

Thermal transport from first principles: the Boltzmann transport equation

Andrea Cepellotti
Ph.D. student
École Polytechnique Fédérale de Lausanne,
Theory and Simulation of Materials

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Outline

- Thermal transport and Boltzmann Equation
- Phonons from first-principles
- Solutions of the Boltzmann transport equation (BTE):
Relaxation time approximation + variational method
- Applications: layered and 2D materials
- Breakdowns of the Fourier law

Equilibrium

Material (...where mostly phonons carry heat)



Bose-Einstein phonon distribution:
$$\bar{n}_\nu = \frac{1}{e^{\hbar\omega_\nu/k_B T} - 1}$$

$\nu=(q,s)$: compact index on phonon wave vectors and branches

Out-of-equilibrium

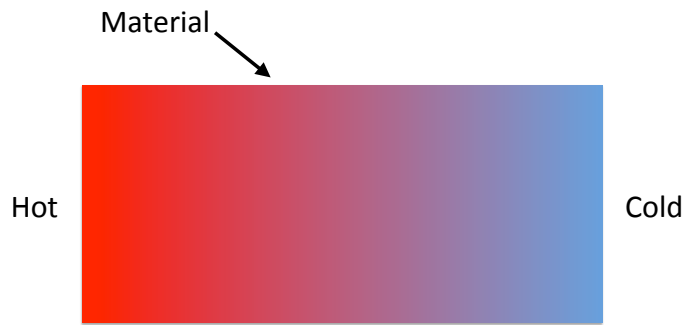
Material



Fourier's law:
$$\mathbf{Q} = -k\nabla T \quad (\text{Macroscopic})$$

Out-of-equilibrium phonon distribution $\bar{n}_\nu \rightarrow n_\nu$

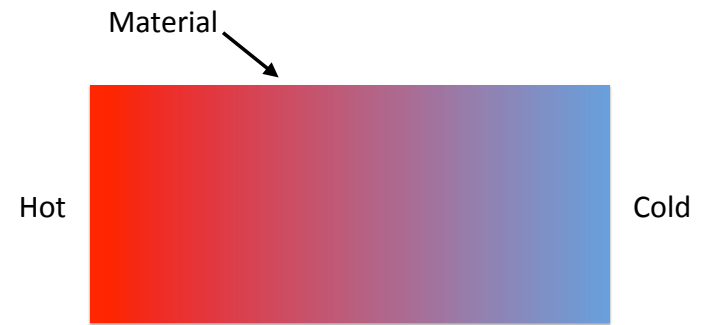
Out-of-equilibrium



Fourier's law: $\mathbf{Q} = \frac{1}{V} \sum_{\nu} n_{\nu} v_{\nu} \hbar \omega_{\nu} = -k \nabla T$ (Microscopic)

Out-of-equilibrium phonon distribution $\bar{n}_{\nu} \rightarrow n_{\nu}$

Out-of-equilibrium

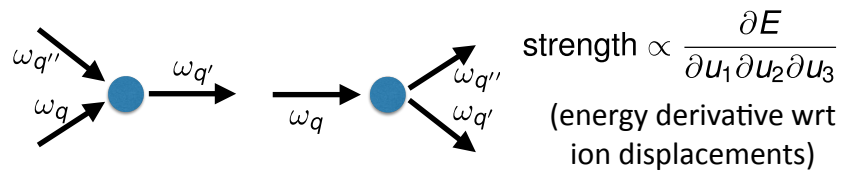


Fourier's law: $\mathbf{Q} = \frac{1}{V} \sum_{\nu} n_{\nu} v_{\nu} \hbar \omega_{\nu} = -k \nabla T$

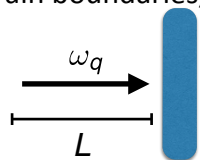
Boltzmann Transport Equation (BTE): $v_{\nu} \nabla T \frac{\partial \bar{n}_{\nu}}{\partial T} = \sum_{\nu'} \Omega_{\nu, \nu'} n_{\nu'}$

Key phonon scattering mechanisms

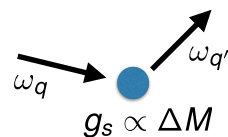
- 3-phonon interaction (decay and coalescence)



- extrinsic scattering (grain boundaries, surfaces, ...)



- mass disorder (isotopes)



3-phonon scattering

Most of the thermal conductivity is determined by the 3-phonon scatterings.

There are two kinds of processes: up or down events. The probabilities are computed with the Fermi Golden rule

For the down process:

Dynamical matrix derivative

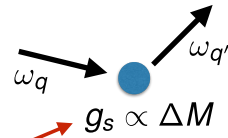
$$P_{q,q'}^{dw} = \frac{2\pi}{N_0 \hbar^2} \sum_{\mathbf{G}, q''} |V^{(3)}(\mathbf{q}, \mathbf{q}'', -\mathbf{q}')|^2 \bar{n}_q \bar{n}_{q''} (\bar{n}_{q'} + 1)$$

Conservation of crystal momentum $\delta_{\mathbf{q}+\mathbf{q}''-\mathbf{q}, \mathbf{G}}$

Conservation of energy $\delta(\hbar\omega_q + \hbar\omega_{q''} - \hbar\omega_{q'})$

Scattering matrix

- Isotope scattering (mass disorder):



$$P_{q,q'}^{mass} = \frac{\pi}{2N_0} \omega_q \omega_{q'} \left[\bar{n}_q \bar{n}_{q'} + \frac{\bar{n}_q + \bar{n}_{q'}}{2} \right] \sum_{s=1}^{\text{modes}} g_s \sum_{\alpha=1}^3 z_q^{s\alpha*} z_{q'}^{s\alpha} \delta(\omega_q - \omega_{q'})$$

- Extrinsic scatterings (e.g. finite size):

$$P_{q,q'}^{size} = \frac{V_q}{L} \bar{n}_q (\bar{n}_q + 1) \delta_{q,q}$$

Computing thermal conductivity

What do we need?

Harmonic properties energies: $\hbar\omega_v$ group velocities: $\partial\hbar\omega_v / \partial q$	Harmonic force constants $\frac{\partial^2 E}{\partial u_1 \partial u_2}$
Anharmonic properties Scattering rates	Anharmonic force constants $\frac{\partial^3 E}{\partial u_1 \partial u_2 \partial u_3}$
Perturbed phonon populations	Solve BTE $v_\nu \nabla T \frac{\partial \bar{n}_\nu}{\partial T} = \sum_{\nu'} \Omega_{\nu,\nu'} \bar{n}_\nu$

First issue

Harmonic properties energies: $\hbar\omega_v$ group velocities: $\partial\hbar\omega_v / \partial q$	Harmonic force constants $\frac{\partial^2 E}{\partial u_1 \partial u_2}$
Anharmonic properties Scattering rates	Anharmonic force constants $\frac{\partial^3 E}{\partial u_1 \partial u_2 \partial u_3}$

How to get them from first principles?

- 1) Frozen phonons
- 2) Density functional perturbation theory (DFPT)

Phonon properties

Lattice Hamiltonian: $H = \sum_{lb} \frac{p_{lb}^2}{2m_b} + V$

Taylor Expansion of the potential energy of a crystal:

$$V \approx V_0 + \sum_{\alpha lb} \frac{\partial V}{\partial u_{\alpha lb}} \Big|_0 + \frac{1}{2} \sum_{\alpha lb \alpha' l' b'} \frac{\partial^2 V}{\partial u_{\alpha lb} \partial u_{\alpha' l' b'}} \Big|_0 u_{\alpha lb} u_{\alpha' l' b'} + \frac{1}{3!} \sum_{\alpha lb \alpha' l' b' \alpha'' l'' b''} \frac{\partial^3 V}{\partial u_{\alpha lb} \partial u_{\alpha' l' b'} \partial u_{\alpha'' l'' b''}} \Big|_0 u_{\alpha lb} u_{\alpha' l' b'} u_{\alpha'' l'' b''}$$

$$= \cancel{V_0} + \cancel{V_1} + V_2 + V_3 + \dots$$

(lowest order) phonon-phonon interactions
 Dynamical matrix:
 phonon energies / velocities

Frozen phonons

- Build a supercell
- Displace the atom (lb) by Δ , compute forces $F_{lb}^\alpha = -\frac{\partial V}{\partial u_{\alpha,lb}}$
- Compute the dynamical matrix: $\phi_{\alpha\alpha'}^{lb'l'b'} = \frac{\partial^2 V}{\partial u_{\alpha,lb} \partial u_{\alpha',l'b'}} \approx -\frac{F_{lb}^\alpha(r_{l'b'}^\alpha + \Delta)}{\Delta}$
- Displace two atoms by Δ , compute forces.
- Compute the anharmonic constants

$$\phi_{\alpha\alpha'\alpha''}^{lb'l'b''} = \frac{\partial^3 V}{\partial u_{\alpha,lb} \partial u_{\alpha',l'b'} \partial u_{\alpha'',l''b''}} \approx \frac{1}{4\Delta} \left[-F_{l''b''}^{\alpha''}(r_{lb}^\alpha + \Delta, r_{l'b'}^{\alpha'} + \Delta) + F_{l''b''}^{\alpha''}(r_{lb}^\alpha + \Delta, r_{l'b'}^{\alpha'} - \Delta) \right.$$

Disadvantages:

- calculations on large (expensive) supercells
- need to check if the displacement is small enough

Density Functional Perturbation Theory

Perturb the potential (move an atom): $V(r) = V_0(r) + \lambda\Delta V(r)$

Find the 1st order wavefunction response to the perturbation

2n+1 theorem: the knowledge of the wavefunction response of a system up to the n -th order in the strength of an external perturbation is sufficient to determine the energy derivative up to order $2n+1$
Gonze and Vigneron, Phys. Rev. B **39**, 13120 (1989)

Compute the second and third derivative of the energy.

For example, the third derivative is:

$$\frac{\partial^3 E^\lambda}{\partial \lambda^3} = 6 \sum_v \langle \psi'_v | \Delta V - \epsilon'_v | \psi'_v \rangle + \int \frac{\delta E_{xc}[n]}{\delta n(r) \delta n(r') \delta n(r'')} \Big|_{n=n_0} n'(r) n'(r') n'(r'') dr dr' dr''$$

It's particularly convenient for DFT codes using a plane-wave basis: the calculation can be performed directly in the reciprocal space!

To reciprocal space

Fourier transform the force constants computed on a grid, to get them at any point of the Brillouin zone:

$$\phi_{\alpha\alpha'}(bb', q) = \sum_l \phi_{\alpha\alpha'}^{0blb'} e^{-iq'l}$$

$$\psi_{\alpha\alpha'\alpha''}(qb, q'b', q''b'') = \sum_{l'l''} \psi_{\alpha\alpha'\alpha''}^{0bl'b',l''b''} e^{-iq'l} e^{-iq''l''}$$

From the first transform of 2nd order force constants we get phonon energies

From the second transform of 3rd order force constants, the scattering probabilities

Note: the FT is the bottleneck of the BTE!

Frozen phonons	DFPT
Easy to implement	Complex to implement
Some parameters to tune	Easy to use
Calculations in a supercell	Calculations in primitive cell
Wavevectors limited by the supercell	Computation at any wave-vector (for plane-wave codes)

Hard to tell what's the best/fastest method for you, ask an expert and then choose!

Frozen phonon softwares: Phonopy, Phon and many others

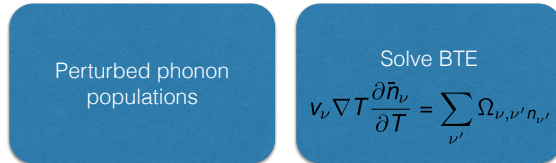
DFPT software: Quantum ESPRESSO, Abinit

Some recommended readings (and references therein):

DFPT: S. Baroni et al., Rev. Mod. Phys. **73**, 515 (2001).

DFPT 3rd-order: L. Paulatto et al., Phys. Rev. B **87**, 214303 (2013)

Second issue



Consider a small perturbation ∇T

$$n_\nu = \tilde{n}_\nu + \tilde{n}_\nu (\tilde{n}_\nu + 1) \nabla T F_\nu$$

(Linear) deviation of the phonon population with respect to the equilibrium distribution

Solution of the BTE

$$F = A^{-1} b$$

- The formal solution is simple in principles, hard in practice: the inversion of the matrix is VERY expensive
- Matrix size: $N \times N$, $N = \# \text{qpoints} \times \# \text{phonon modes}$
- Typical values for silicon: integrate with 30^3 points (not too many...), 6 phonon modes: $N = 2 \times 10^5$
- Notice also that matrix inversion scales as $O(N^3)$!

Boltzmann Transport Equation

The Boltzmann Transport Equation (BTE) in full is:

$$v_\nu \frac{\partial \tilde{n}_\nu}{\partial T} = \sum_{\nu', \nu''} \left[P_{\nu, \nu'}^{\nu''} (F_\nu + F_{\nu'} - F_{\nu''}) + \frac{1}{2} P_{\nu', \nu''}^{\nu} (F_\nu - F_{\nu'} - F_{\nu''}) \right] + \sum_{\nu'} P_{\nu, \nu'}^{\text{isot}} (F_\nu - F_{\nu'}) + P_\nu^{\text{extr}} F_\nu$$

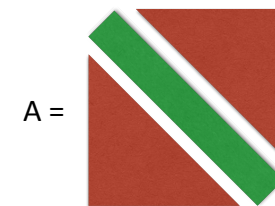
Omini, Phys. Rev. B 53, 9064 (1996)

(often you'll find it written in articles like the equation above)
Let's introduce the scattering matrix A, the BTE is simply as:

$$AF = b$$

Scattering matrix properties

A can be decomposed in two parts:



$$A_{\nu, \nu'}^{\text{out}} = \frac{\tilde{n}_\nu (\tilde{n}_\nu + 1)}{\tau_\nu} \delta_{\nu, \nu'}$$

Depopulation

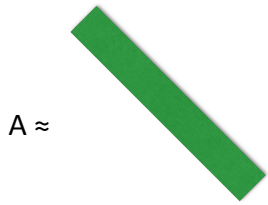
$$A_{\nu, \nu'}^{\text{in}} = - \sum_{\nu''} (P_{\nu, \nu''}^{\nu'} - P_{\nu, \nu'}^{\nu''} + P_{\nu', \nu''}^{\nu}) + P_{\nu, \nu'}^{\text{isot}}$$

Repopulation

Relaxation time:
(average time between scatterings)

$$\frac{1}{\tau_\nu} = \frac{1}{\tau_\nu^{\text{3ph}}} + \frac{1}{\tau_\nu^{\text{isot}}} + \frac{1}{\tau_\nu^{\text{extr}}}$$

Single mode relaxation time approximation (SMA)



$$A_{\nu, \nu'}^{\text{out}} = \frac{\bar{n}_\nu (\bar{n}_\nu + 1)}{\tau_\nu} \delta_{\nu, \nu'} \quad F = A^{-1} b \approx \frac{b}{A^{\text{out}}}$$

The inversion of a diagonal matrix is very simple, it's something we can do analytically!

Exact solutions

We can compute the thermal conductivity using the complete matrix (i.e. solving the problem exactly.)

Note first:

- A is symmetric: $A_{\nu, \nu'} = A_{\nu', \nu}$
- A is positive definite. i.e. \forall vector x : $x \cdot Ax \geq 0$

It has a very nice physical meaning!

$$A_{\nu, \nu'} = \left[\sum_{\nu'', \nu'''} \left(P_{\nu, \nu''}^{\nu'''} + \frac{P_{\nu'', \nu'''}^\nu}{2} \right) + \sum_{\nu''} P_{\nu, \nu''}^{\text{isot}} + P_\nu^{\text{be}} \right] \delta_{\nu, \nu'} + \sum_{\nu''} \left(P_{\nu, \nu''}^{\nu''} - P_{\nu, \nu''}^{\nu''} + P_{\nu', \nu''}^\nu \right) + P_{\nu, \nu'}^{\text{isot}}$$

Single mode relaxation time approximation (SMA)

The Boltzmann transport equation is often solved in the SMA (because it's simple!). Physical interpretation:

- Consider the time between phonon collisions: phonon lifetime (τ_ν).
- SMA: suppose that every time a phonon scatters, heat-flux is dissipated in the process. The BTE is simplified:

$$v_\nu \nabla T \frac{\partial \bar{n}_\nu}{\partial T} = -\frac{n_\nu - \bar{n}_\nu}{\tau_\nu} \quad \bar{n}_\nu = \frac{1}{e^{\hbar\omega_\nu/k_B T} - 1}$$

- The SMA-BTE can be solved analytically, the thermal conductivity simply becomes:

$$k = \frac{1}{V k_B T^2} \sum_\nu \bar{n}_\nu (\bar{n}_\nu + 1) (\hbar\omega_\nu)^2 v_\nu^2 \tau_\nu$$

Entropy of phonons

Let's use the Boltzmann entropy

$$S = k_B \ln W$$

The entropy of an ensemble of bosons is:

$$S = -k_B \int [n_\nu \ln n_\nu - (n_\nu + 1) \ln(n_\nu + 1)] d\nu$$

The result is true, strictly speaking, for non-interacting phonons close to equilibrium... We cheat a little, and hope it still works close to equilibrium (where $n_\nu - \bar{n}_\nu$ is small)

Entropy production

$$S = -k_B \int [n_\nu \ln n_\nu - (n_\nu + 1) \ln(n_\nu + 1)] d\nu$$

Let's compute the time derivative, and expand in Taylor series to first order.

There's some algebra, but the end result is:

$$\frac{dS}{dt} \approx -\frac{1}{T} \int F_\nu \frac{dn_\nu}{dt} d\nu + \frac{1}{T} \int \nabla T \frac{dF_\nu}{dt} d\nu$$

There are two terms: in the first, two phonon populations are coupled, in the second there's only one phonon population

Diffusion entropy

The term $F \cdot b$ is related to the diffusion entropy:

$$\begin{aligned} \left. \frac{dS}{dt} \right|_{\text{diff}} &= -\frac{1}{T} F \cdot b \nabla T \\ &= \frac{1}{T} \int F_\nu \bar{n}_\nu (\bar{n}_\nu + 1) \nabla T \mathbf{v}_\nu \hbar \omega_\nu \\ &= \frac{1}{T} \int (n_\nu - \bar{n}_\nu) \mathbf{v}_\nu \hbar \omega_\nu \\ &= \frac{\mathbf{Q}}{T} \end{aligned}$$

$$\frac{dS}{dt} \approx -\frac{1}{T} \int F_\nu \frac{dn_\nu}{dt} d\nu + \frac{1}{T} \int \nabla T \frac{dF_\nu}{dt} d\nu$$

The second term implies the increase of the internal energy with time.

$$U = \int n_\nu \hbar \omega_\nu d\nu$$

We don't allow it ($dU/dt=0$) and set it to zero

Focus on the first term.

$$\frac{dS}{dt} \approx -\frac{1}{T} \int F_\nu \frac{dn_\nu}{dt} d\nu$$

The BTE is essentially: $\frac{dn_\nu}{dt} = \left. \frac{\partial n_\nu}{\partial t} \right|_{\text{diff}} + \left. \frac{\partial n_\nu}{\partial t} \right|_{\text{scatt}}$

Thus, we suppose we can split the entropy in two terms, diffusion + scattering

Electric diffusion entropy

If we were to study electrical currents (the Boltzmann theory for electrons is almost the same), the thermal gradient would be replaced by an electrical field and we would find:

$$\begin{aligned} \left. \frac{dS}{dt} \right|_{\text{field}} &= -\frac{1}{T} F \cdot b e \mathbf{E} \\ &= \frac{1}{T} \int F_\nu \mathbf{v}_\nu \cdot \frac{\partial \bar{n}_\nu}{\partial \mathcal{E}_\nu} e \mathbf{E} d\nu \\ &= -\frac{1}{T} \mathbf{E} \cdot \mathbf{e} \int v_\nu (n_\nu - \bar{n}_\nu) d\nu \\ &= -\frac{1}{T} \mathbf{E} \cdot \mathbf{J} \end{aligned}$$

Joule Heat

Thermodynamical interpretation of the BTE

- We start with the BTE: $AF = b$

- Take a scalar product:

$$\frac{\nabla T}{T} F \cdot AF = \frac{\nabla T}{T} Fb$$

- Let's define the production of scattering entropy as:

$$\left. \frac{dS}{dt} \right|_{\text{scatt}} = \frac{\nabla T}{T} F \cdot AF$$

- The BTE can be interpreted as:

$$\left. \frac{dS}{dt} \right|_{\text{scatt}} = - \left. \frac{dS}{dt} \right|_{\text{diff}}$$

Variational principle 2

We could solve the BTE by trying to minimise the entropy production.

Alternatively, (and more conveniently) we can maximise a thermal conductivity functional

$$k = \max_F \frac{1}{k_B T^2 V} (2F \cdot b - F \cdot AF)$$

Property of the functional:

- It's a quadratic form
- The stationary point exists and is unique

Variational principle 1

The matrix A is positive definite $\Rightarrow \frac{dS}{dt} \geq 0$ 2nd law of thermodynamics

Solving the BTE means finding the phonon population (F) such that

$$\frac{dS}{dt} = 0$$

Therefore, rather than solving an algebraic equation, we can minimize the entropy-production functional!

The thermal conductivity can be defined in terms of the two entropies:

$$k = \frac{1}{k_B T^2 V} (2F \cdot b - F \cdot AF)$$

Past approaches

- Build a trial function, with some variational parameters
- Compute the conductivity functional
- Optimise the variational parameters

Example: Hamilton and Parrot, Phys. Rev. **178**, 1284 (1969)

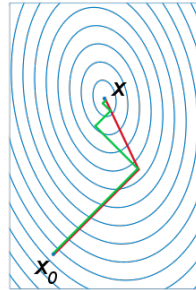
$$F_\nu = \frac{\mathbf{q} \cdot \nabla T}{|\mathbf{q}| |\nabla T|} \sum_n \alpha_n q^n$$

Already with only n=1 you can improve upon the relaxation time approximation. In exchange, you increase the complexity of the calculation.

Conjugate gradient

Iteratively try to improve the conductivity:

- Initial guess F_0
- Loop:
 - $F_{k+1} = F_k + \alpha_k (b - AF_k)$



- check convergence on $k = \frac{1}{k_B T^2 V} (2F \cdot b - F \cdot AF)$

Mathematically stable, always convergent!

Applications

SMA	Variational
Inexpensive	Moderately expensive (~10 times SMA)
It's an approximation!	Exact

References:

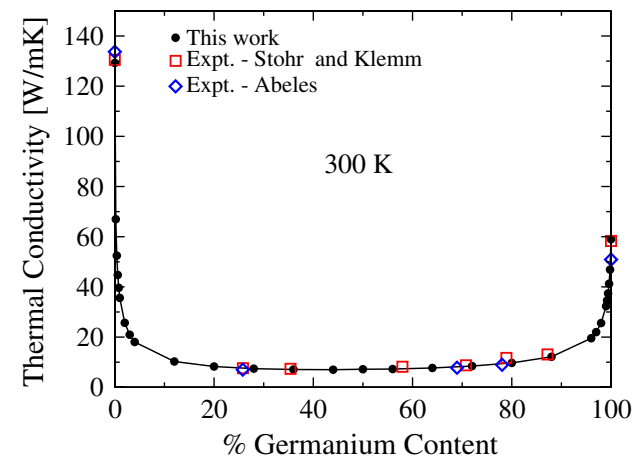
- J.M. Ziman, *Electrons and Phonons*, Oxford university press (1964)
- R.A.H. Hamilton et al., *Phys. Rev.* **178**, 1284 (1969)
- G. Fugallo et al., *Phys. Rev. B* **88**, 045430 (2013)

Iterative (non-variational) methods:

- M. Omini and A. Sparavigna, *Phys. Rev. B* **53**, 9064 (1996)
- D.A.Broido et al., *Phys. Rev. B* **72**, 014308 (2005)

When to use what? (no definitive answer, but more on this later)

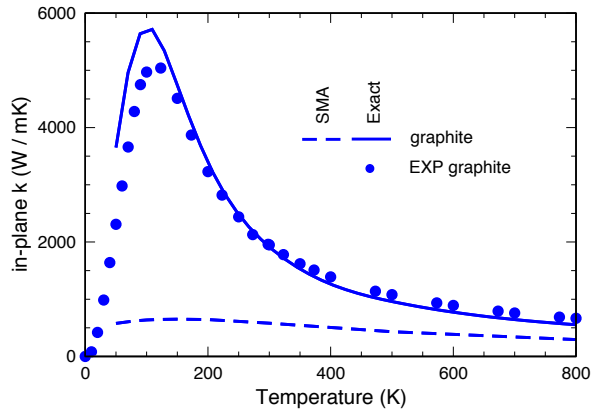
Silicon Germanium



J. Garg et al.,
PRL **106**,
045901 (2011)

The first-principles BTE + SMA often works very well (in 3D)

Graphite in-plane

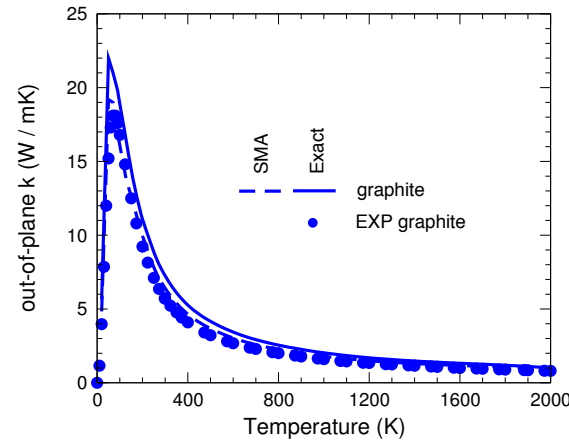


Fugallo et al.,
NanoLett. **14**,
6109 (2014)

Sometimes the SMA
can be incorrect,
even in 3D materials,
and even at high
temperatures.

The simulation results are in good agreement with experiments on graphite, but only if the BTE is solved exactly!

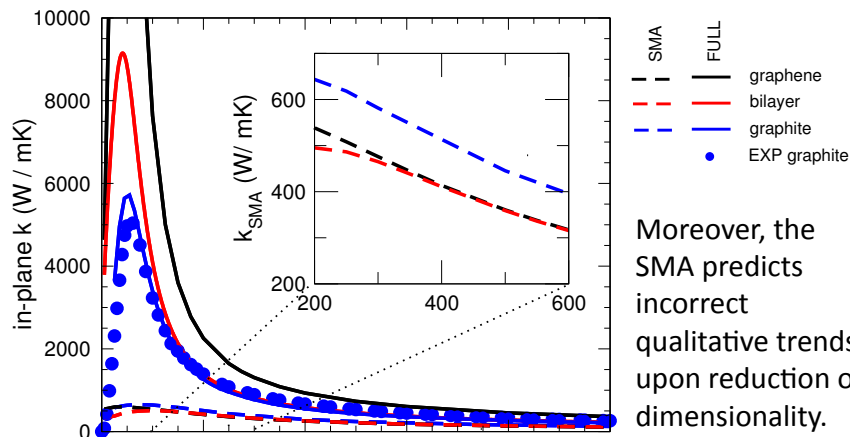
Graphite out-of-plane



To make things
more complicated,
SMA errors are
direction
dependent.

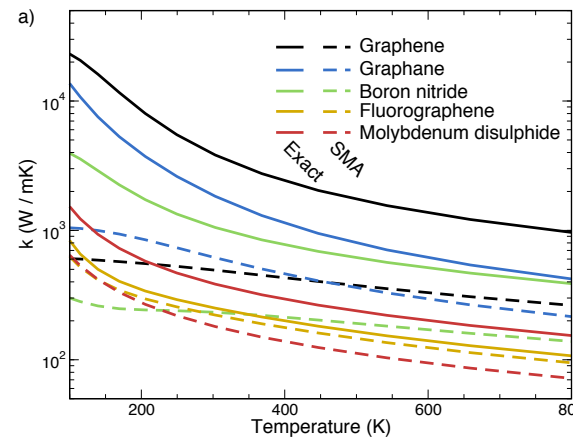
In the out-of-plane
direction, the SMA
works well (few %
error)

Graphite to graphene



Moreover, the
SMA predicts
incorrect
qualitative trends
upon reduction of
dimensionality.

Thermal transport in 2D materials

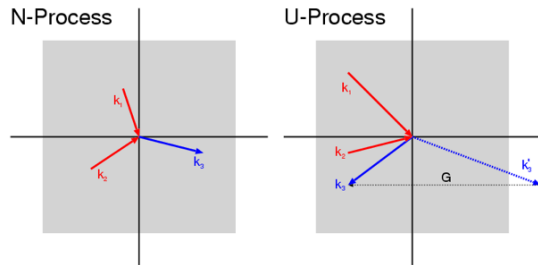


The physics of phonon
transport in 2d
materials shares many
similarities with
graphene

The exact variational
solution is always
required when dealing
with 2D materials and/
or planar materials.

What do these materials have in common?

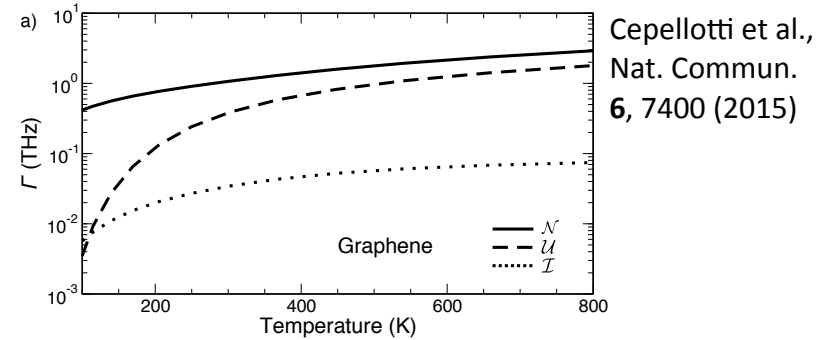
Umklapp vs Normal



- Normal (N) scattering conserve mechanical momentum
- Umklapp (U) scattering do not conserve momentum.

It can be shown that only U contribute explicitly to thermal resistivity (U scattering can reverse the direction of the heat flux)

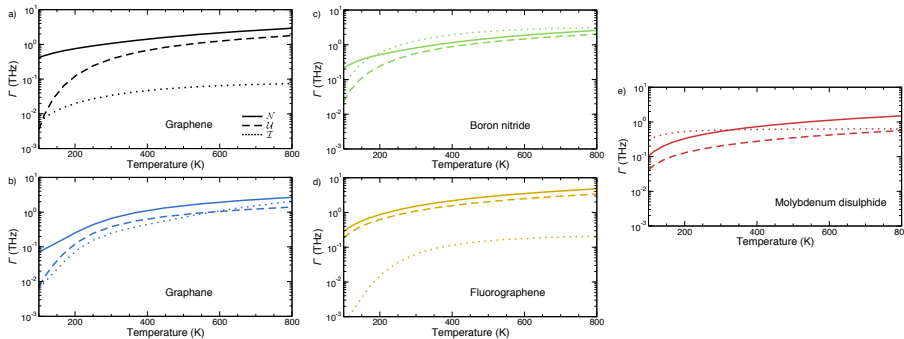
Graphene scattering rates



Using SMA quantities (i.e. lifetimes), we can check that normal processes take place with highest frequency

$$\text{Average scattering rate: } \Gamma^i = \frac{\sum_{\nu} C_{\nu} 2\pi / \tau_{\nu}^i}{\sum_{\nu} C_{\nu}}$$

Scattering rates



On average, Normal processes are the most frequent at any temperature in the 2D materials studied. The mechanical momentum of phonons is thus a well conserved quantity.

Failure of the SMA

The failure of the SMA in 2D materials is induced by the large number of normal scattering events

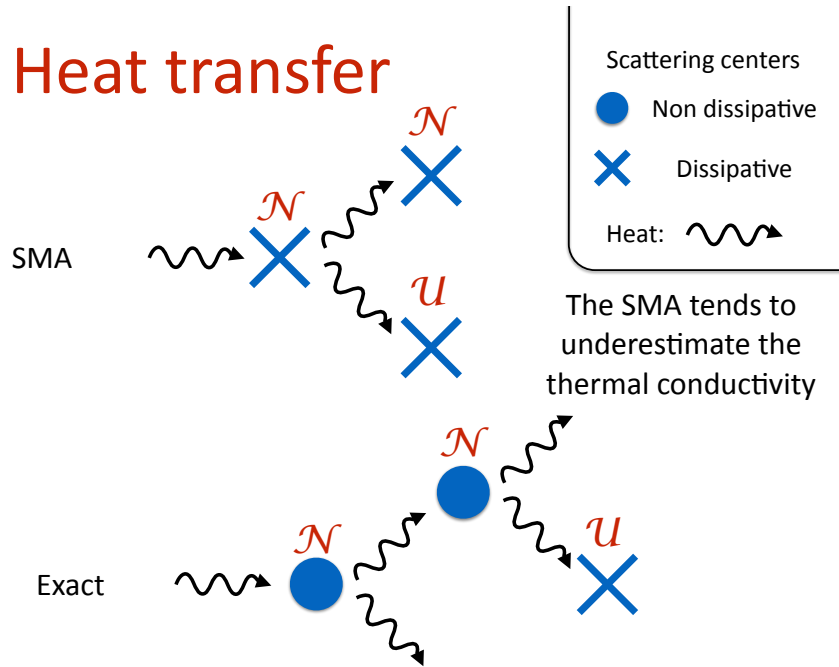
Even at high temperature, phonon lifetimes are dominated by normal processes:

$$\frac{1}{\tau} = \frac{1}{\tau_{\mathcal{R}}} + \frac{1}{\tau_{\mathcal{N}}} \approx \frac{1}{\tau_{\mathcal{N}}}$$

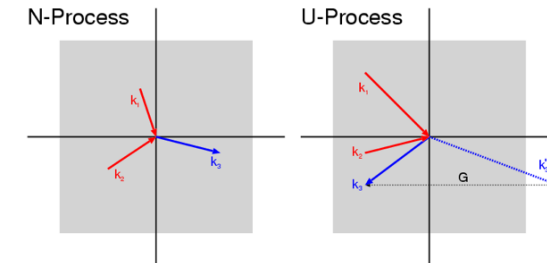
Therefore, the thermal conductivity is largely determined by N processes (that shouldn't give any thermal resistance!):

$$k = \frac{1}{Nk_B T^2} \sum_{\nu} \bar{n}_{\nu} (\bar{n}_{\nu} + 1) (\hbar\omega_{\nu})^2 v_{\nu}^2 \tau_{\mathcal{N}}$$

Heat transfer



Umklapp freezing?



A similar situation happens in Umklapp freezing: at low temperatures, only acoustic phonons close to the Gamma point (with very small momentum) can be excited.

Can we use low-temperature methods to describe the conductivity of 2D materials at room temperature?

Callaway model

$$\mathcal{L} = -k_B \int [n_\nu \ln n_\nu - (n_\nu + 1) \ln(n_\nu + 1)] d\nu - \beta E - \mathbf{V} \cdot \mathbf{P}$$

$$\mathbf{P} = \int \hbar \mathbf{q} n_\nu d\nu$$

The drifting distribution is the most probable distribution under the constraint of momentum conservation.

$$\frac{\delta \mathcal{L}}{\delta n_\nu} = 0 \quad \Rightarrow \quad n_\nu^{\text{drift}} = \frac{1}{e^{\hbar(\omega_\nu - \mathbf{q} \cdot \mathbf{V}) / k_B T} - 1}$$

Callaway model

Let's keep a relaxation time model and take advantage of the concept of the drifting distribution.

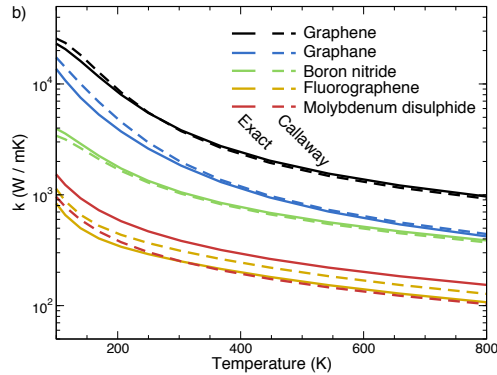
We distinguish Resistive (R) from Normal (N) scattering events. The former relax the distribution to the Bose-Einstein equilibrium, whereas the latter relax to the drifting distribution:

$$v_\nu \nabla T \frac{\partial \bar{n}_\nu}{\partial T} = -\frac{n_\nu - \bar{n}_\nu}{\tau_\nu^R} - \frac{n_\nu - n_\nu^{\text{drift}}}{\tau_\nu^N}$$

Phys. Rev. **113**, 1046 (1959)

This method was originally developed to describe the thermal conductivity of Germanium at cryogenic temperatures, where N processes dominate (under Umklapp freezing)

Callaway model

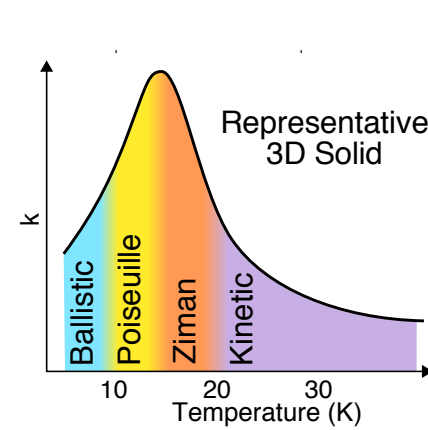


The model is simple and reproduces well the results of the exact solution of the BTE.

Transport is dominated by the presence of N processes

Room-temperature conditions of 2D materials are analogous to low-temperature conditions of solids characterised by Umklapp freezing.

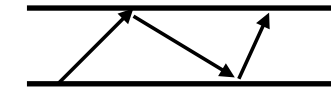
Phonon-transport regimes



Ballistic	$\epsilon \gg \mathcal{N}$ and $\epsilon \gg \mathcal{R}$
Poiseuille	$\mathcal{N} \gg \epsilon \gg \mathcal{R}$
Ziman	$\mathcal{N} \gg \mathcal{R} \gg \epsilon$
Kinetic	$\mathcal{R} \gg \mathcal{N}$ and $\mathcal{R} \gg \epsilon$

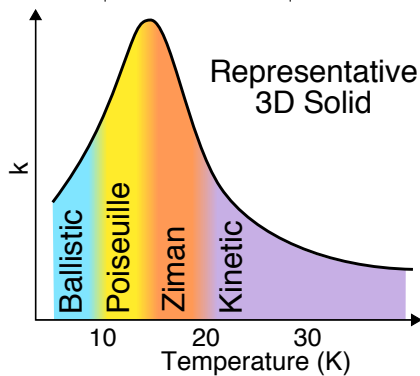
Scattering rates of extrinsic (E), Normal (N) and resistive (R) processes

Ballistic regime:



Typically poorly described in the BTE, with the scattering rate $\frac{1}{\tau_v} = \frac{v_v}{L}$

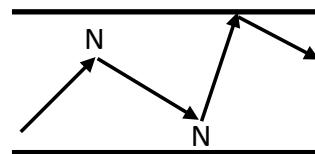
Phonon-transport regimes



Ballistic	$\epsilon \gg \mathcal{N}$ and $\epsilon \gg \mathcal{R}$
Poiseuille	$\mathcal{N} \gg \epsilon \gg \mathcal{R}$
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Kinetic	$\mathcal{R} \gg \mathcal{N}$ and $\mathcal{R} \gg \epsilon$

Scattering rates of extrinsic (E), Normal (N) and resistive (R) processes

Poiseuille regime:

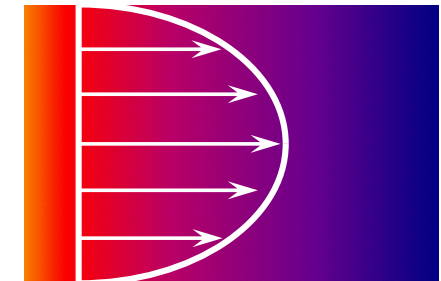


N processes dominate, and the phonon fluid feels the "walls"

Poiseuille regime

$$\mathcal{N} \gg \epsilon \gg \mathcal{R}$$

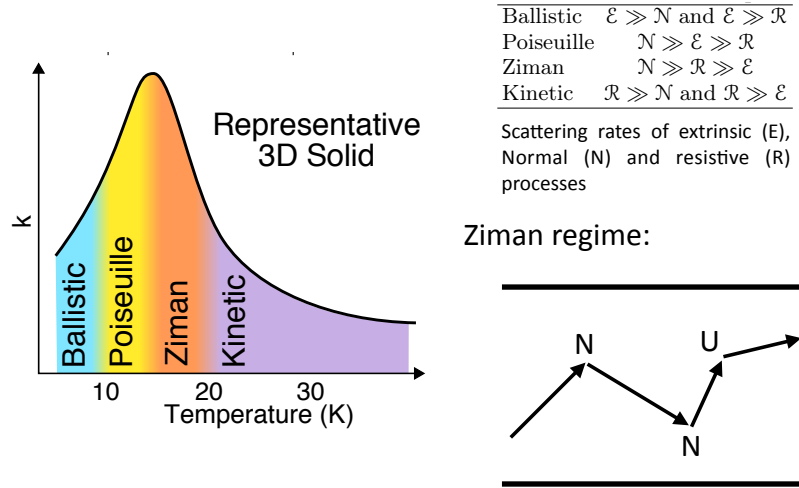
- Internal scattering dominated by N processes, and heat dissipation happening due to extrinsic processes (surfaces, ...)



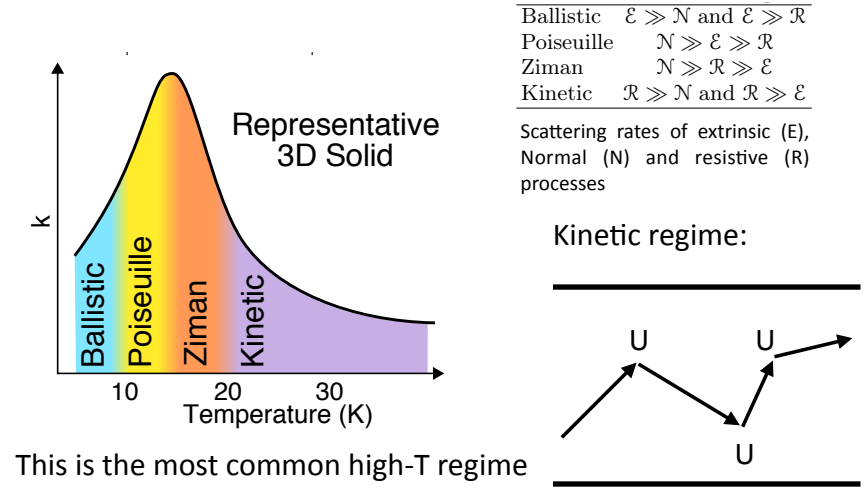
- Called Poiseuille after the similarities with the flow of a viscous fluid in a pipe.

(Picture from *Nat. Commun.* 6, 7290 (2015))

Phonon-transport regimes

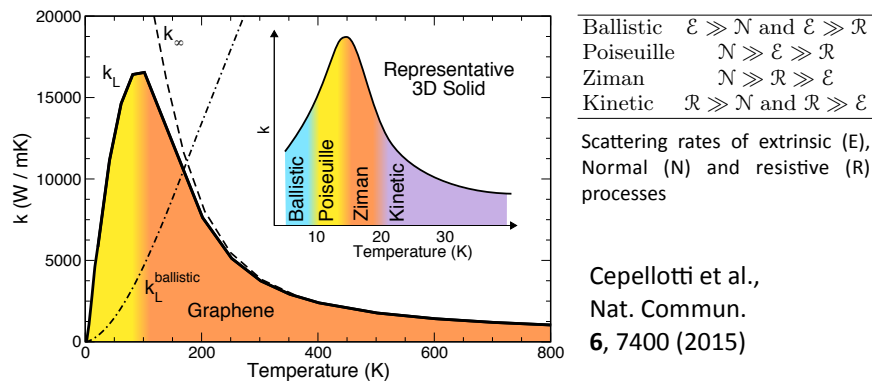


Phonon-transport regimes



This is the most common high-T regime where SMA is expected to work (often)

2D phonon-transport regimes



Breakdowns of Fourier's law

Hydrodynamic phonon transport has been observed (in few materials) at cryogenic temperatures. In 2D materials, it's present at room temperature

Fourier's law from the BTE

Consider the BTE (for simplicity, we work with the relaxation time approximation):

$$v_\nu \frac{\partial \bar{n}_\nu}{\partial T} \nabla T = - \frac{n_\nu - \bar{n}_\nu}{\tau_\nu}$$

$$v_\nu \bar{n}_\nu (\bar{n}_\nu + 1) \frac{\hbar \omega_\nu}{k_B T^2} \nabla T = - \frac{n_\nu - \bar{n}_\nu}{\tau_\nu}$$

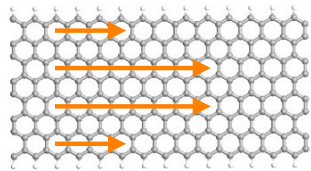
Multiply the BTE by: $\sum_\nu v_\nu \hbar \omega_\nu \tau_\nu$

The BTE becomes:

$$\sum_\nu \bar{n}_\nu (\bar{n}_\nu + 1) v_\nu^2 (\hbar \omega_\nu)^2 \tau_\nu \nabla T = - \sum_\nu (n_\nu - \bar{n}_\nu) \hbar \omega_\nu v_\nu$$

$$k \nabla T = -Q$$

The BTE "contains" the Fourier's law



Heat flux in small systems with rough edges is space dependent, more conducting at the centre.

But if the heat is thermalised on a distance (mean free path) smaller than the sample size, then k is roughly constant.

To estimate the mean free path, we perturb the scattering operator with:

$$P_\nu^{\text{extr}} \propto \frac{v_\nu}{L}$$

Its physical meaning: any phonon, with velocity v_ν , will be thermalised after it has traveled for a distance L .

$$\tau_\nu^{\text{extr}} v_\nu = \frac{L}{v_\nu} v_\nu = L \quad (\text{Nothing travels further than a distance } L)$$

Validity of Fourier's law

$$Q = -k \nabla T$$

Can we always use Fourier's law to reconstruct the temperature profile? i.e. when is k a constant of the material?

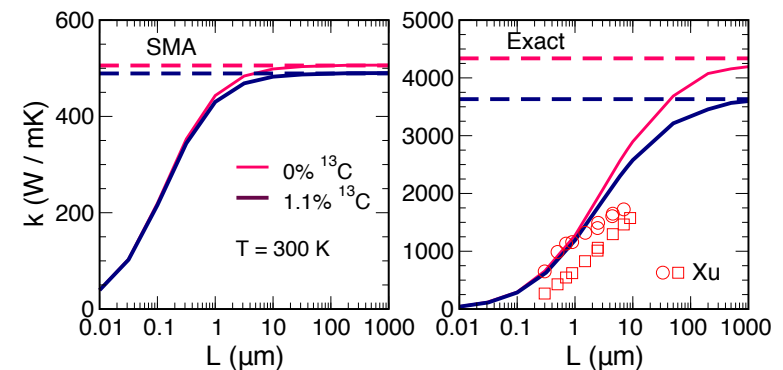
If the material is infinite (thermodynamic limit), the law holds and k is constant.

If the material is finite, the BTE needs to be solved in real space, with boundary conditions!

$$n_\nu \rightarrow n_\nu(x) \quad v_\nu \nabla n_\nu(x) = - \frac{n_\nu(x) - \bar{n}_\nu(x)}{\tau_\nu} \quad \nabla n_\nu \neq \frac{\partial n_\nu}{\partial T} \nabla T$$

k becomes space dependent: $Q(x) = -k(x) \nabla T$
and we should solve the BTE rather than the Fourier's law!

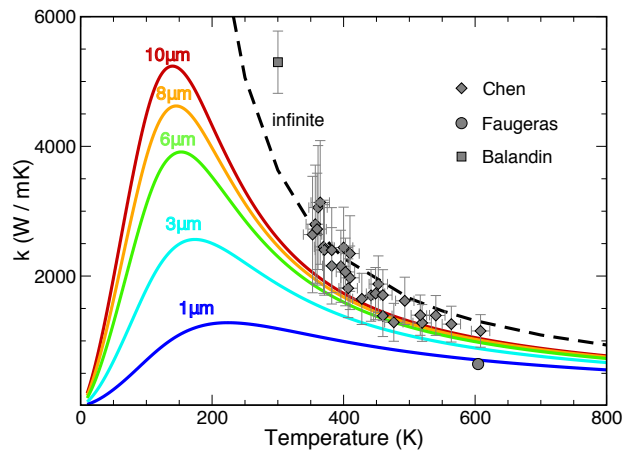
Graphene's MFP



Sim: *Nano Lett.* **14**, 6109 (2014) Exp: *Nat. Commun.* **5**, 3689 (2014)

In graphene, the mean free paths extends up to 1mm (T=300K)
The intrinsic thermal conductivity is defined only for larger samples
Below that, Fourier's law does not hold, and we should use the BTE!

Comparison with experiments?



Balandin Nano Lett. **8**, 902 (2008)
 Chen, ACS Nano **5**, 321 (2011)
 Faugeras, ACS Nano **4**, 1889 (2010)

The comparison between simulation results and experiments is not fully justified:

Simulations describe an infinite crystal, while measurements are on small systems.

Some experiments infer their results from the Fourier's law, which does not hold.

More work to be done!

Fourier's law in the time domain

Energy balance equation for phonons:
 (C=specific heat, \mathbf{Q} =heat flux):

$$C \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{Q} = 0$$

Fourier's law: $\mathbf{Q} = -k \nabla T$

Combining the two one obtains the diffusion equation:

$$\frac{1}{k} C \frac{\partial T}{\partial t} - \nabla^2 T = 0$$

Some fundamental problems: the diffusion equation leads to an infinite propagation velocity under a temperature pulse.

Fourier's law in the time domain

One can correct the Fourier equation to include the build-up time of the temperature response:

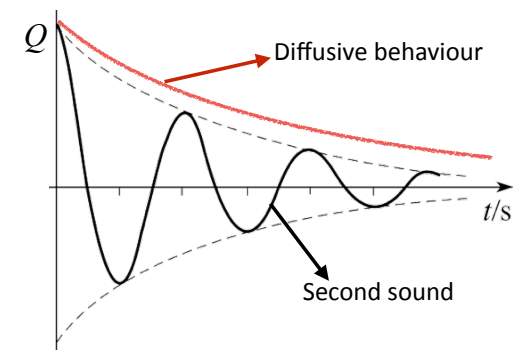
$$\tau_{ss} \frac{\partial \mathbf{Q}}{\partial t} + \mathbf{Q} = -k \nabla T \quad C \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{Q} = 0$$

The temperature profile is thus given by thermal waves:

$$\frac{\partial T^2}{\partial t^2} + \frac{1}{\tau_{ss}} \frac{\partial T}{\partial t} - (v_{ss})^2 \nabla^2 T = 0$$

We define second sound as the case in which the thermal profile can be described by a wave equation

Second sound profile



In response to a temperature pulse, a wave-packet of phonons is created, which is dissipated in a characteristic time τ_{ss}

Often the time dependent oscillations are smoothed out quickly, so that most of the times only the diffusive behaviour is observed

Second sound from BTE

The second sound expression can also be derived from the first-principles BTE:

1. The energy continuity equation can be obtained from the BTE
2. Assume that: $n_\nu \approx n_\nu^{\text{drift}}$

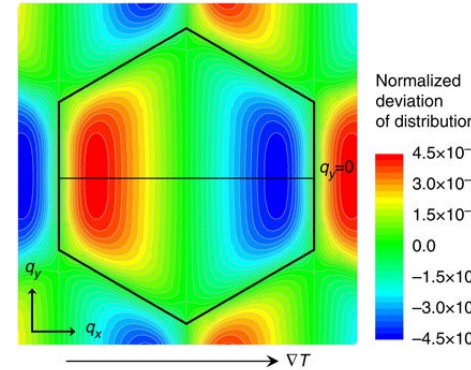
Assume also the Callaway approximation to the scattering operator. The (time dependent) BTE can be written as:

$$\left\langle \frac{1}{\tau R} \right\rangle^{-1} \frac{\partial Q(\mathbf{x}, t)}{\partial t} + k \nabla T(\mathbf{x}, t) + Q(\mathbf{x}, t) = 0$$

In this way we obtain a closed expression for the second sound lifetime

Thus, the parameters for second sound can be obtained from the BTE

Drifting distribution



ZA mode in graphene
(Picture from *Nat. Commun.* **6**, 7290 (2015))

Second sound requires:

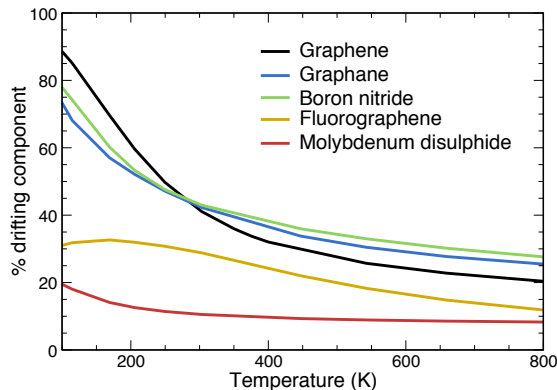
$$n_\nu \approx n_\nu^{\text{drift}}$$

The approximation holds if the deviation function F is linear in momentum

$$n_\nu \approx \bar{n}_\nu + \bar{n}_\nu (\bar{n}_\nu + 1) \nabla T F_\nu$$

$$n_\nu^{\text{drift}} = \frac{1}{e^{(\hbar\omega_\nu - \mathbf{q} \cdot \mathbf{V}) / k_B T} - 1} \approx \bar{n}_\nu + \bar{n}_\nu (\bar{n}_\nu + 1) \frac{\mathbf{q} \cdot \mathbf{V}}{k_B T}$$

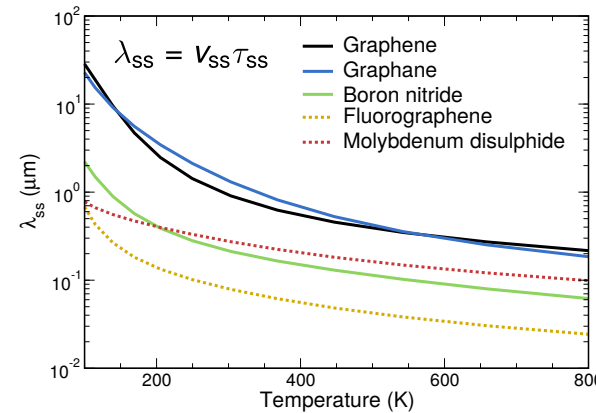
Linearity of the solution



We quantify the amount of the linearity in the out-of-equilibrium distribution by defining a scalar product:

$$\frac{\sum_\nu C_\nu F_\nu q_{||}}{\sqrt{\sum_\nu C_\nu F_\nu^2} \sqrt{\sum_\nu C_\nu q_{||}^2}}$$

Second sound length



$\lambda_{ss} = v_{ss} \tau_{ss}$
Nat. Commun. **6**, 7400 (2015)

Heat can propagate in the form of a wave over distances of 1 micron at room temperature in graphene, a distance well compatible with current dimensions of samples.

Second sound propagation:

$$\frac{\partial^2 T}{\partial t^2} + \frac{1}{\tau_{ss}} \frac{\partial T}{\partial t} - (v_{ss})^2 \nabla^2 T = 0$$

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- **Nicola Marzari**, *École Polytechnique Fédérale, Lausanne*

Conclusions

- First principles phonons + BTE: accurate, parameter-free results
- Two main approaches to compute phonons from first principles: frozen phonon and DFPT (my favourite!)
- The (linearised) BTE can be solved in the relaxation-time approach or (since recently) in an exact way, as with the variational method.
- The relaxation time approximation fails in layered/2D materials
- The BTE provides insights on thermodynamic properties of the system, like the entropy, or the validity of Fourier's law
- The BTE can distinguish between different thermal conductivity regimes (ballistic, kinetic, hydrodynamic)