2x2x2 Supercell, > 200ps AIMD / data point

WHY?

Experiment:

Semi-empirical MD:
Distance $dr$ finite at all temperatures!

Switches are an intrinsic feature of the dynamics.
pristine $\text{ZrO}_2$

$E_{\text{barrier}}$

140 / 70 meV
Vacancies **reduce** the barrier, but **retain** the topology!

**pristine ZrO$_2$**

- **$E_{\text{barrier}}$**
  - *without latt. relax.*: 140 / 70 meV
  - *with latt. relax.*: 80 / 40 meV

**6.25 mol-% ZrO$_{1.5}$ doped ZrO$_2$**

- **$E_{\text{barrier}}$**
  - *without latt. relax.*: 140 / 70 meV
  - *with latt. relax.*: 80 / 40 meV
Y cations affect the topology, but not the barriers!
pristine ZrO$_2$

6.25 mol-% ZrO$_{1.5}$ doped ZrO$_2$

E$_{\text{barrier}}$

140 / 70 meV

80 / 40 meV

80 / 30 meV

160 / 100 meV

6.25 mol-% YO$_{1.5}$ doped ZrO$_2$

6.25 mol-% YO$_{1.5}$ + 3.125 mol-% TiO$_2$
doped ZrO$_2$

Ti cations even \textbf{increase} the barriers!
6.25 mol-% YO\textsubscript{1.5} + 3.125 mol-% TiO\textsubscript{2} doped ZrO\textsubscript{2}

E\textsubscript{barrier} = 160 / 100 meV

thermal cond. (% wrt pure ZrO\textsubscript{2})

Barrier for Switches (meV)

YO\textsubscript{1.5} (mol-%)

experiment: 313K

tetragonal ZrO\textsubscript{2}

fully stabilized cubic ZrO\textsubscript{2}

pristine ZrO\textsubscript{2}

6.25 mol-% ZrO\textsubscript{1.5} doped ZrO\textsubscript{2}

140 / 70 meV

without latt. relax.

with latt. relax.
Occurrence, character and degree of anharmonicity can be tailored by doping!
## FIRST-PRINCIPLES APPROACHES

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*Ab initio* Green-Kubo approach allows the **accurate** and **predictive** computation of **lattice thermal conductivities $\kappa$** at **arbitrarily high temperatures**!