UNIVERSITÉ DE LORRAINE

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Laboratoire énergies & mécanique théorique et appliquée

Thermal exchanges at the nanoscale, Monte Carlo phonon transport

David LACROIX

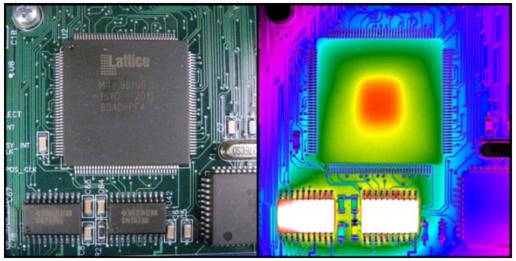
Outline

- **Heat transport in nano & microstructures, basics, models and challenges**
- **Using Monte Carlo technique to solve the Boltzmann transport equation for phonons**
  - Application of MC-BTE tool to appraise thermal properties in nanostructures
  - Improvement of MC-BTE by coupling with ab-initio calculations
  - MC-BTE & Green-Kubo
  - MC-BTE calculations for TE materials (if time not exceed !)
- **Summary and perspectives**

Heat transport in nano & microstructures.

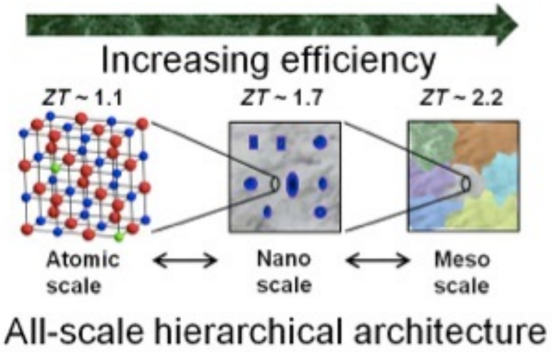
Basics, models and challenges

Tailoring heat transport in nano & microstructures

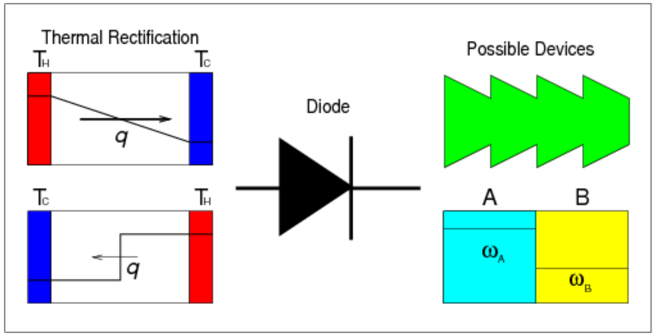


Challenges

- **Control of overheating**
  - minimize failure,
  - hotspots occurrence
  - improve performance of materials
  - etc
- **Tailoring heat transport properties**
  - thermoelectric material improvement
  - thermal cloaking, thermal rectification
  - etc
- **Thermal management applications**
  - electronic, optical, optoelectronic and thermoelectric devices,
  - thermal diode
  - etc



Nature 489, 414–418 (2012)



http://telab.vuse.vanderbilt.edu/research.html

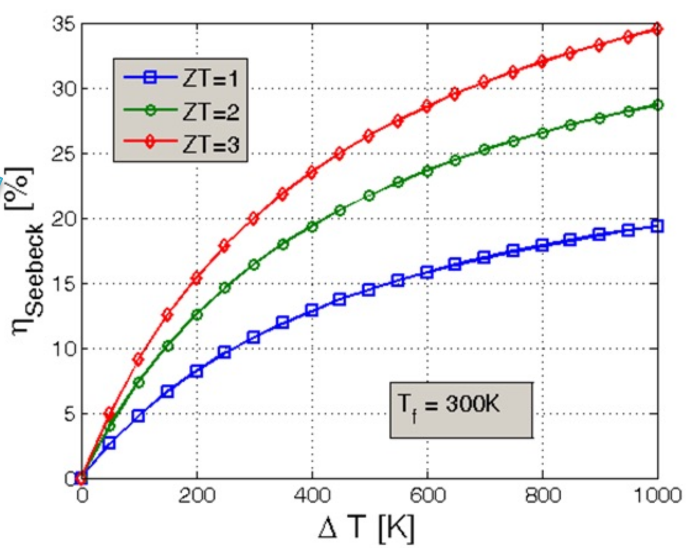
Phonons and thermoelectricity

In semiconductors for thermoelectricity "phonons" and "electrons" are both energy carriers that must be taken into account to design efficient materials, **i.e. with large figure of merit ZT**.

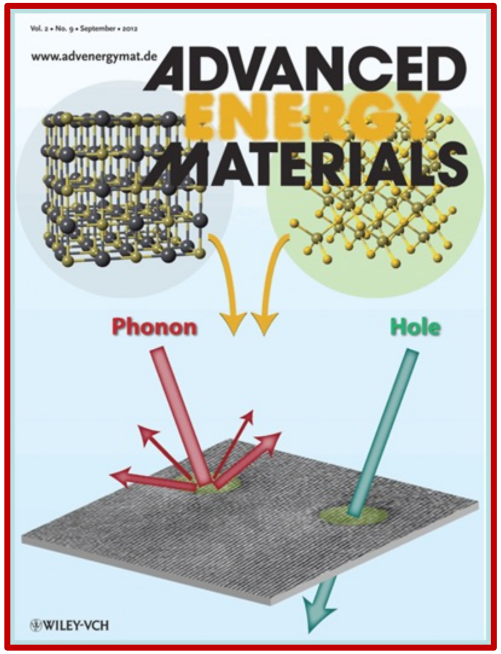
$$ZT = \frac{\sigma \alpha^2 T}{\kappa}$$

High ZT leads to increase conversion efficiency:

$$\eta_{Seebeck} = \left(1 - \frac{T_f}{T_c}\right) \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + T_f / T_c}$$



Phonon engineering

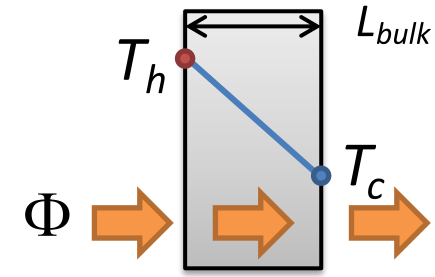


Advanced Energy Materials, Sept 2012

Heat transport in nano & microstructures

Basics

- Heat transfer at the nanoscale differs from what occurs in bulk material:
  - Fourier's law needs to be considered with caution
  - Heat transport equation is no longer valid
  - Thermal properties of materials depend on **length scales** and temperature
- Heat transport varies between diffusive and ballistic regimes



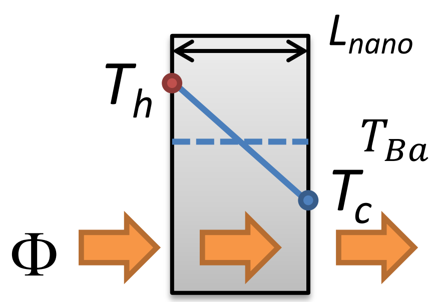
$$\Phi = -k\nabla T$$

$$\rho C \frac{dT}{dt} = \nabla.(k\nabla T) + q_{vol}$$

k_{nano} ???

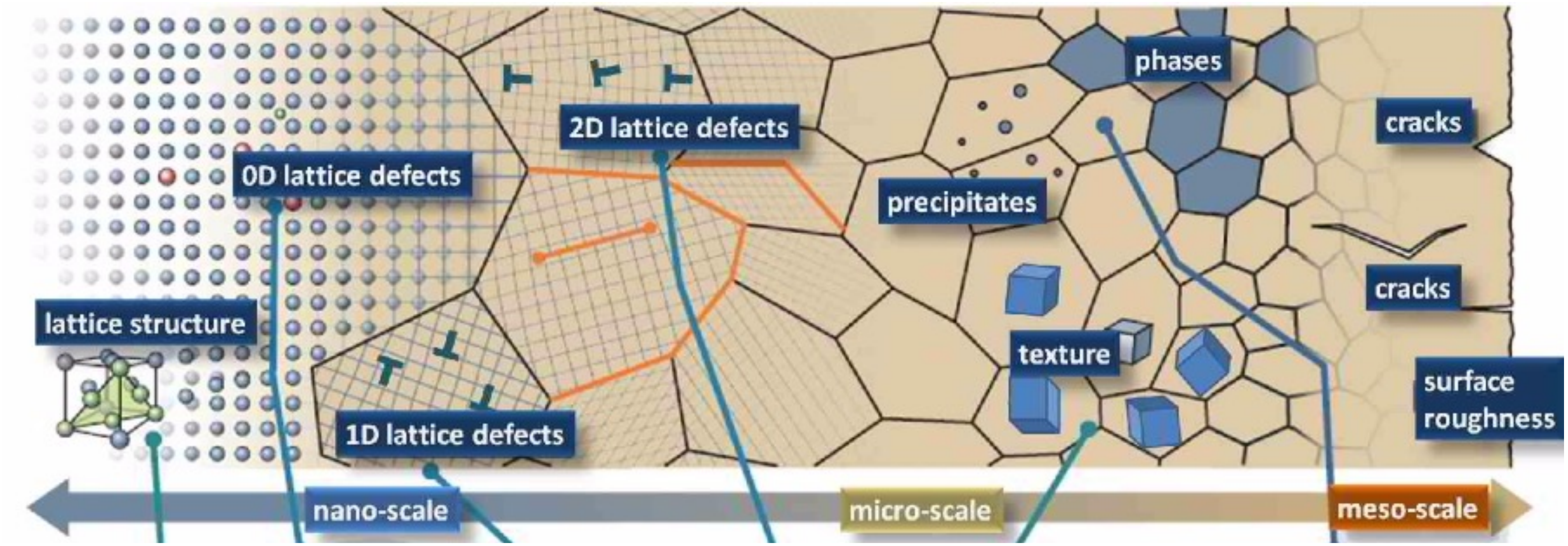
dT/dx ???

Approach based on heat carrier transport: "phonons"



$$T_{Ballistic} = \left(\frac{T_h^4 + T_c^4}{2}\right)^{1/4}$$

Heat transport modeling, a multiscale issue



http://www.dierk-raabe.com/

DFT	MD	MC	FEM, FVM
few atoms & electrons	**thousands of atoms**	**crystals**	**structures**
~ 1nm	10~100nm	100nm ~ 100µm	100µm ~ above

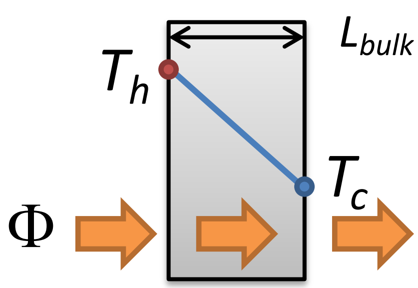
Heat transport, Monte Carlo methods 1

Monte Carlo methods refers to techniques that use statistical tools to model energy carriers displacements and scattering mechanisms. This techniques are used in several domain, in the field of thermal transport there are:

- Radiative heat transfer of semi-transparent (absorbing, scattering & emitting media), through the resolution of the Radiative Transfer Equation (RTE)
- Conductive heat transfer at macroscale ("Marcheurs Brownien"), through the solution Heat equation
- Heat transport at microscale with the resolution of Boltzmann Transport Equation (BTE) for phonons

Heat transport, Monte Carlo methods 2

Monte Carlo methods relies on the use of probability distributions. Basic case of Heat Equation solution with "Browian walkers" :



$$\Phi = -k\nabla T$$

$$\rho C \frac{dT}{dt} = \nabla.(k\nabla T) + q_{vol}$$

How provide a statistical approach to solve this equation without using PDE. Basic assumptions :

- Transport is in the diffuse regime (Diffusion coefficient is known)
- Energy carriers all transport the same amount of energy
- Displacement of Energy carriers follows a Normal distribution
- Location of Energy carriers is determined with uniform distribution

V. Gonneau, IJHMT, 184, 122261

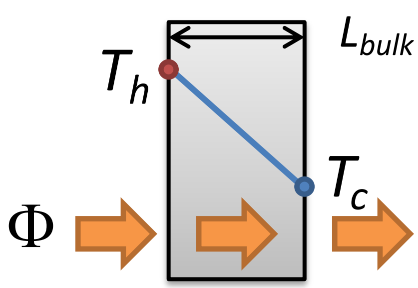
Heat transport, Monte Carlo methods 3

"Browian walkers" : Let assume 1D model (along L_{bulk}), the system is discretized in intervals dL= L_{bulk}/N_x. The applied thermal gradient is $\Delta T_{hc}=(T_h-T_c)/L_{bulk}$. This quantity drives the amount of energy carried by each walkers δh_r

$$\delta h_r = \rho_r C_r V \frac{\Delta T_{hc}}{M_r}$$

With M_r the number of Brownian walkers

V. Gonneau, IJHMT, 184, 122261



$$\Phi = -k\nabla T$$

$$\rho C \frac{dT}{dt} = \nabla.(k\nabla T) + q_{vol}$$

The temperature at time t and location i, is defined as :

$$T_t^i = T_r + \frac{M_t^i \times \delta h_r}{\rho_r C_r V^i}$$

Each energy carrier position is set according a uniform probability distribution

$$x_0^i = L_{bulk} \times \mathcal{R}_U$$

Each energy carrier displacement is ruled by material thermal diffusivity as :

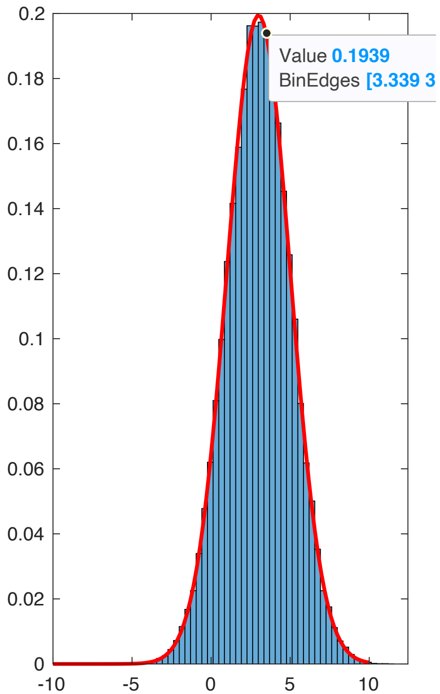
$$x_{t+1}^i = x_t^i + \sqrt{2\,a\,\delta t} \times \mathcal{R}_N$$

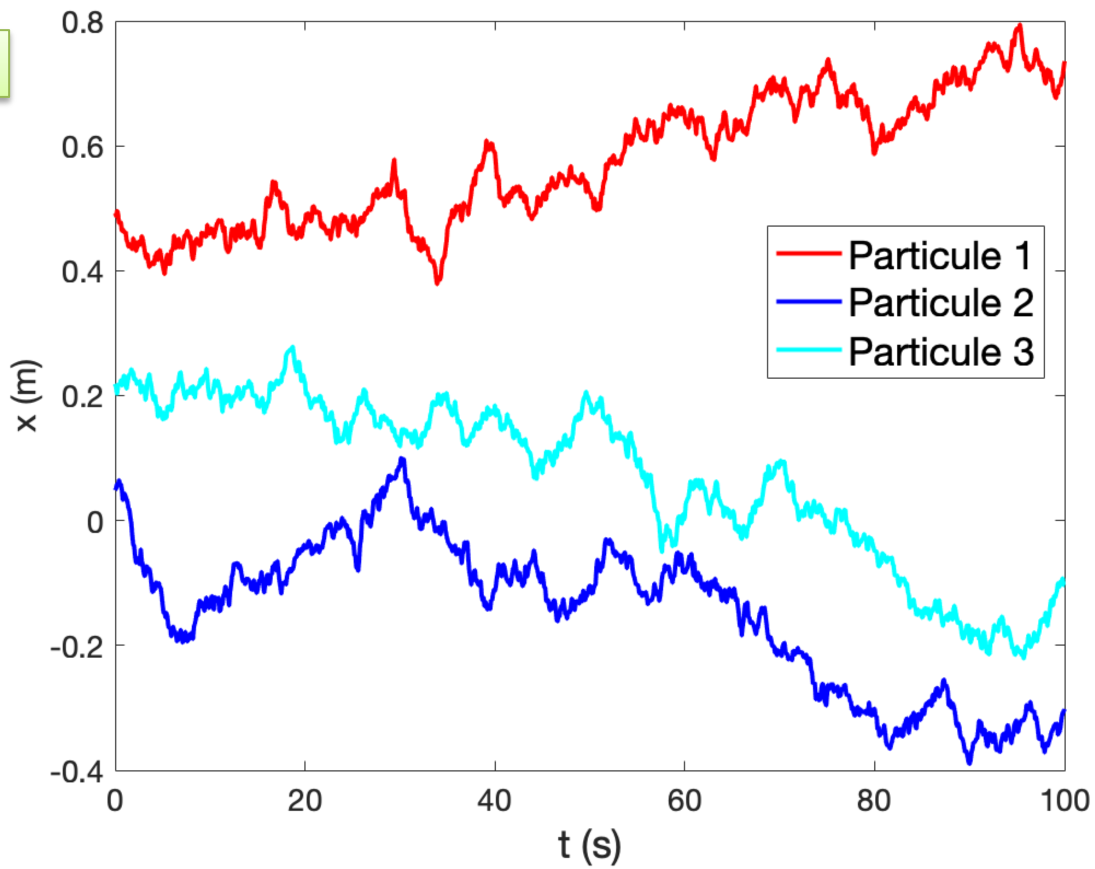
With $\mathcal{R}_U$ and $\mathcal{R}_N$ a random numbers drawn on uniform and normal centered probability distribution

Heat transport, Monte Carlo methods 4

Displacements of walkers allows energy carriers in excess on the hot side to flow toward the cold size.

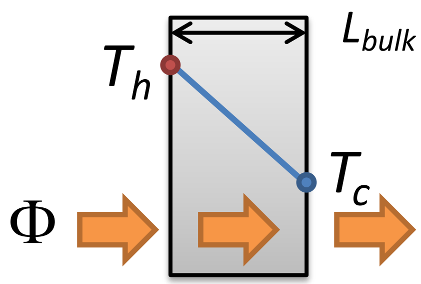
$$x_{t+1}^{i} = x_{t}^{i} + \sqrt{2\,a\,\delta t} \times \mathcal{R}_N$$





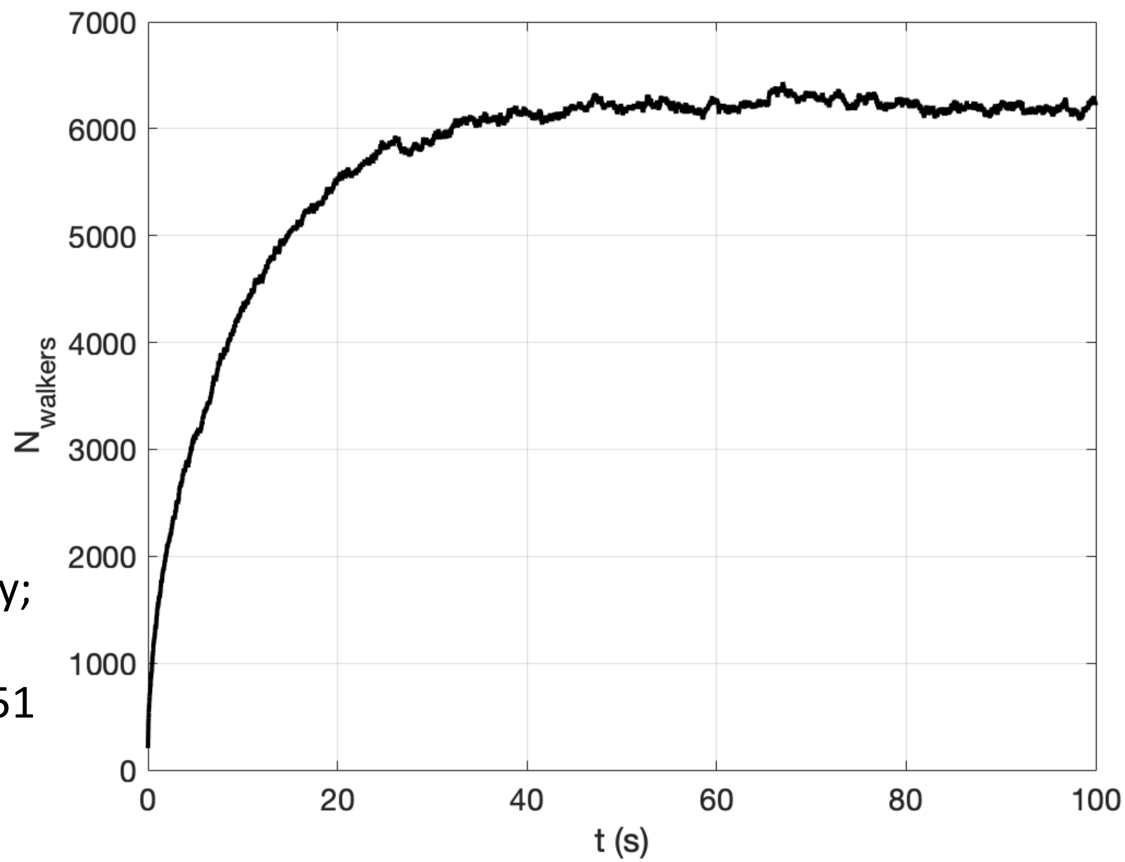
Heat transport, Monte Carlo methods 5

Hot and cold size act as blackbodies (absorbing and emitting Brownian walkers at the prescribed temperatures



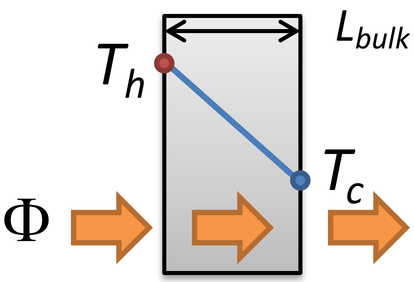
Example : Test case on bulk Si;
k_{Si} = 151 W/mK
Initially M_r=250 all in hot blackbody;
T_r=0°C, with ΔT_{hc}=10°C
L=0.1m ; δt = 5e-4s ; Nt =2e4 ; Ni=51

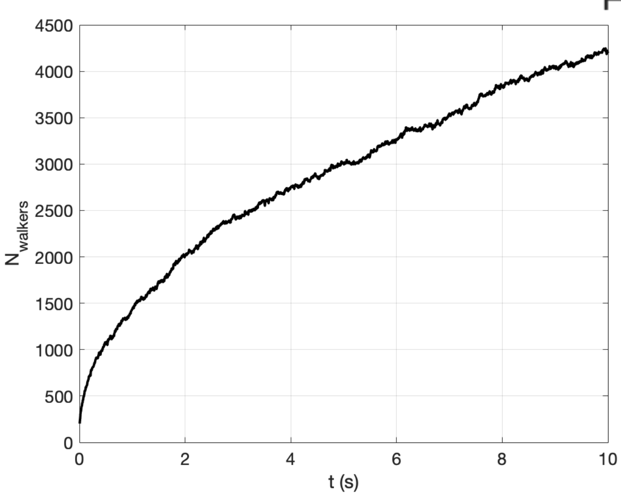
$$T_t^i = T_r + \frac{M_t^i \times \delta h_r}{\rho_r C_r V^i}$$

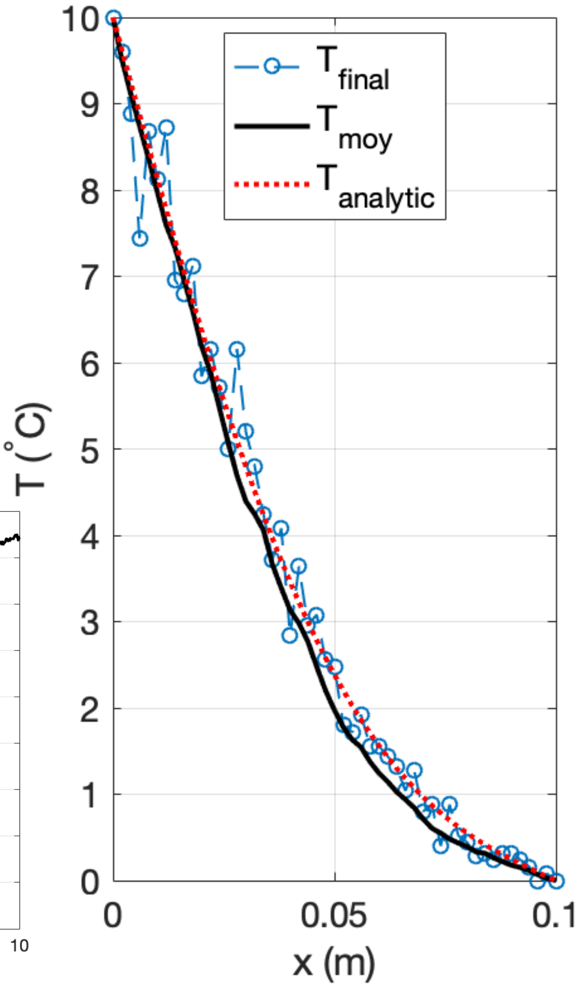


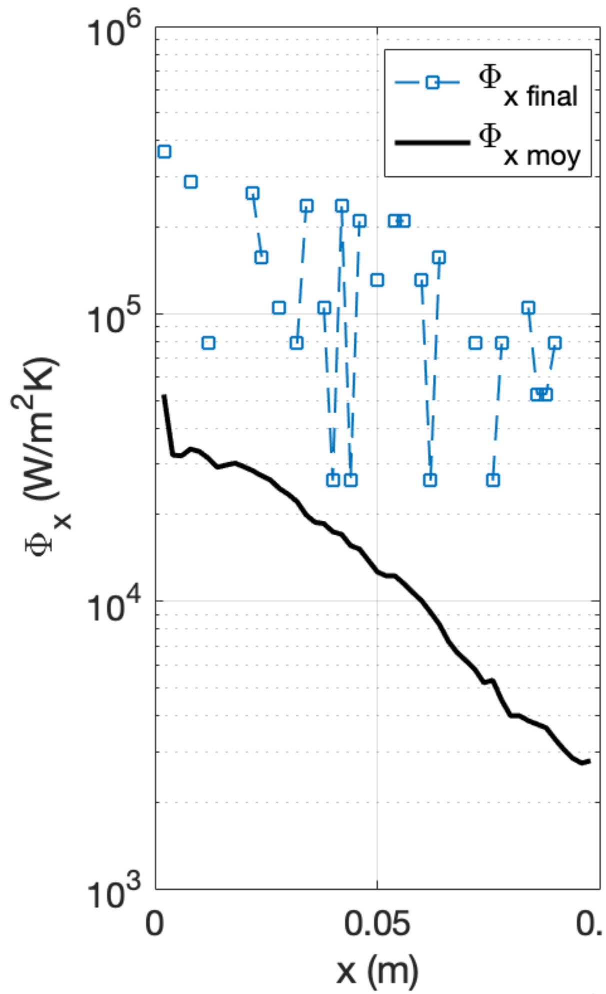
Heat transport, Monte Carlo methods 6

Transient state can be recovered



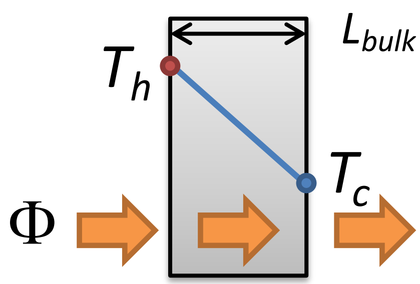




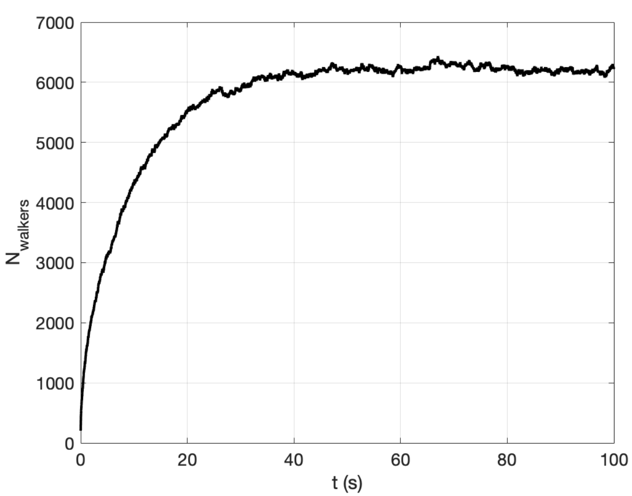


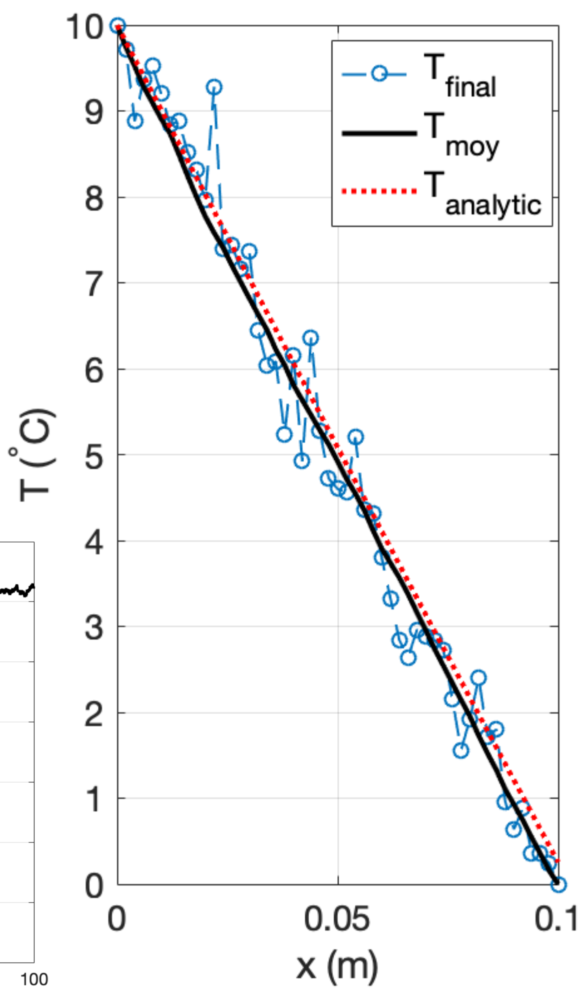
Heat transport, Monte Carlo methods 7

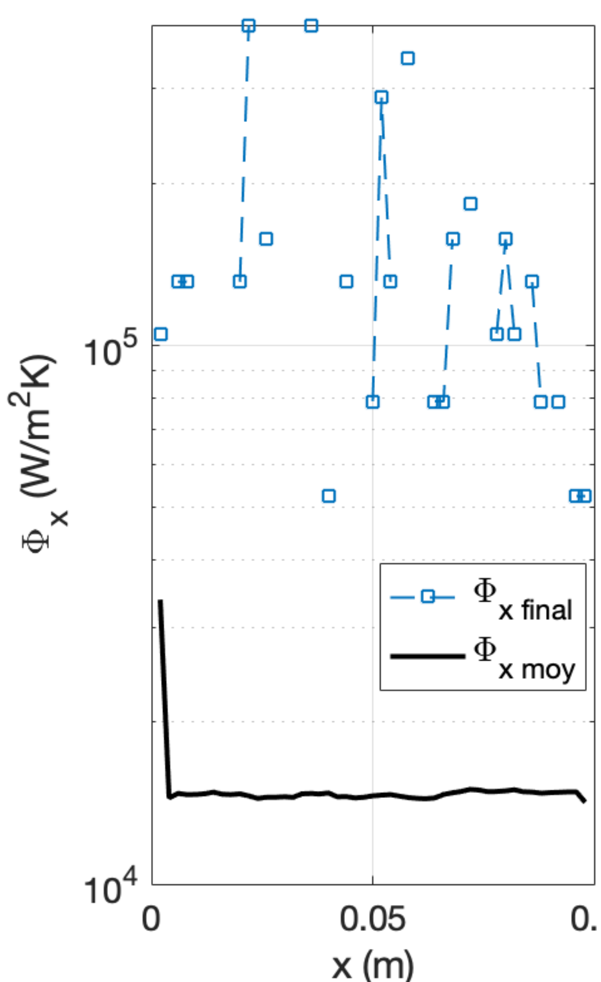
Steady state is recovered



k_{MC} = 151.25 W/mK







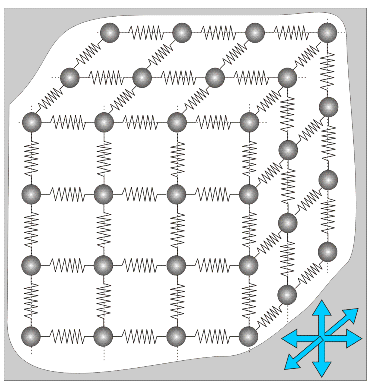
Monte Carlo technique to solve the Boltzmann transport equation for phonons

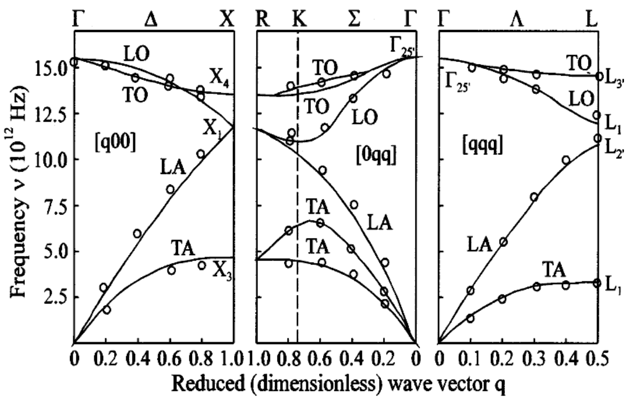
Phonons and heat propagation

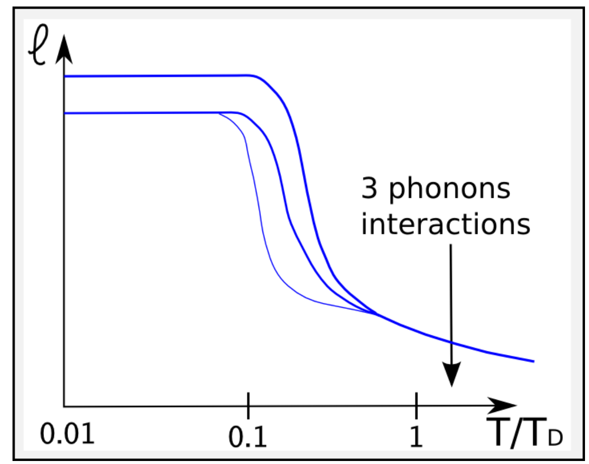
In semiconductors “phonons” are quasiparticles that characterize the vibrational motions of a lattice. They propagate heat and can be either considered as wave or particles.

$\Lambda \equiv \ell$: phonon mean free path

Vibration ↔ Dispersion relations



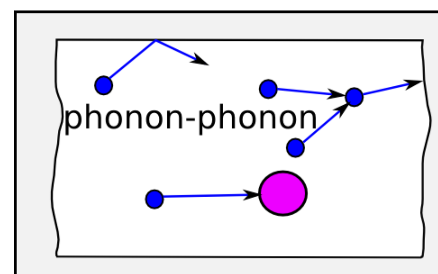




Kinetic model for thermal conductivity:

$$k = \frac{1}{3}\rho\, C\, v_g\, \Lambda \quad ; \quad \Lambda = v_g \tau$$

Scattering mechanisms



Boltzmann transport equation for phonons

Phonons obey to the **Boltzmann Transport Equation (BTE)**. When considered as particles their motion and interactions (scattering) in nanostructures depends on: temperature, dispersion properties and scattering lifetimes of the considered material.

The BTE is solved in the frame of the relaxation time approximation by a Monte Carlo method.

BTE

$$\frac{\partial \mathrm{f}}{\partial t} + \nabla_{\mathrm{K}} \omega \cdot \nabla_{\mathrm{r}} \mathrm{f} + F \cdot \nabla_{\mathrm{p}} \mathrm{f} = \left.\frac{\partial \mathrm{f}}{\partial t}\right|_{scat}$$

Relaxation time approximation

$$\left.\frac{\partial \mathrm{f}}{\partial t}\right|_{scat} = \frac{\mathrm{f}_{\omega} - \mathrm{f}_{\omega}^{0}}{\tau(\omega)}$$

$\mathbf{f}$ is the distribution function
$\leftrightarrow$ number of phonons

$$\mathrm{N}(t,\mathrm{r}) = \frac{1}{V} \sum_{\mathrm{K}} \mathrm{f}(t,\mathrm{r},\mathrm{K})$$

Problem: $\tau(\omega)$ appraisal is not explicit. Analytic expressions can be found for some bulk materials (Si, Ge, GaN, C, etc) but littérature is poor for complex compounds

Solution? Ab-initio calculation of τ

Monte Carlo solution of the BTE

The MC solution of the BTE for phonons lies on several steps:

Initialization

- Design of the nanostructure geometry and discretization
- Prescription of boundary conditions
- Initialization of the phonon state in the discretized cells

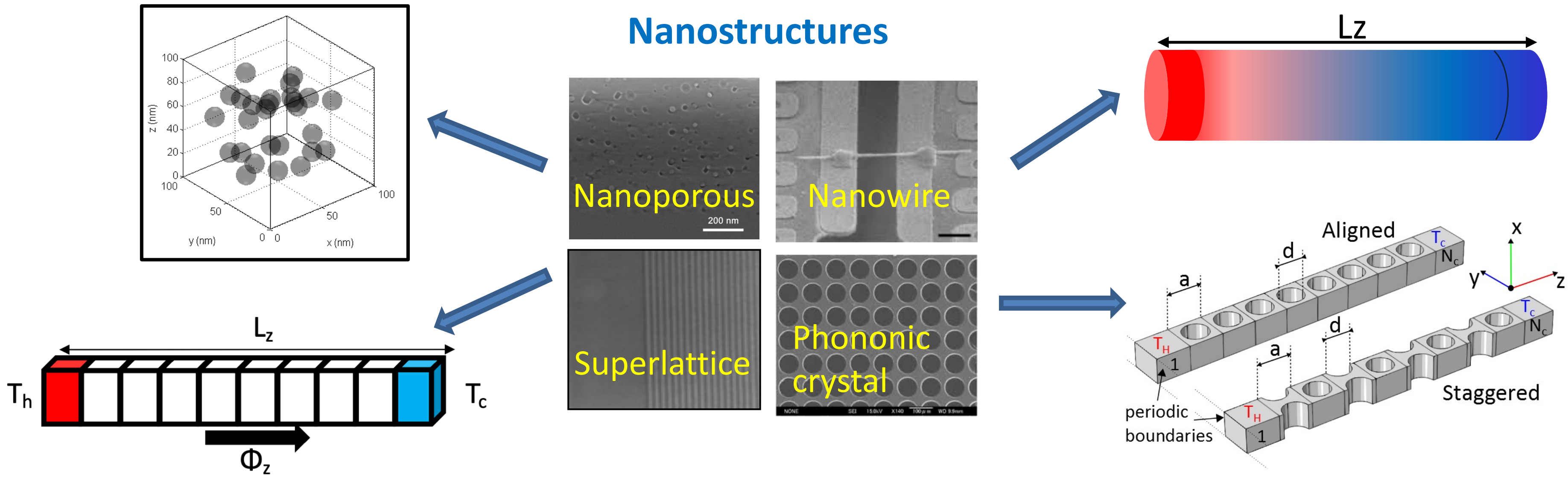
Iterative process

- Motion of phonon during a time step
- Scattering of phonon to restore thermodynamic equilibrium
- Calculation of local temperature and heat flux

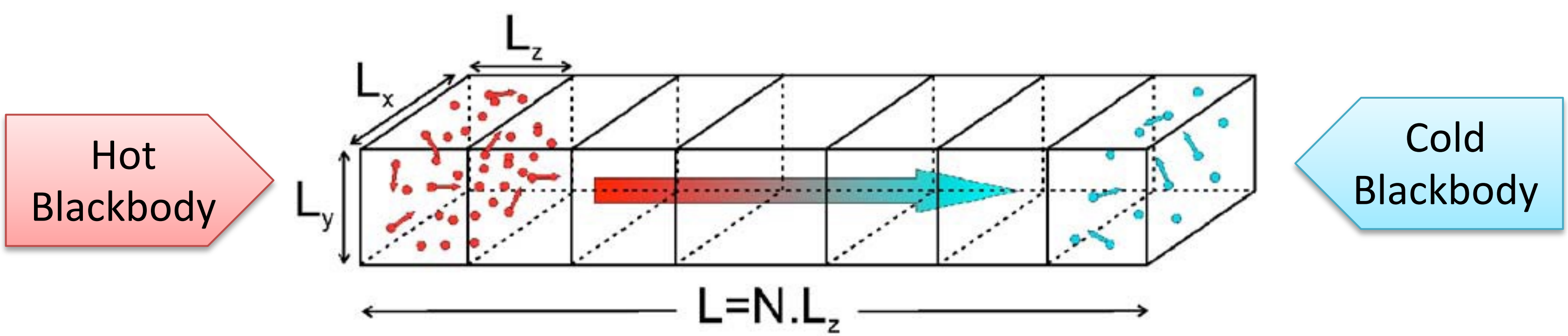
Post-processing

- Derivation of thermal conductivity
- Assessment of other quantities (phonon spectrum vs mfp, phonon phase function, etc)

Monte Carlo solution of the BTE - initialization



Structures are discretized taking into account periodicities
Temperatures are prescribed in first and last cells (blackbodies)

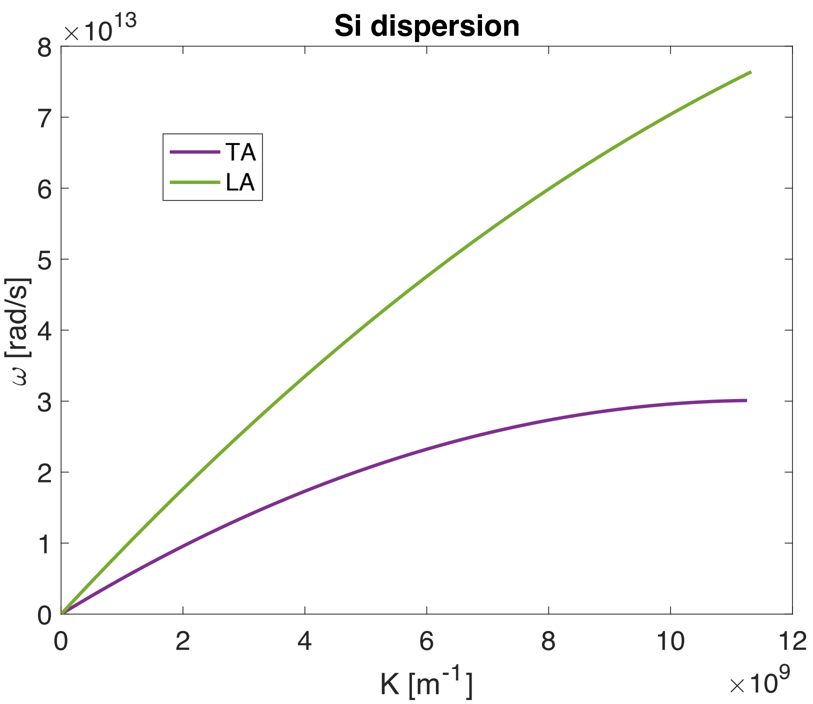


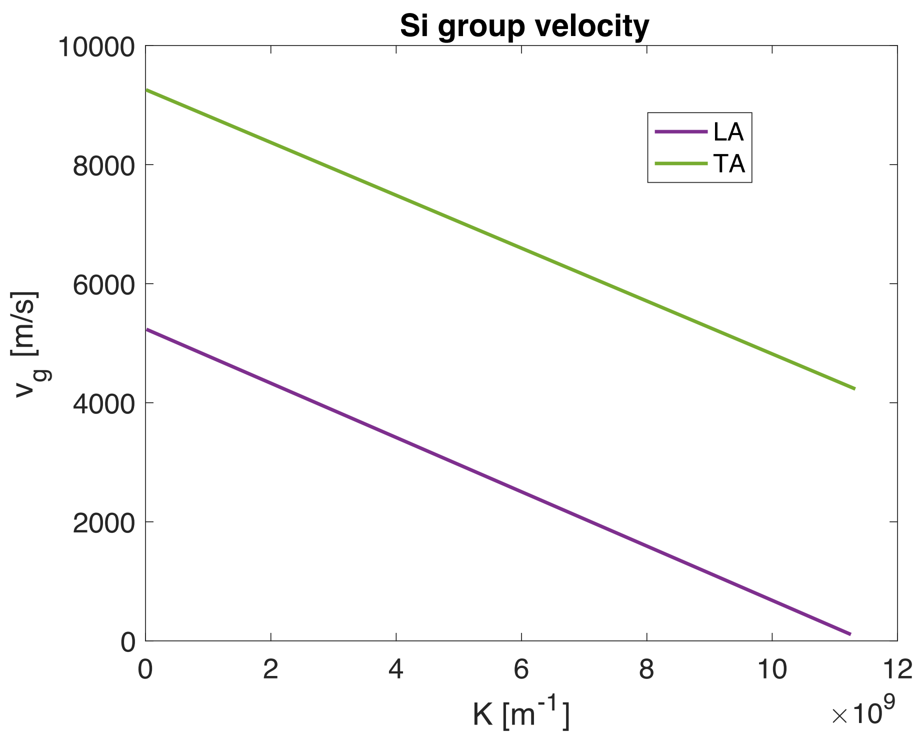
Monte Carlo solution of the BTE - initialization

Temperatures are prescribed in first and last cells (blackbodies)

➡ **Phonon energy is known at the initial stage**

Density of state $D_p(\omega) = \frac{K^2 V}{2\pi^2 V_g}$





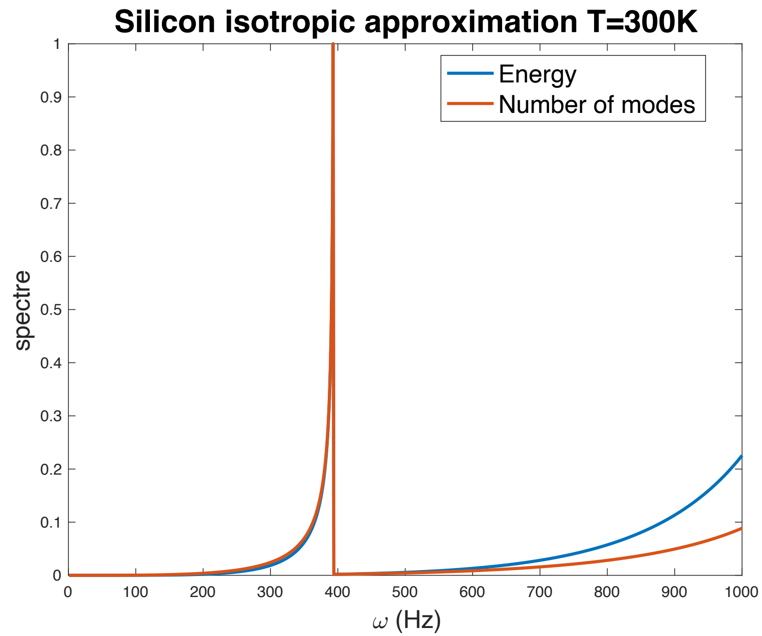
Energy within a cell

$$E = \int_\omega \sum_p \frac{1}{\exp(\hbar\omega/k_B T) - 1} D_p(\omega) g_p \hbar\omega \, d\omega$$

Number of mode within a cell

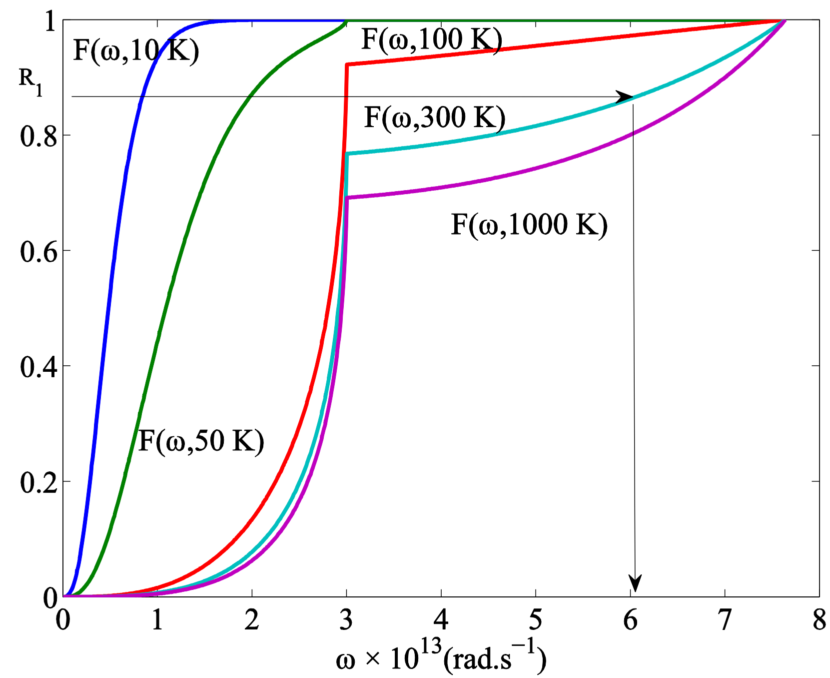
$$N = \int \sum_p \frac{1}{\exp(\hbar\omega/k_B T) - 1} D_p(\omega) g_p \, d\omega$$

Monte Carlo solution of the BTE - initialization



Energy within a cell

Number of modes within a cell



Cumulative distribution function

$$F(X)=\frac{\int_0^X \sum_p f^0(\omega,T)D_p(\omega)g_p\hbar\omega\, d\omega}{\int_0^{\omega\max} \sum_p f^0(\omega,T)D_p(\omega)g_p\hbar\omega\, d\omega}$$

1. Sampling of a phonon population (energy bundles) at a given temperature T, according to dispersion relations (isotropic). Random location of phonons.

Monte Carlo solution of the BTE – transport and scattering

1. Sampling of a phonon population (energy bundles) at a given temperature T, according to dispersion relations (isotropic). Random location of phonons.

$$E = \int_{\omega} \sum_p \frac{1}{\exp(\hbar\omega / k_B T) - 1} D_p(\omega) g_p \hbar\omega \, d\omega$$

Number sampling

$$N_{tot} = {}^{N_{th}}/_{W_n}$$

Energy sampling

$$N_{tot} = {}^{E_{th}}/_{\delta E} = W_e$$

ω, p, v_g

$\mathcal{R}_1 \Leftrightarrow \omega$ with $F(\omega)$

$$P_{LA-TA} = {}^{N_{LA}}/_{(N_{LA} + N_{TA})}$$

$\mathcal{R}_2 < P_{LA-TA} \Leftrightarrow p = LA$
$\mathcal{R}_2 > P_{LA-TA} \Leftrightarrow p = TA$

ω, p known $\Rightarrow v_g$ from dispersion

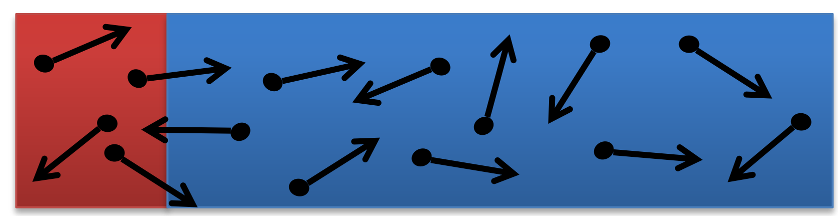
$\mathcal{R}_3, \mathcal{R}_4, \mathcal{R}_5 \Leftrightarrow x, y, z$

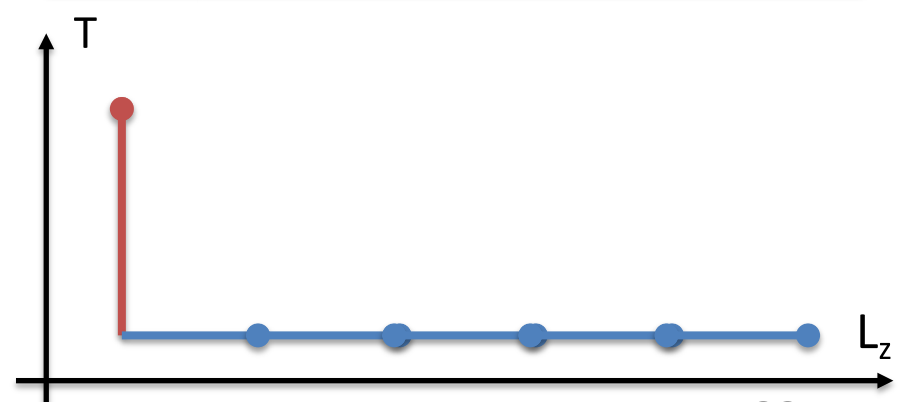
Number sampling

$$E_{MC-n} = \sum_{i=1}^{N_{tot}} \hbar\omega_i$$

Energy sampling

$$E_{MC-e} = \sum_{i=1}^{N_{tot}} \delta \mathrm{E}$$

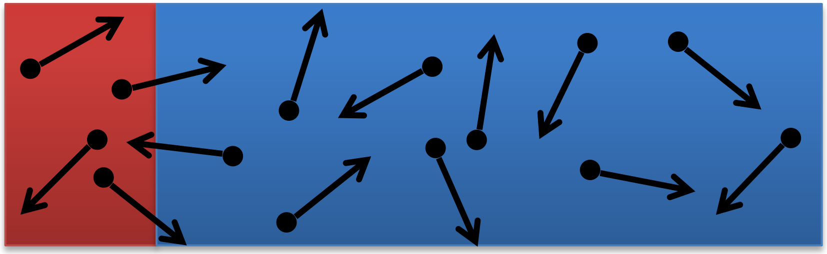




Monte Carlo solution of the BTE – transport and scattering

2. Follow phonon displacement according to their group velocity and boundary conditions

$$\frac{\partial f}{\partial t} + \nabla_K \omega \cdot \nabla_r f + F \cdot \nabla_p f = \left.\frac{\partial f}{\partial t}\right|_{scat}$$

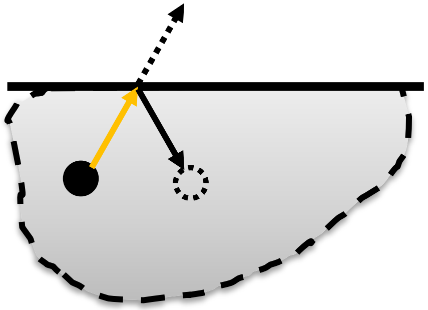


$$r(t+\delta t) = r(t) + v_g(\omega, p)\,\delta t$$

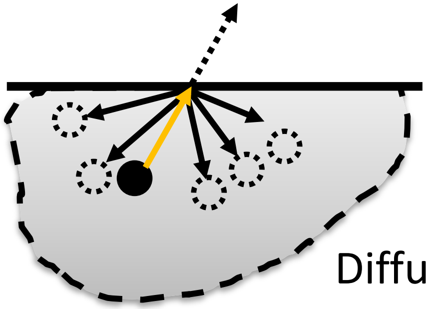
Two possibilities:

- Free displacement along initial propagation direction
- Collision with a boundary (edge of the system, pore, inclusion, etc.)

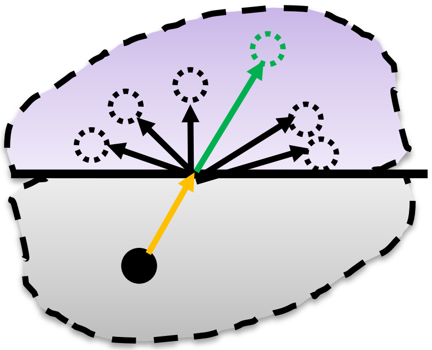
Free displacement



Specular reflection



Diffuse reflection

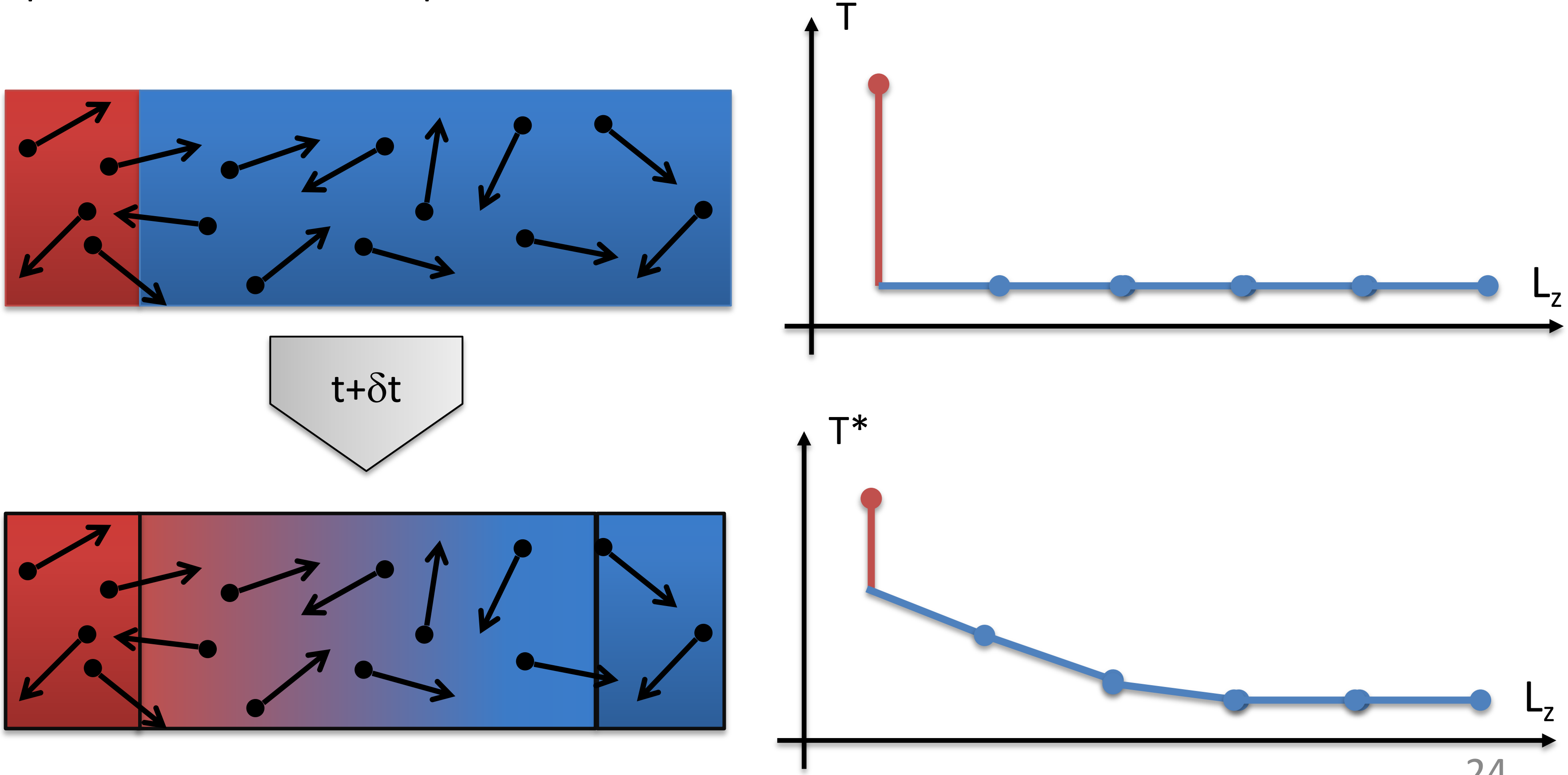


Diffuse or specular transmission

Monte Carlo solution of the BTE – transport and scattering

2. After displacement (drift stage) “local pseudo” Temperature T* (out of equilibrium) is computed in each cell of the domain.

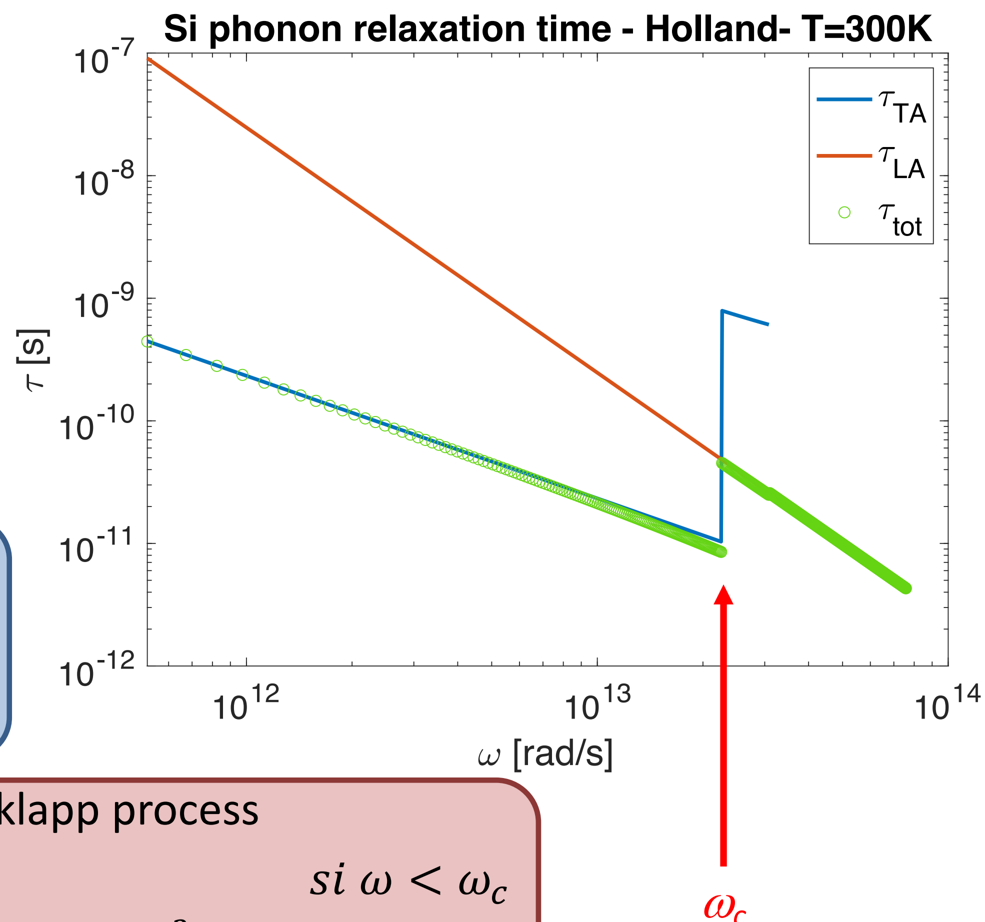
All the phonons are displaced within the structure; they carry a part of the energy that depends on the local temperature.



Monte Carlo solution of the BTE – transport and scattering

3. Proceed to phonon scattering with respect to the Matthiesen rule, calculation of E and T

$$\tau(\omega,p,T)^{-1} = \sum_{process} \tau_{process}(\omega,p,T)^{-1}$$



Lifetimes of scattering processes (Normal, Umklapp, Impurity) are derived from M.G. Holland for Si and Ge

M.G. Holland, PR ***132****, 2461-2471*

Normal process

$$\tau_{N,LA}^{-1} = \tau_{U,LA}^{-1} = B_L \omega^2 T^3$$

$$\tau_{N,TA}^{-1} = B_{TN} \omega T^4$$

Impurity

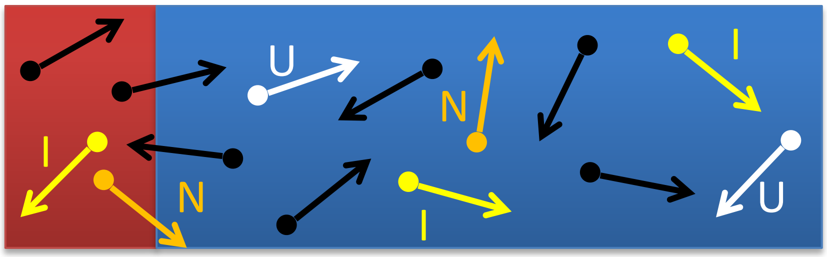
$$\tau_I^{-1} = B_I \omega^4$$

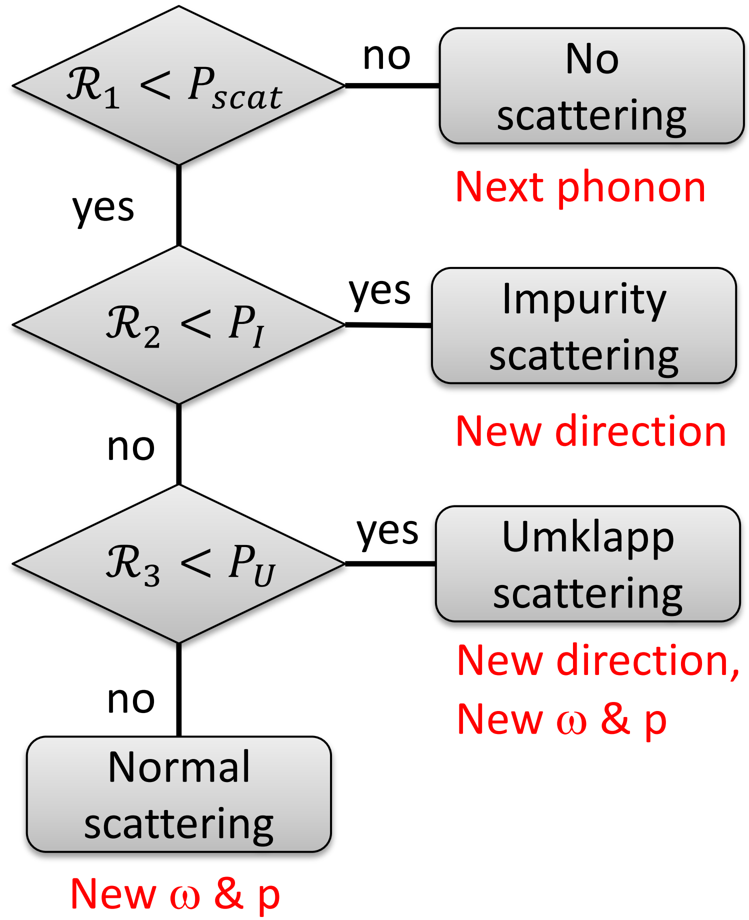
Umklapp process

$$\tau_{U,TA}^{-1} = \begin{cases} 0 & si\ \omega < \omega_c \\ B_{TU} \times \dfrac{\omega^2}{\sinh(\hbar\omega/k_B T)} & si\ \omega > \omega_c \end{cases}$$

Monte Carlo solution of the BTE – transport and scattering

3. Proceed to phonon scattering with respect to the Matthiesen rule, calculation of E and T





Scattering probability is randomly addressed

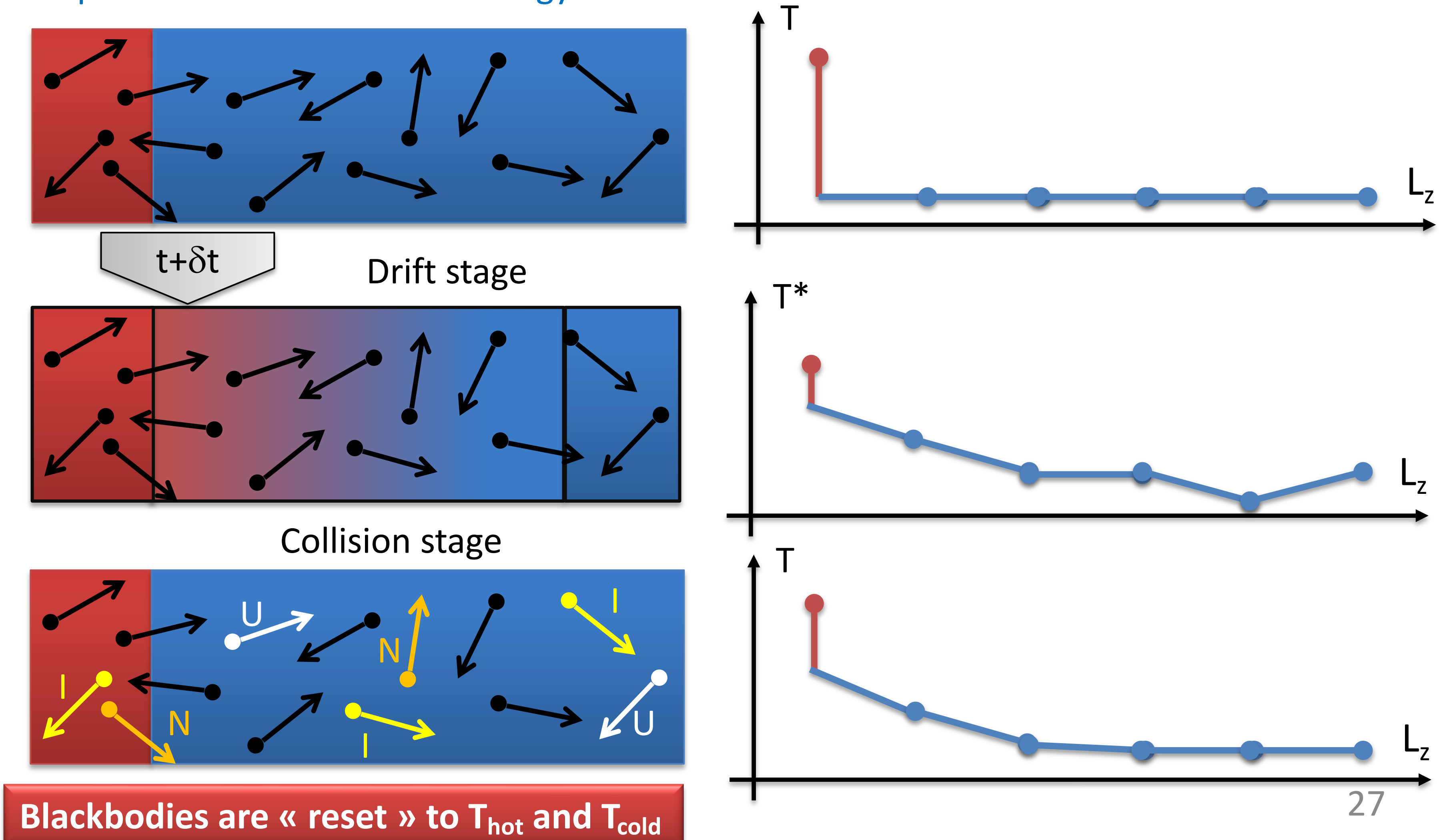
$$P_{scat} = 1 - \exp\left[\frac{-\delta t}{\tau(\omega, p, T)}\right]$$

$$P_{I,p}(\omega, T^*) = \frac{\tau_I^{-1}(\omega)}{\tau_I^{-1}(\omega) + \tau_{N,p}^{-1}(\omega, T^*) + \tau_{U,p}^{-1}(\omega, T^*)}$$

$$P_{U,p}(\omega, T^*) = \frac{\tau_{U,p}^{-1}(\omega)}{\tau_{N,p}^{-1}(\omega, T^*) + \tau_{U,p}^{-1}(\omega, T^*)}$$

Monte Carlo solution of the BTE – transport and scattering

2. After scattering, the energy in each cell is calculated, as well as phonon heat flux, temperature is derived from energy.



Monte Carlo solution of the BTE – post processing

4. Extract T and Φ according to the local phonon distribution in the nanostructure

$$\Phi_z = \sum_{i=1}^{N} \frac{\hbar \omega_i V_{gz}}{V}$$

Silicon nanofilm

Lz = 2µm

δt = 1ps

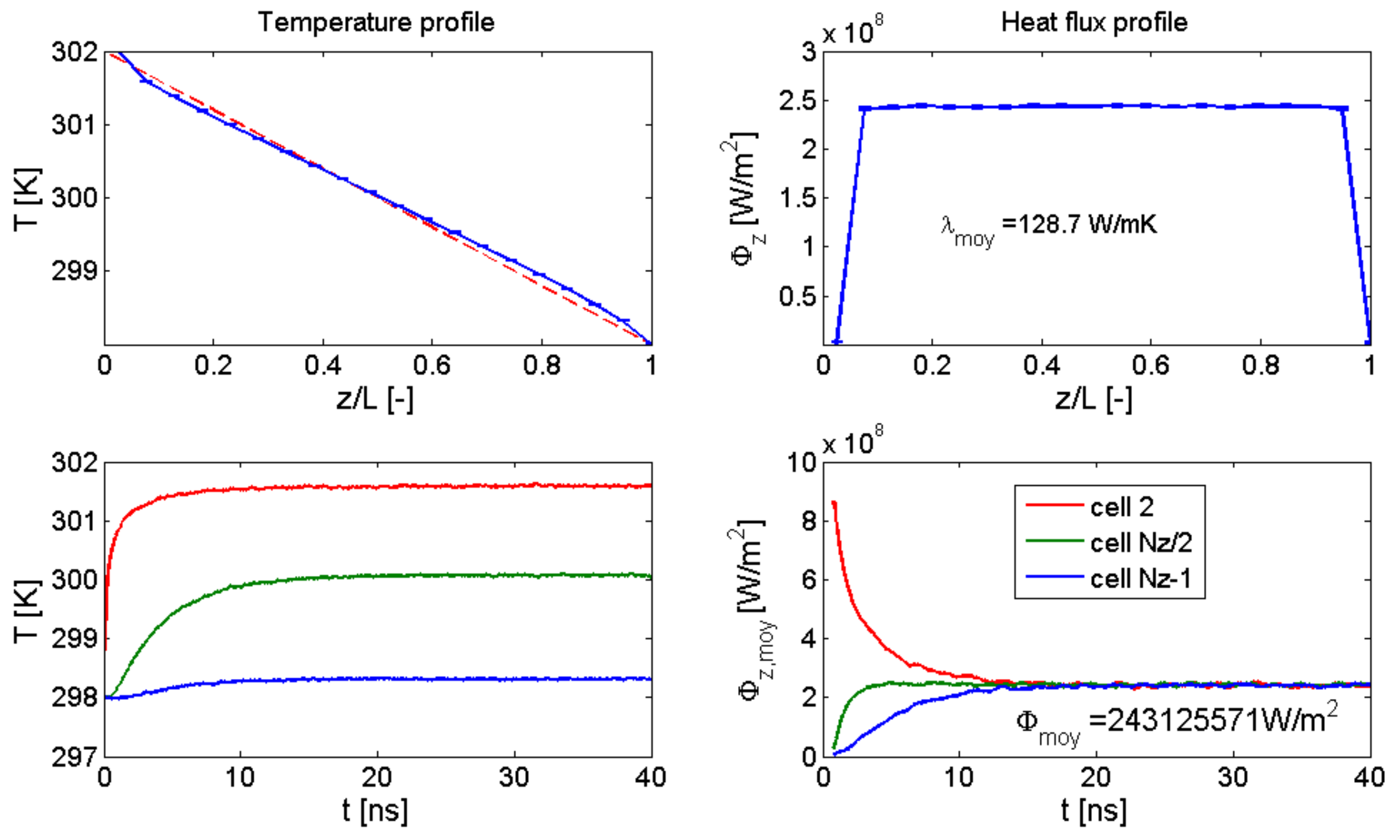
Nz = 20 cells

40000 time steps

8 cores / 6 hours

Cross plane TC

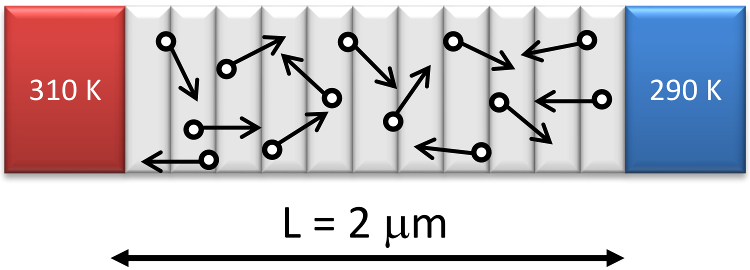
k = 128.7 W/m K



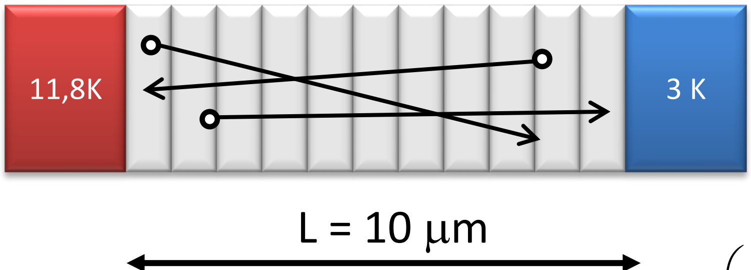
Application of MC-BTE tool to appraise thermal properties in nanostructures

Monte Carlo simulations – Nanofilms 1

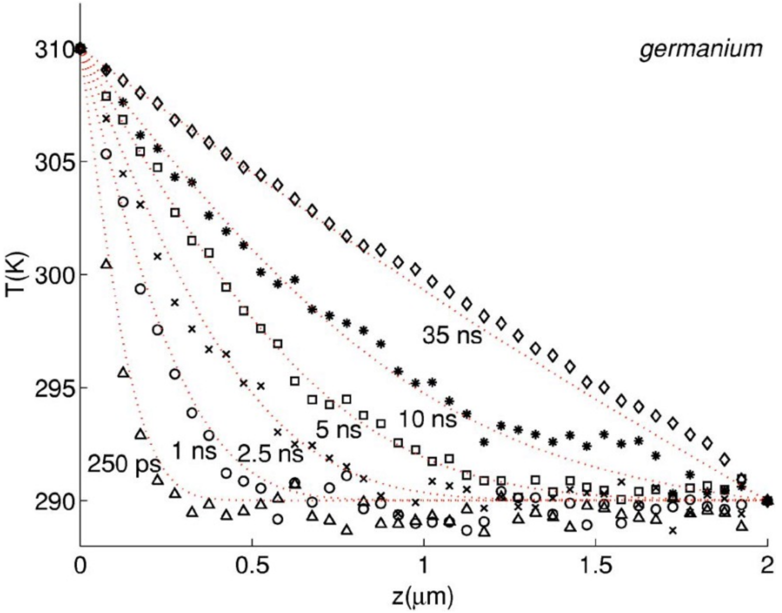
Diffuse regime

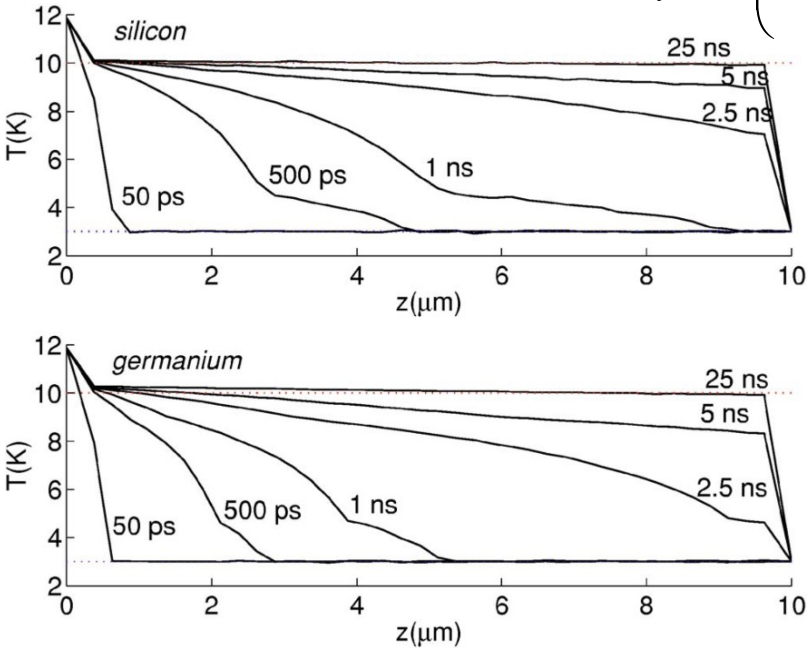


Ballistic regime



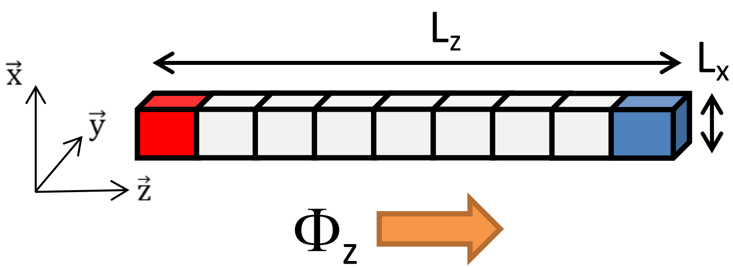
$$T_{final} = \left(\frac{T_c^4 + T_f^4}{2} \right)^{1/4}$$





*D. Lacroix, PRB **72**, 064305, 2005*

Monte Carlo simulations – Nanofilms 2



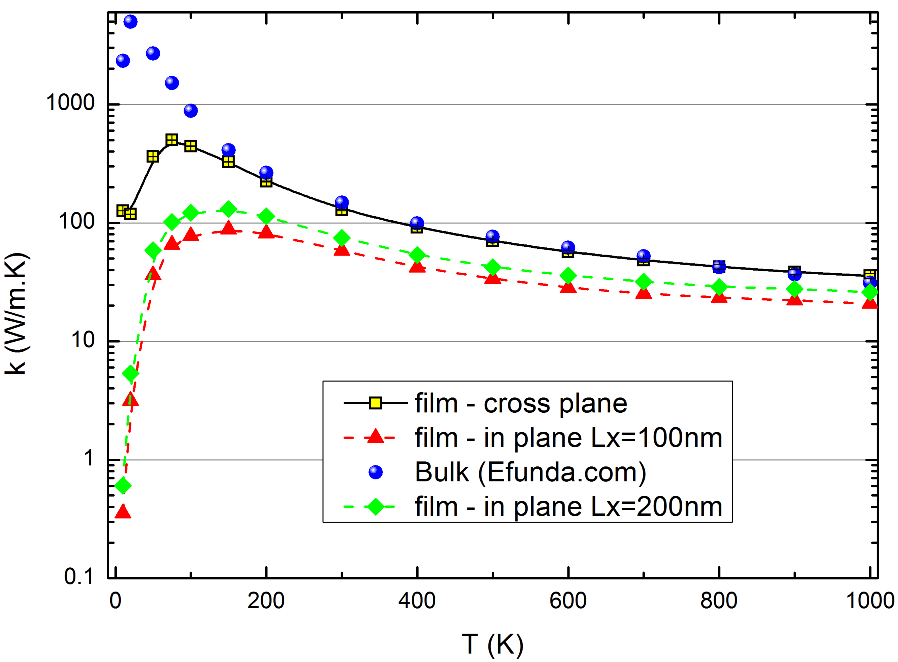
Rx, Ry: reflections
D: diffuse
S: Specular

Film In-plane: Rx = D, Ry = S

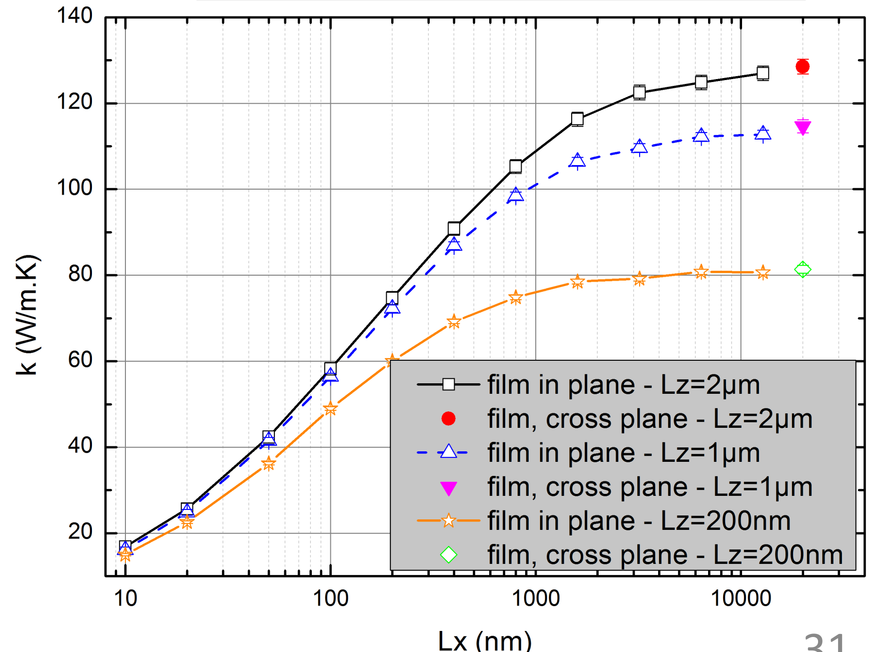
Wire: Rx = D, Ry = D

Bulk /film Cross-plane: Rx = S, Ry = S

Thermal conductivity in Si vs T; Lz = 2µm

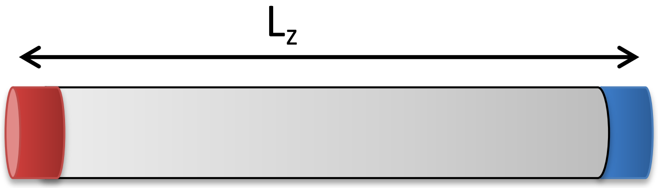


In-plane & cross-plane TC in Si film vs Lx

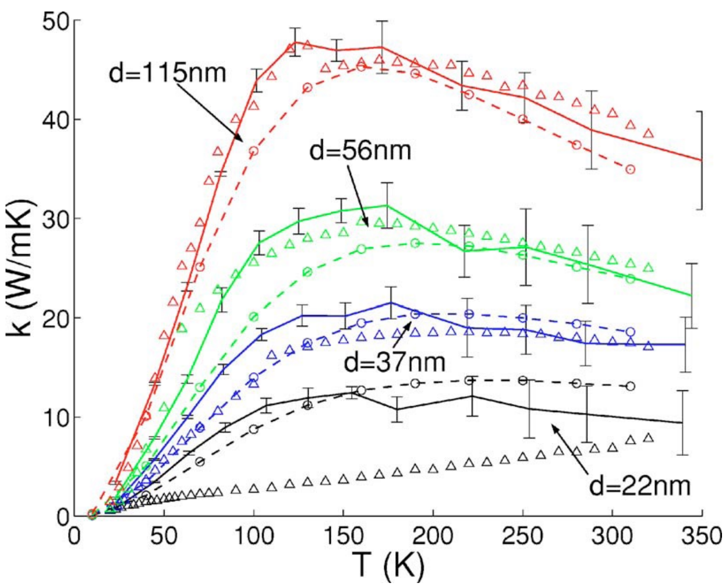


Monte Carlo simulations – Nanowires 1

Smooth nanowires



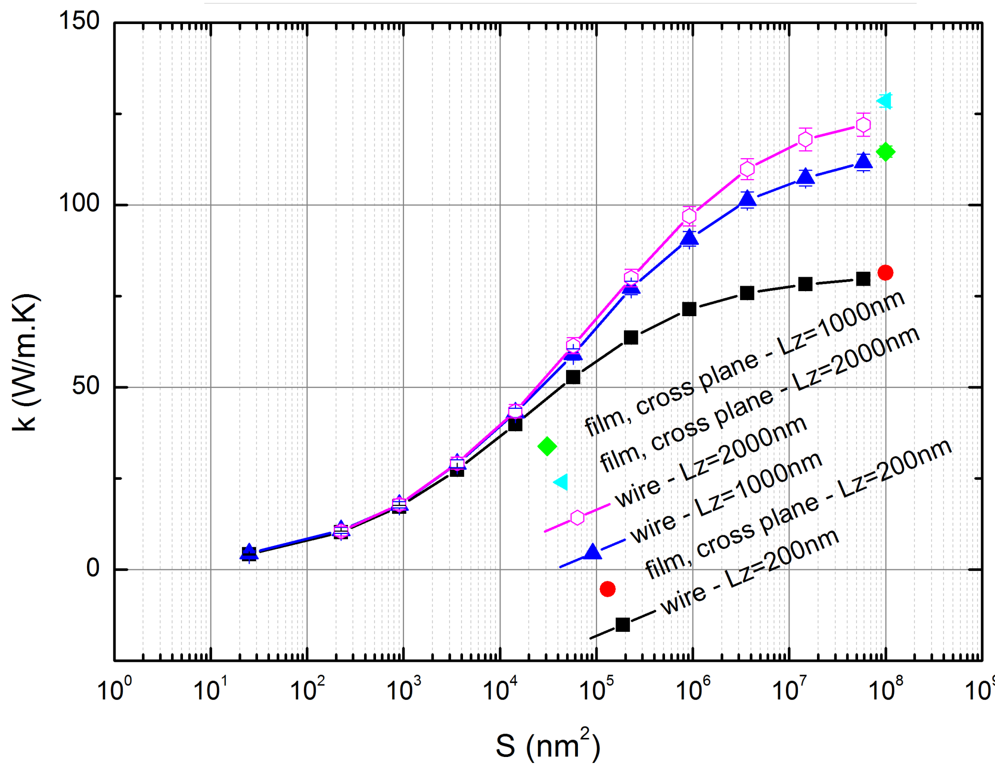
Si nanowire TC vs T



*D. Lacroix, APL **89**, 103104*

*D. Li, APL **83**, 2934*

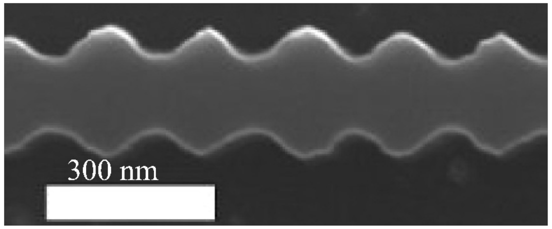
Si nanowire TC vs cross-section



Simulations match experiments, except for very thin diameters (bulk limit)

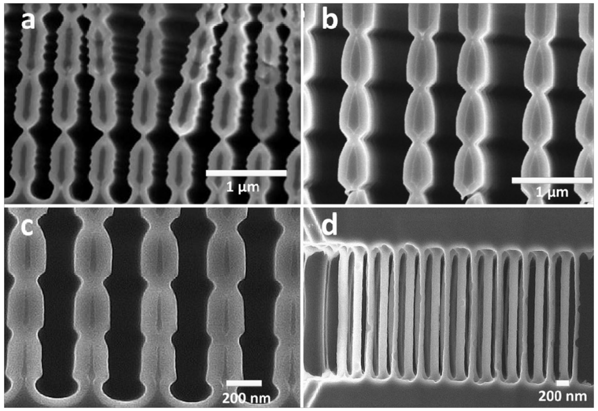
Monte Carlo simulations – Nanowires 2

Corrugated and modulated nanowires



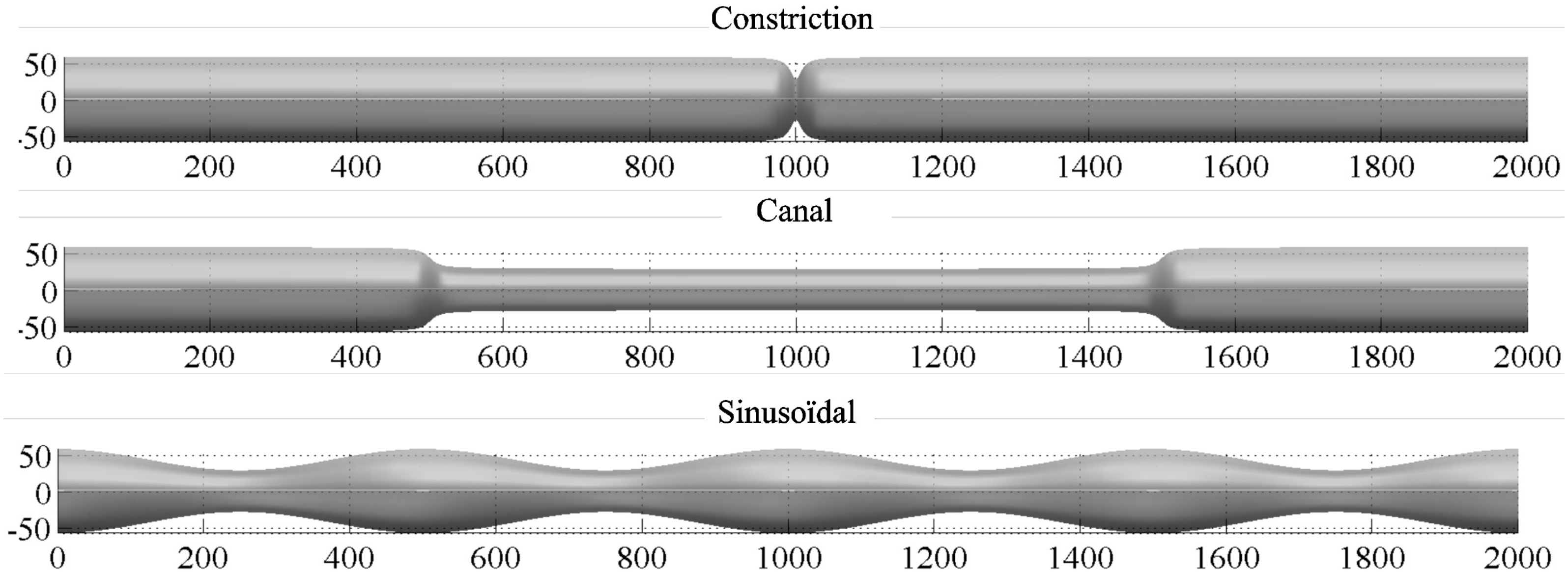
*C. Blanc, APL **103**, 043109*

Si Nanowires with shaped modulation



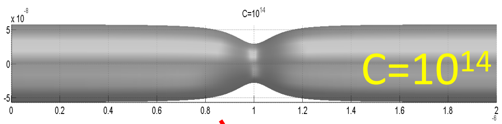
*E. Buitrago, Microelectronic Engineering **97**, 345–348*

MC design of modulated nanowires



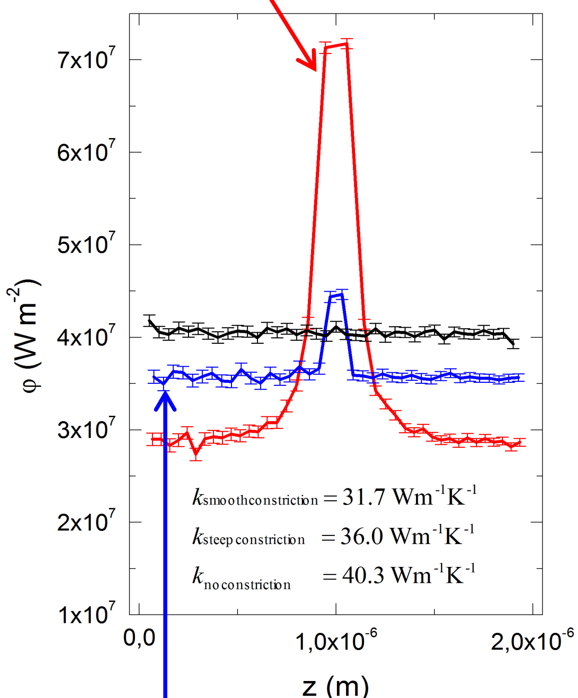
Monte Carlo simulations – Nanowires 3

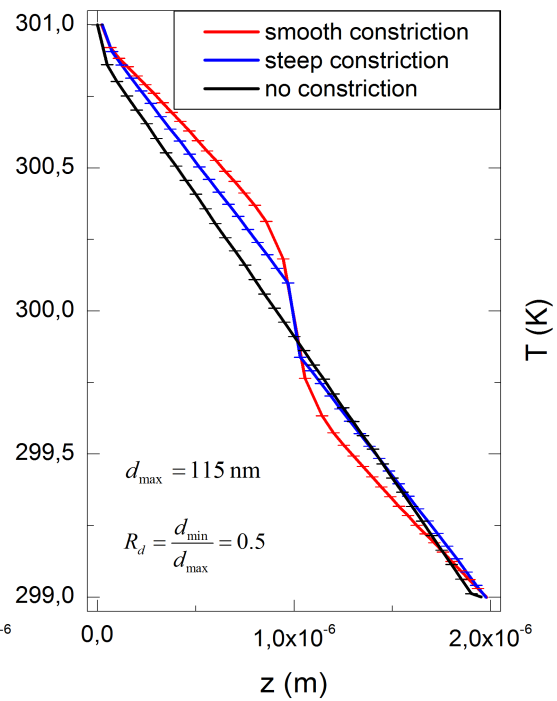
Smooth and steep constrictions

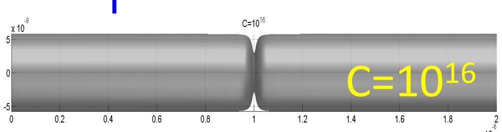


C is a constriction parameter

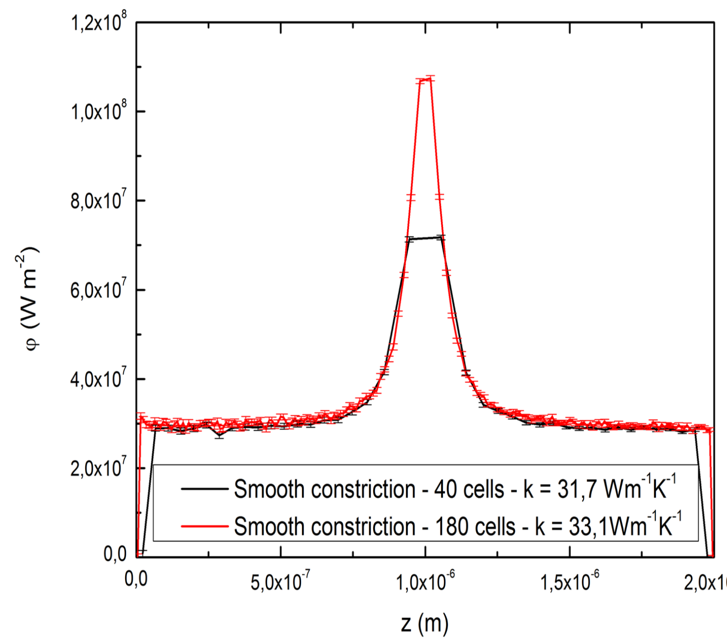
$$d(z) = d_{\max}\left[1 - \frac{(1-R_d)}{1 + C(z-z_0)^2}\right] \quad ; \quad R_d = \frac{d_{\min}}{d_{\max}}$$







Spatial discretization impact

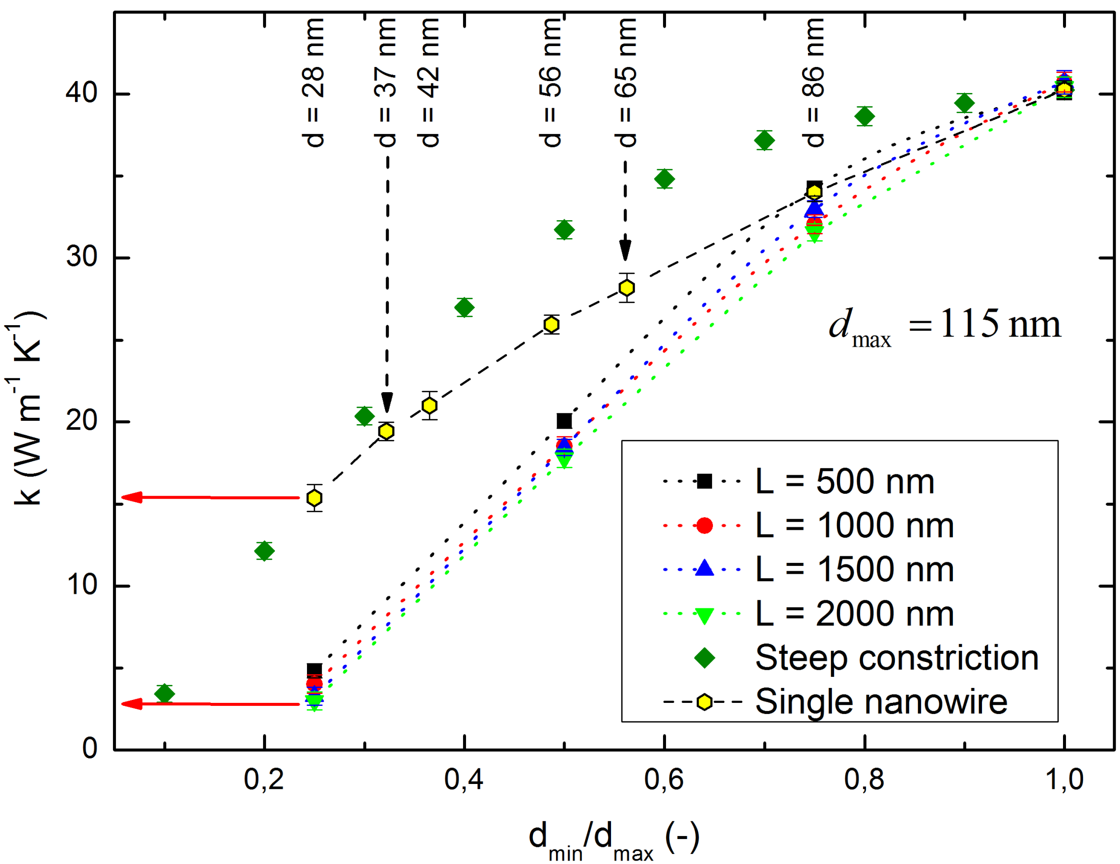


$k_{smooth} < k_{steep}$ ⇒ importance of Λ_b

*V. Jean, IJHMT **86**, 648-645*

Monte Carlo simulations – Nanowires 4

Long constriction 'canal shape'

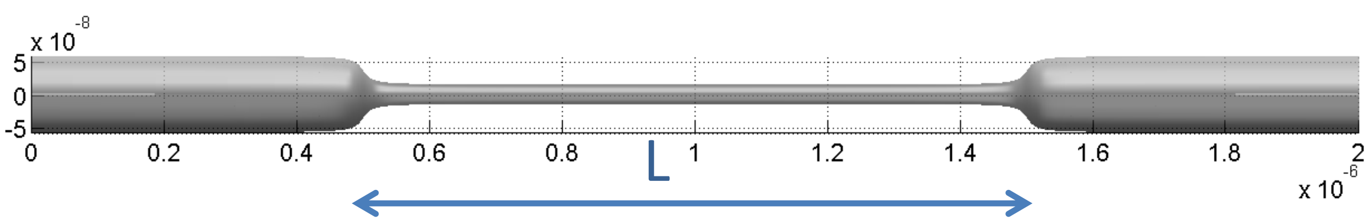


TC in canal NW smaller than in single NW with the minimal diameter

No significant effect of 'canal' length,

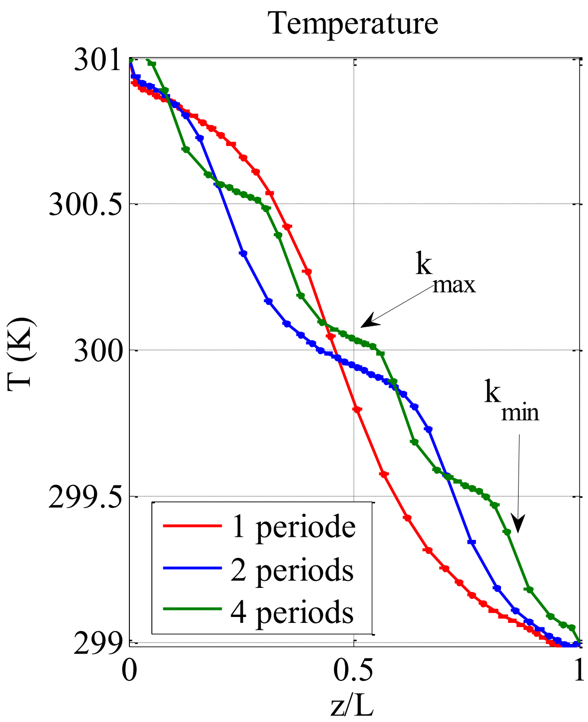
Constriction resistance

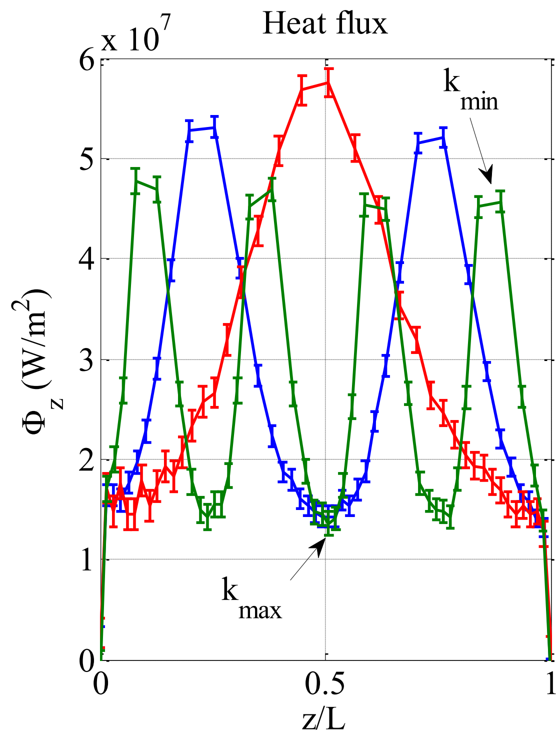
*V. Jean, IJHMT **86**, 648-645*

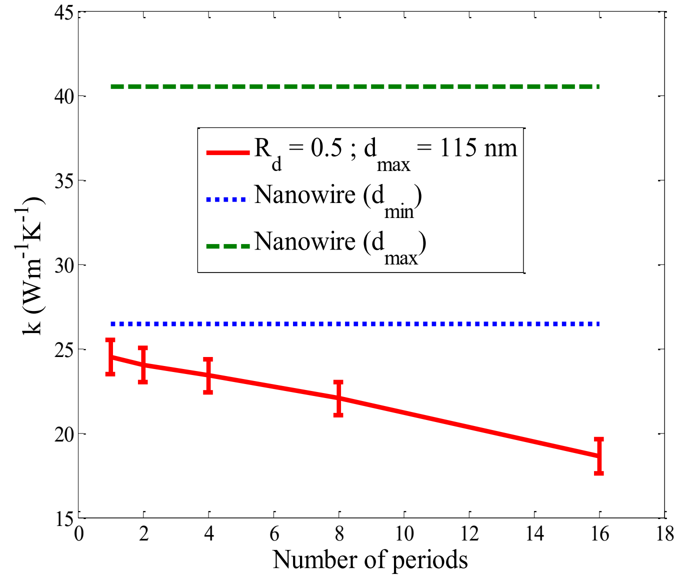


Monte Carlo simulations – Nanowires 5

Modulated nanowire

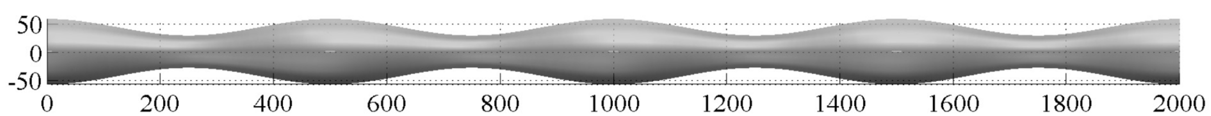






Increase of period number leads to a decrease of the thermal conductivity

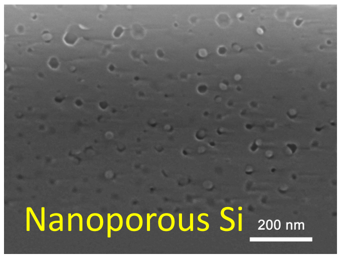
4 periods nanowire

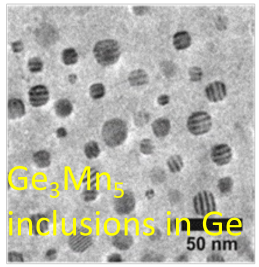


*V. Jean, IJHMT **86**, 648-645*

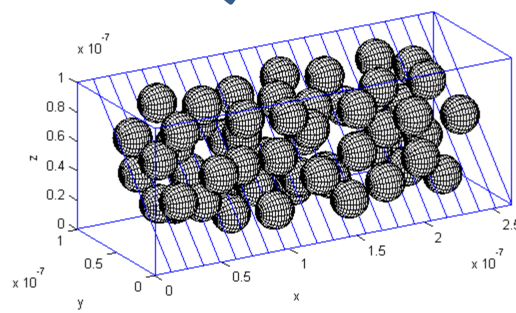
Monte Carlo simulations – Porous membranes

Porous membranes/membranes with inclusions

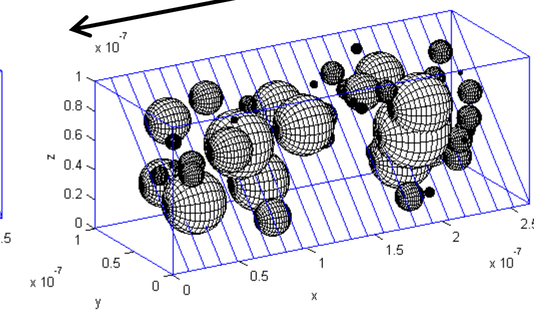




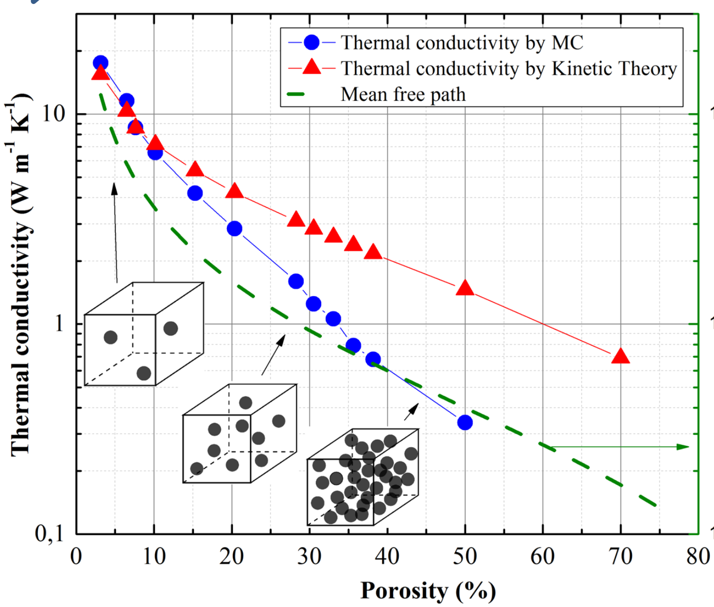
L_z =250nm



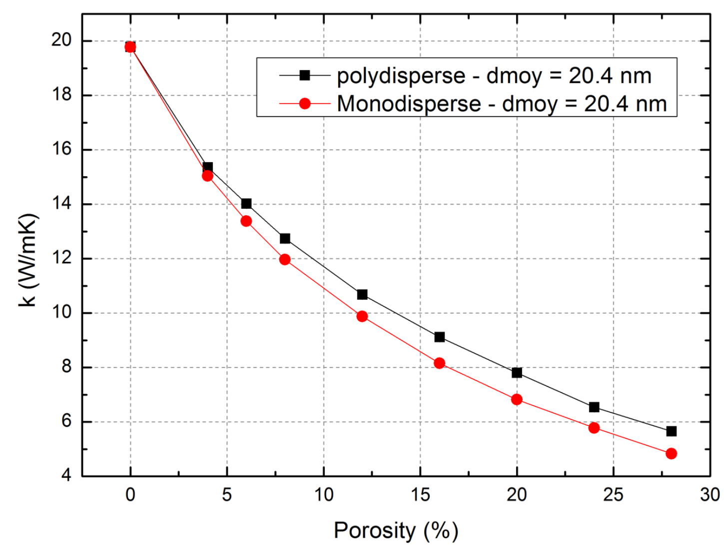
Monodisperse inclusions



Polydisperse inclusions



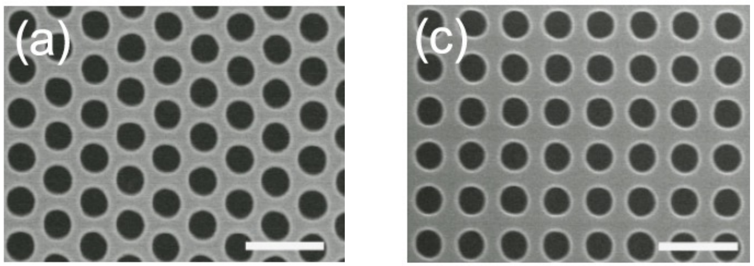
*V. Jean, JAP **115**, 024304*



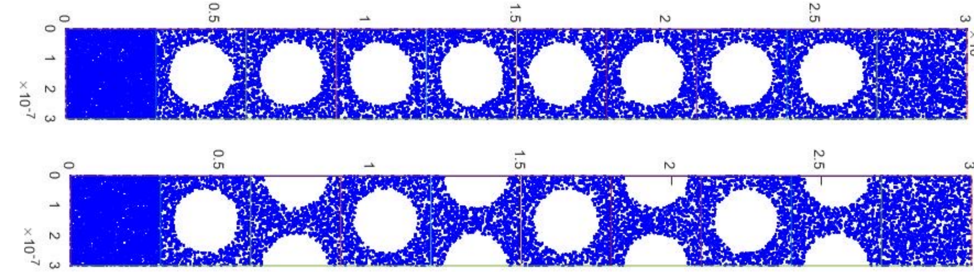
ANR Grant - Mesophon

Monte Carlo simulations – PnC membranes 1

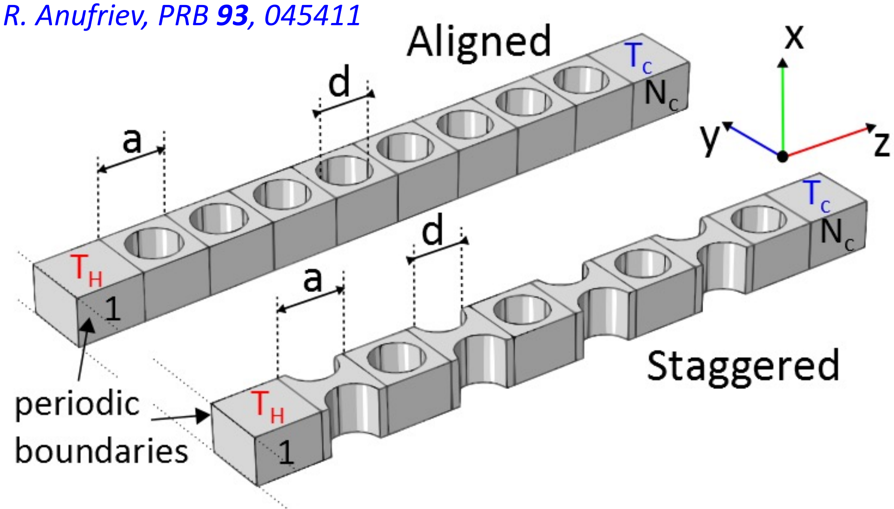
Phononic (PnC) Si membranes

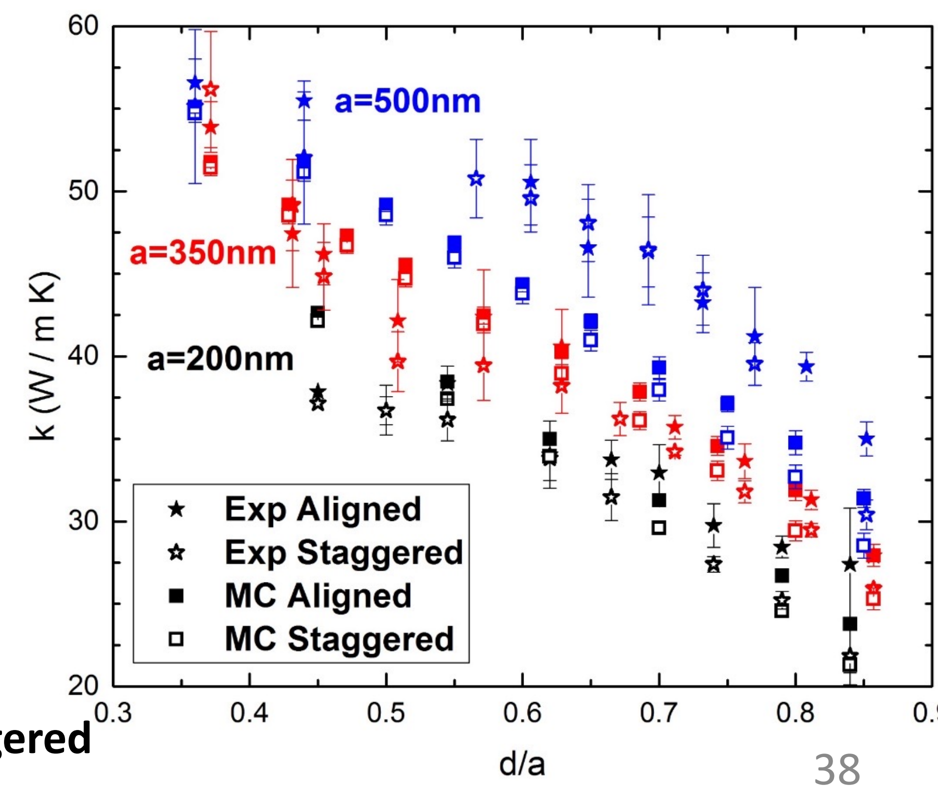


'Staggered' 'Aligned'



*R. Anufriev, PRB **93**, 045411*





Good agreement between experiments & simulations

The TC is always lower when pores are in staggered configuration for a same S/V ratio

Monte Carlo simulations – PnC membranes 2

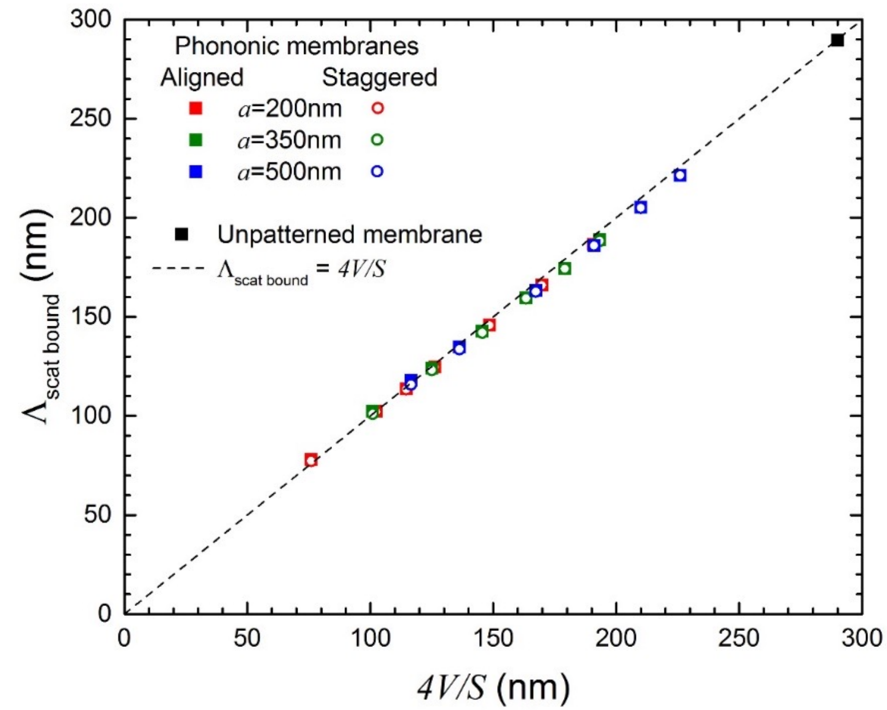
Boundary scattering mean free path as a function of the volume to surface scattering ratio

$$\Lambda_{scat\text{-}bound}(d,a,h) = \frac{v_g\,\delta t}{\ln\left(\frac{N_{ph}}{N_{ph} - N_{scat\text{-}bound}}\right)}$$

MC computing, ray tracing like method, million of phonons are launched ion one small time-step δt#0.1ps

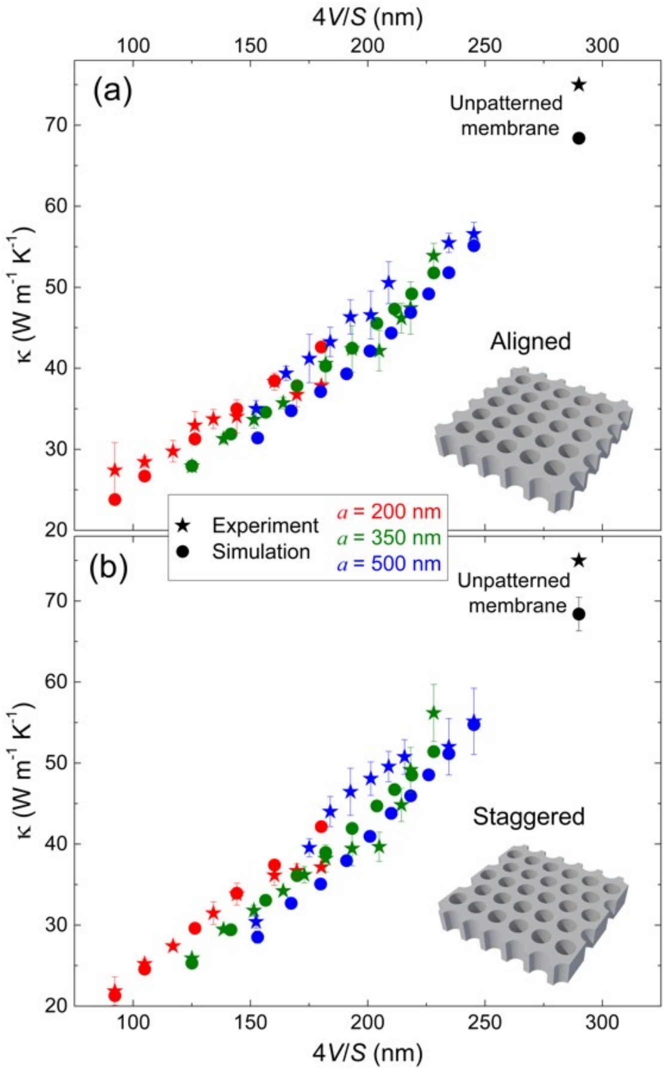
In case of diffusive heat conduction, the boundary scattering MFP is equal to four times volume-to-surface ratio.

$$\Lambda_{scat\text{-}boundh}(d,a,h) = \frac{4V}{S} = \frac{4ha^2 - \pi hd^2/4}{\pi hd + 2\left(a^2 - \pi d^2/4\right)}$$



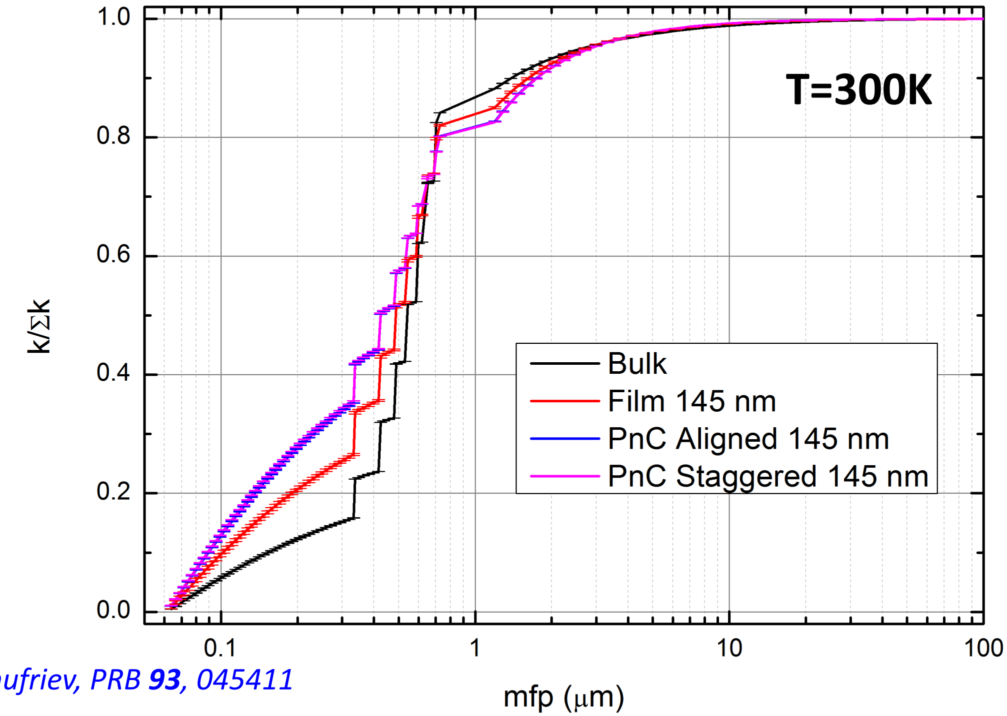
Linear trend, theoretical behavior is retrieved for diffuse medium as PnC membranes

Monte Carlo simulations – PnC membranes 3



Accumulated TC in PnC Si membranes

Extracted from MC computations, the contribution of phonon frequencies to the total TC



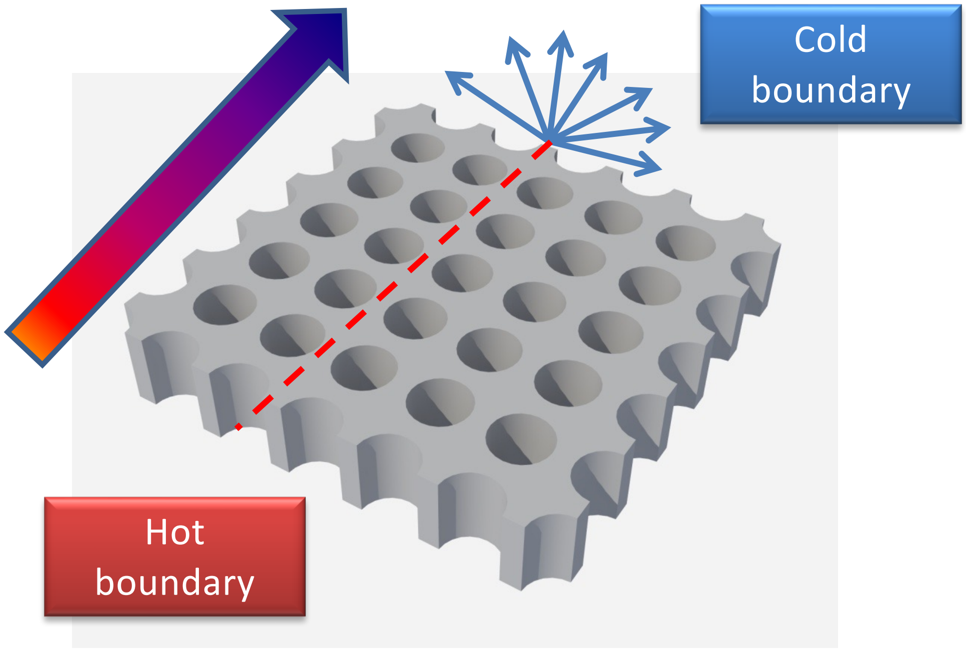
*R. Anufriev, PRB **93**, 045411*

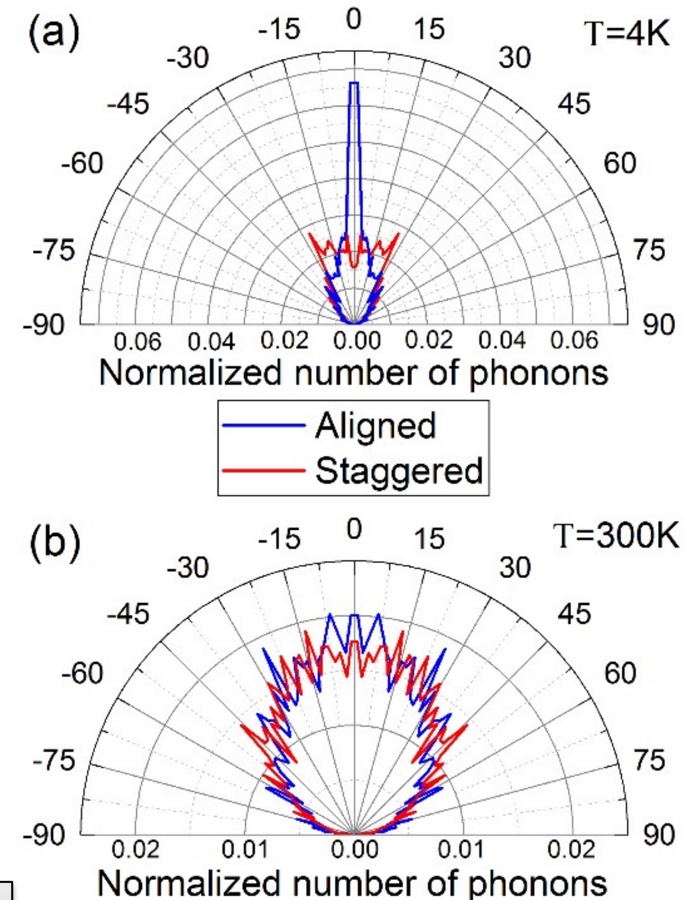
Bulk : 50% of TC due to phonon with mfp < 500nm
PnC : 65% of TC due to phonon with mfp < 500nm

Phonon transport in those membranes is mostly diffusive due to multiple diffuse boundary scattering processes

Monte Carlo simulations – PnC membranes 4

Angular distribution of transmitted phonons





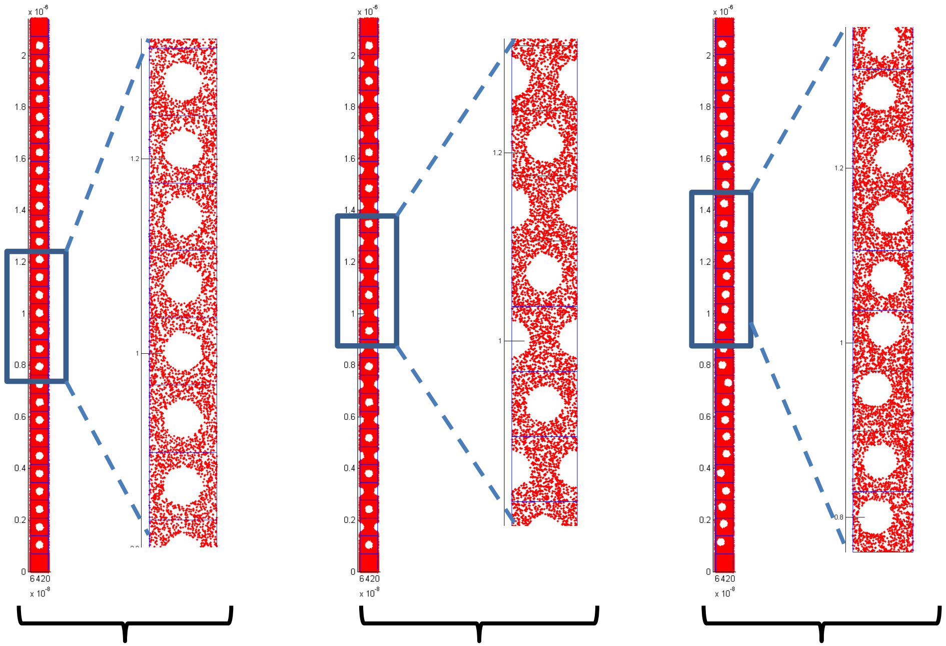
At low temperature, ballistic transport is either observed for aligned and staggered PnC. At room temperature, diffuse transport leads to isotropic distribution.

a=160nm; d=126nm

*R. Anufriev, PRB **93**, 045411*

MC simulations - Disordered porous membranes 1

Ordered - Disordered PnC membranes

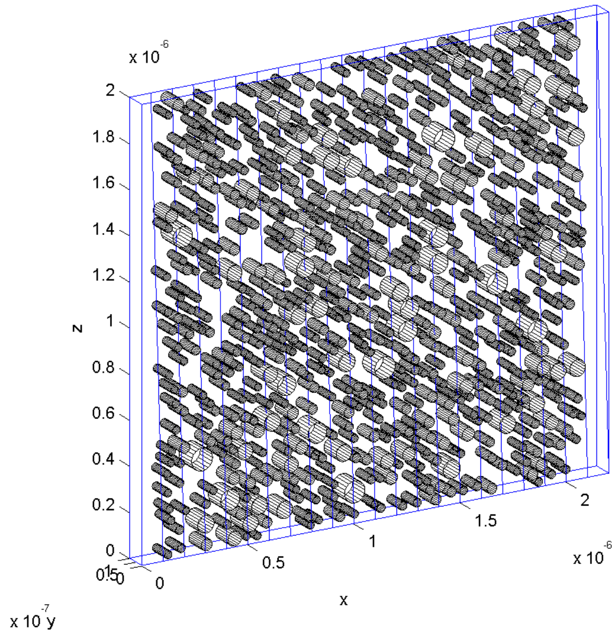


Aligned

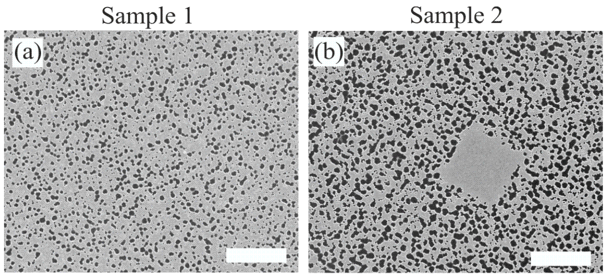
Staggered

Random

Highly disordered membranes, With polydispersed holes

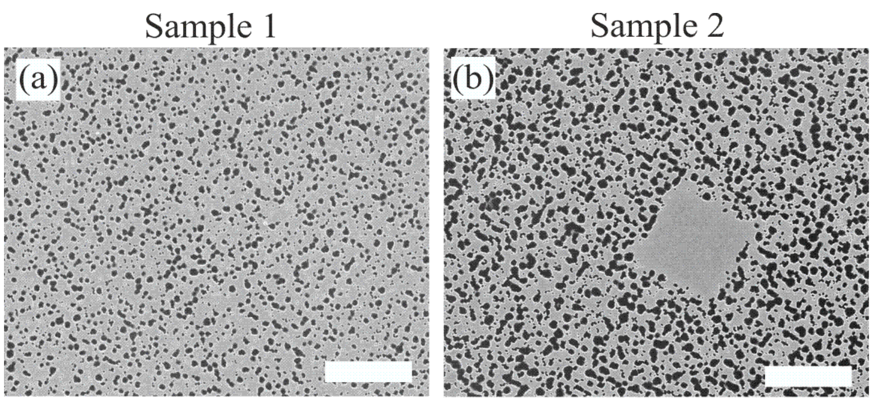


(Lx=100nm; Ly=Lz=2μm)

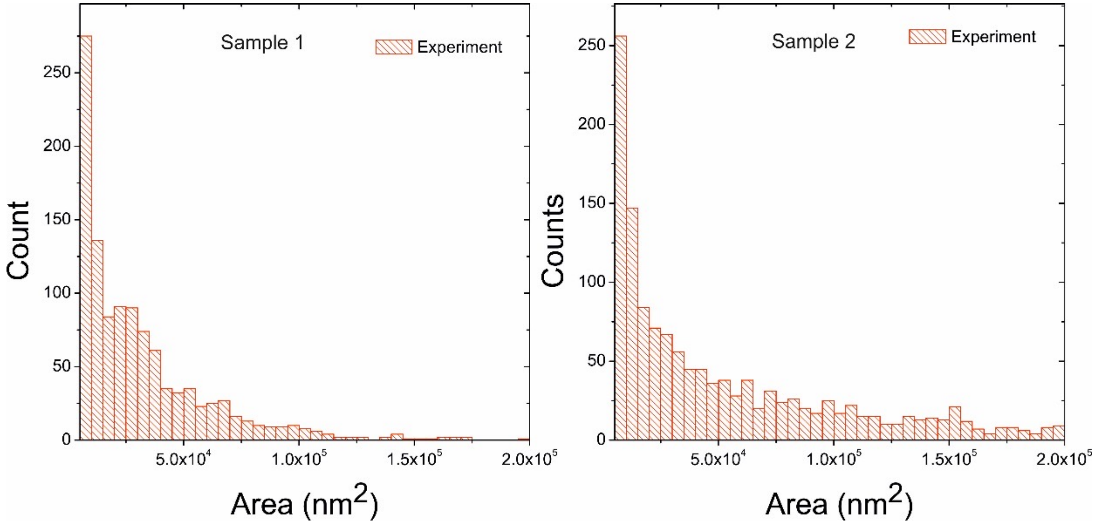


MC simulations - Disordered porous membranes 2

SEM of DPM Si membranes



Pore size distribution



Thin membrane : 100nm
Porosity : 25% for S1 and 37% for S2

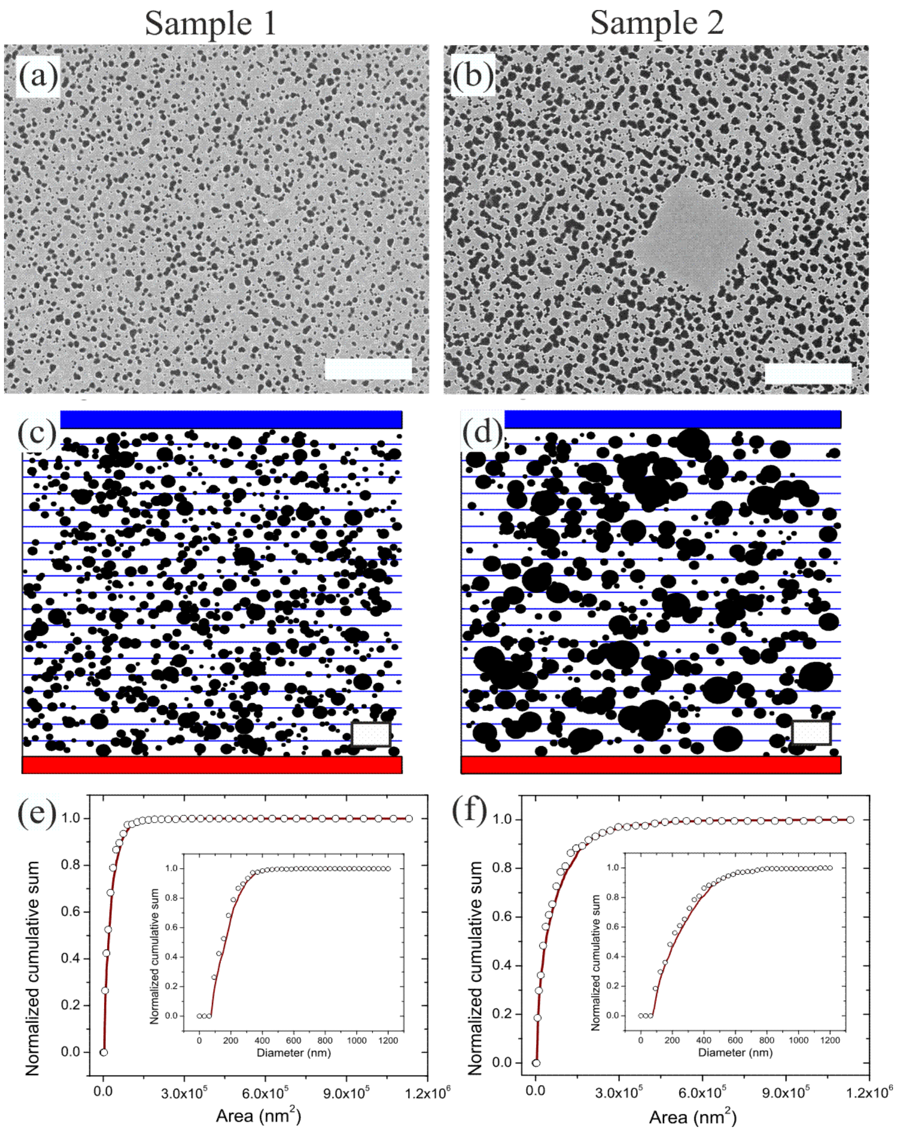
Low thermal conductivity (two lasers Raman spectroscopy):

- Plain membrane : k = 60 W/m K
- S1 : k = 19 +/-3 W/m K
- S2 : k = 11 +/-3 W/m K

Complicated geometries that can be handled with MC

MC simulations - Disordered porous membranes 3

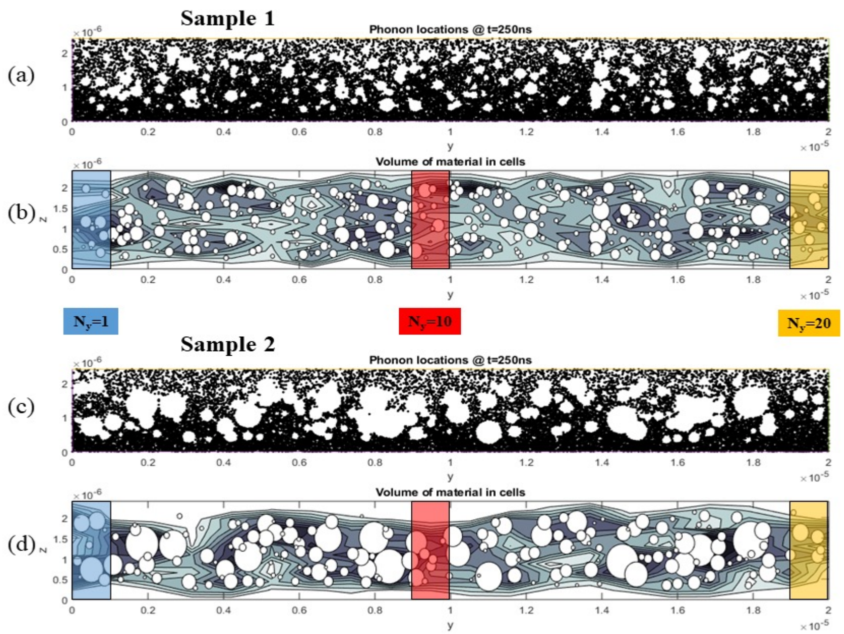
SEM of DPM Si membranes

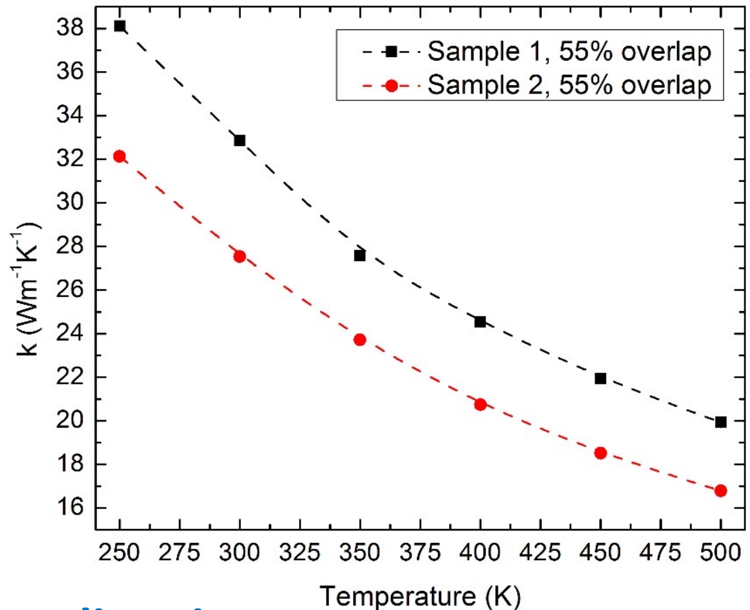


1. With the pore distribution, a cumulative probability is constructed to mimic pore sampling with MC.
2. Pores allowed to overlap
3. Simulations are done by applying a thermal gradient and following phonons on membrane of : 0.1µm x 2µm x 10µm
4. MC calculations are parallelized over 16 nodes

We derive : Temperature, fluxes and equivalent TC.

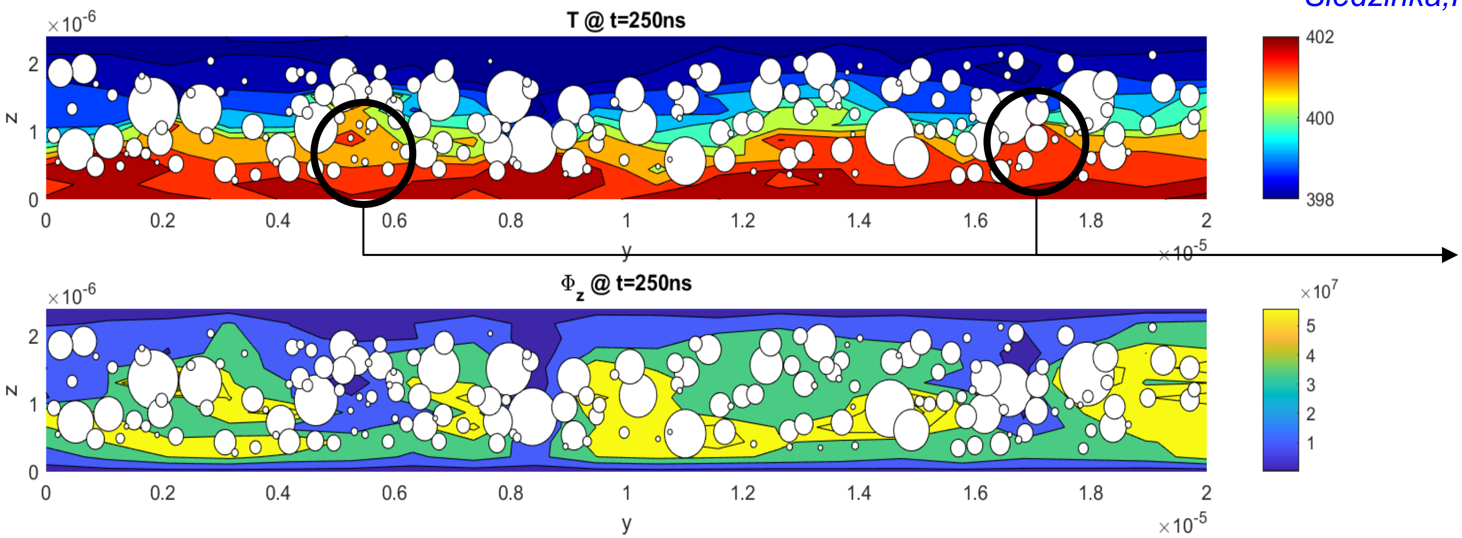
MC simulations - Disordered porous membranes 4





2D map of temperature and heat flux in z direction

Sledzinka,Nanotechnology 30, 265401



Good agreement between Exp and MC

Visualisation of hot spots on the membrane

Summary (Pros/Cons)

- Efficient and fast technique to recover TC in various nanostructures from ~10nm to ~10µm
- Efficient for low to high temperatures, (ballistic to diffusive regimes)
- Allows to combine several materials (superlattices, nanoinclusions, etc.)
- Accuracy easily controlled through MPI simulations

- Limited to isotropic dispersion relations
- Phonon relaxation times provided according to analytic expressions (calibration stage on bulk cases)

Improvement of MC-BTE by coupling with ab-initio calculations

Monte Carlo simulations, ab-initio coupling 1

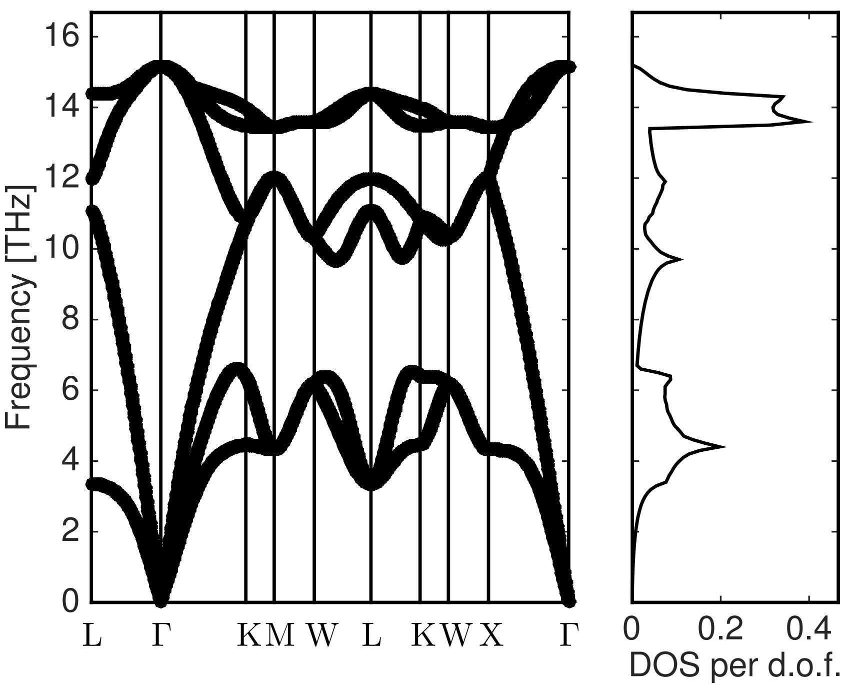
The MC solution of the BTE for phonon has a main weakness, the necessity to have an explicit formulation of phonon lifetimes of the studied material.

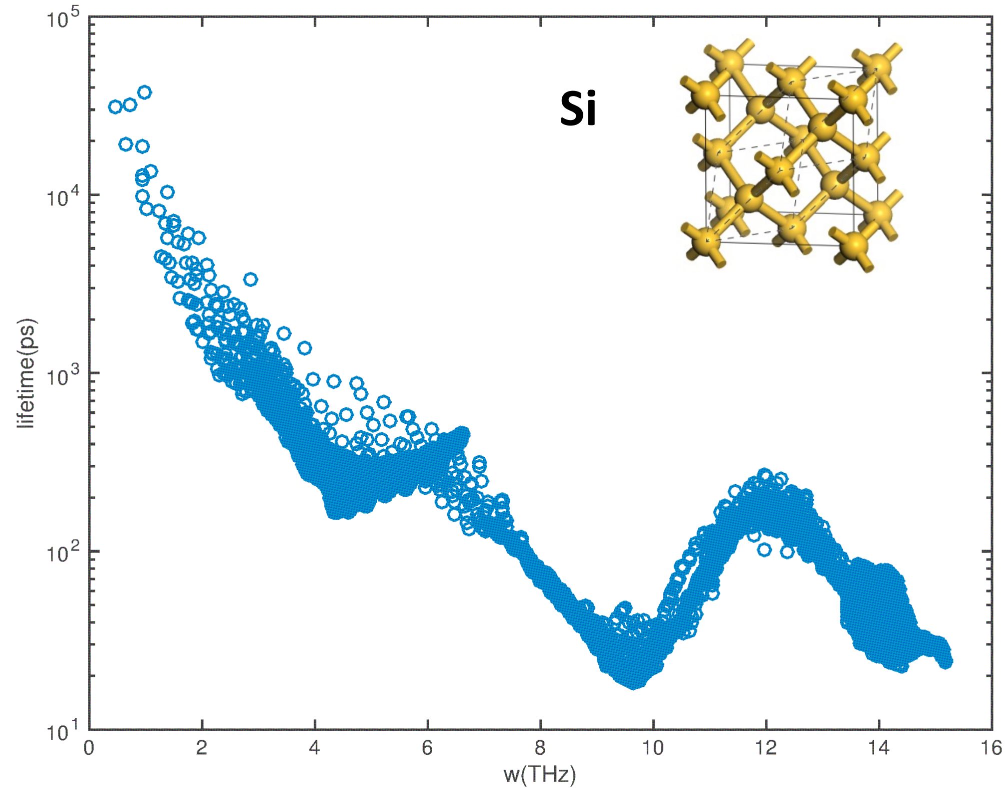
- **Idea**: replace analytic lifetime expressions of basic materials (Si, Ge, etc) by the one provided by DFT calculations
- Use the real dispersion properties of the material (frequency, polarization branches including optical modes & group velocities)

Monte Carlo simulations, ab-initio coupling 2

DFT calculations: Dispersion properties & phonon lifetimes

Discretization of the first Brillouin zone on a 31x31x31 K grid





Monte Carlo simulations, ab-initio coupling 3

The MC-ab initio solution of the BTE for phonons lies on the same principle as above: discretization, BC, initialization, phonon drift and phonon scattering.

Changes are related to:

- Use of a K space discretization instead of frequency one
- All phonon branches are considered including optical ones
- The scattering term of the BTE is the DFT calculated phonon lifetime

For each K point j, at a given time t, a phonon is sampled in a cell and carries a given number of modes "n_j^t" given by the Bose-Einstein distribution

$$n_j^t = \frac{1}{\exp\left({}^{\hbar\omega_i}/_{k_B T}\right) - 1}$$

MC simulation will compute n_j^t variations due to phonon displacement and scattering

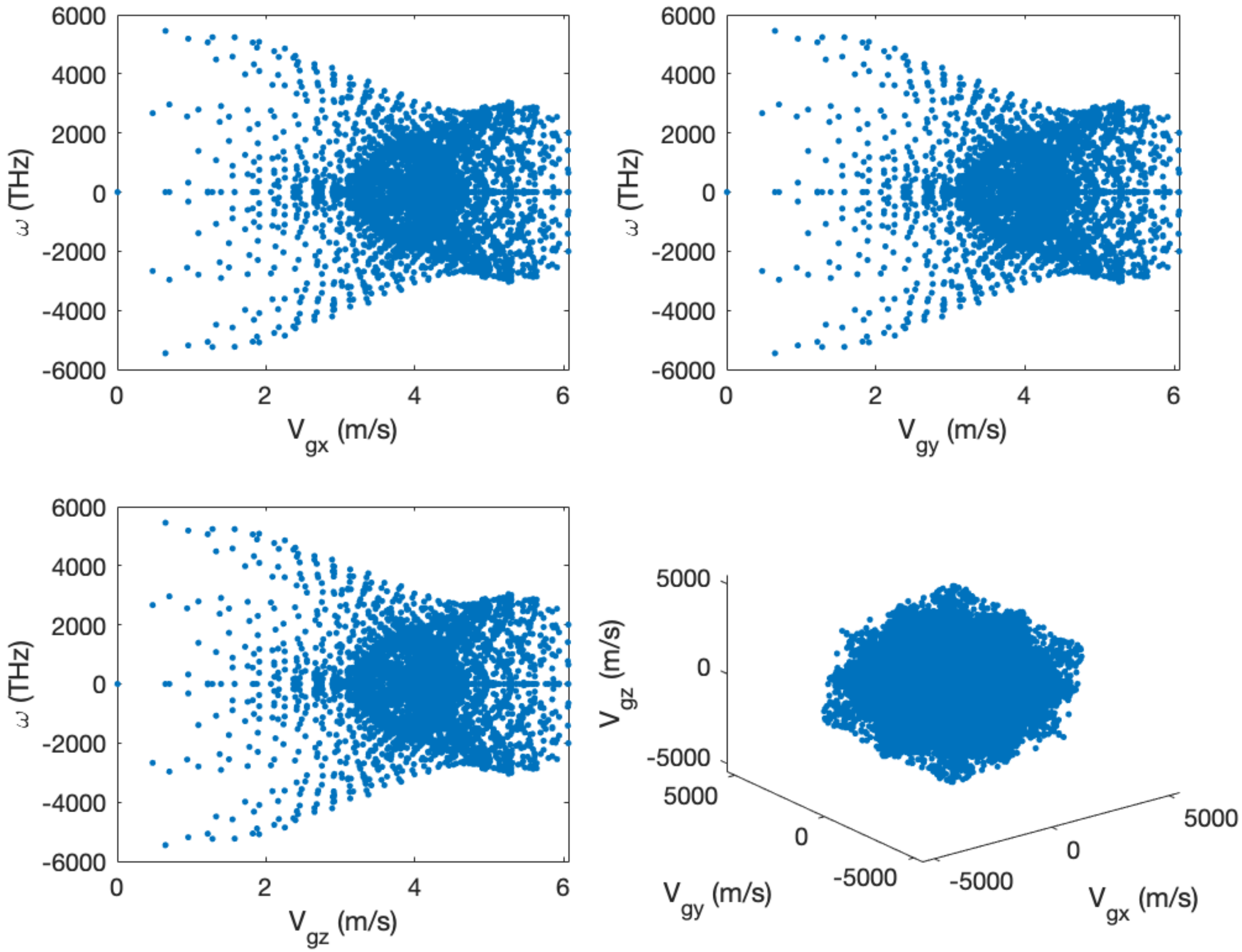
Monte Carlo simulations, ab-initio coupling 3

MC – ab-initio coupling procedure

1. Generation of the phonon properties from DFT inputs for each phonon mode in a given T range : $\omega(K_x, K_y, K_z, p)$, $V_{gx}(K_x, K_y, K_z, p)$, $V_{gy}(K_x, K_y, K_z, p)$, $V_{gz}(K_x, K_y, K_z, p)$, $\tau(K_x, K_y, K_z, p, T)$
2. Definition of the weighting factor : W that gives the initial number of phonons in each domain cell : $N_p = K_1 \times K_2 \times K_3 \times p \times W$
3. Definition of the system geometry (thin film, nanowire, …) and of the initial applied temperatures
4. Initialization of the phonon bundle (location x, y, z) in each cell at the initial stage according to the prescribed T.

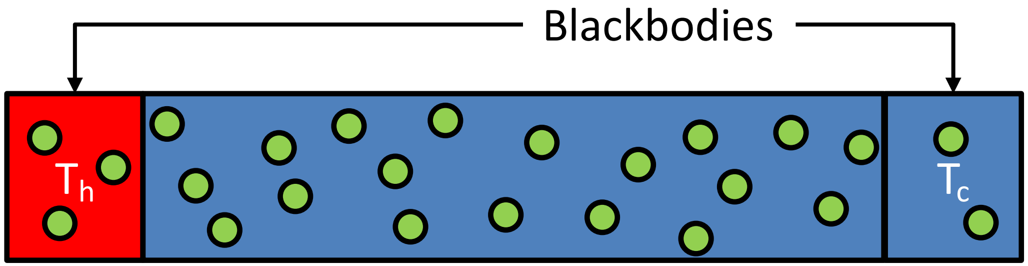
Monte Carlo simulations, ab-initio coupling 4

Group velocities – Si TA branch – DFT calculations



Monte Carlo simulations, ab-initio coupling 5

MC – ab-initio initialization



A reference temperature T_{ref} is set such as $T_{ref}<T_c$
Energy carried by phonon
Modes is proportional to
$(T-T_{ref})$

Occupation number n_j^t is computed for each discretized mode

$$n_j^t = \frac{1}{\exp\left({}^{\hbar\omega_j}\!/_{k_B T}\right) - 1} - n_{ref,j}^t \qquad n_{ref}(K,p) = \frac{1}{\exp\left({}^{\hbar\omega_{K,p}}\!/_{k_B T_{ref}}\right) - 1}$$

With index j defined by (K_x, K_y, K_z, p)

Energy within a cell thus becomes

$$E(t,T) = E_{ref} + \frac{1}{W(K_1K_2K_3)V_{UC}} \sum_{i=1}^{W} \sum_{j=1}^{K_1K_2K_3p} \hbar\ \omega_j \left(\frac{1}{2} + n_j^t\right)$$

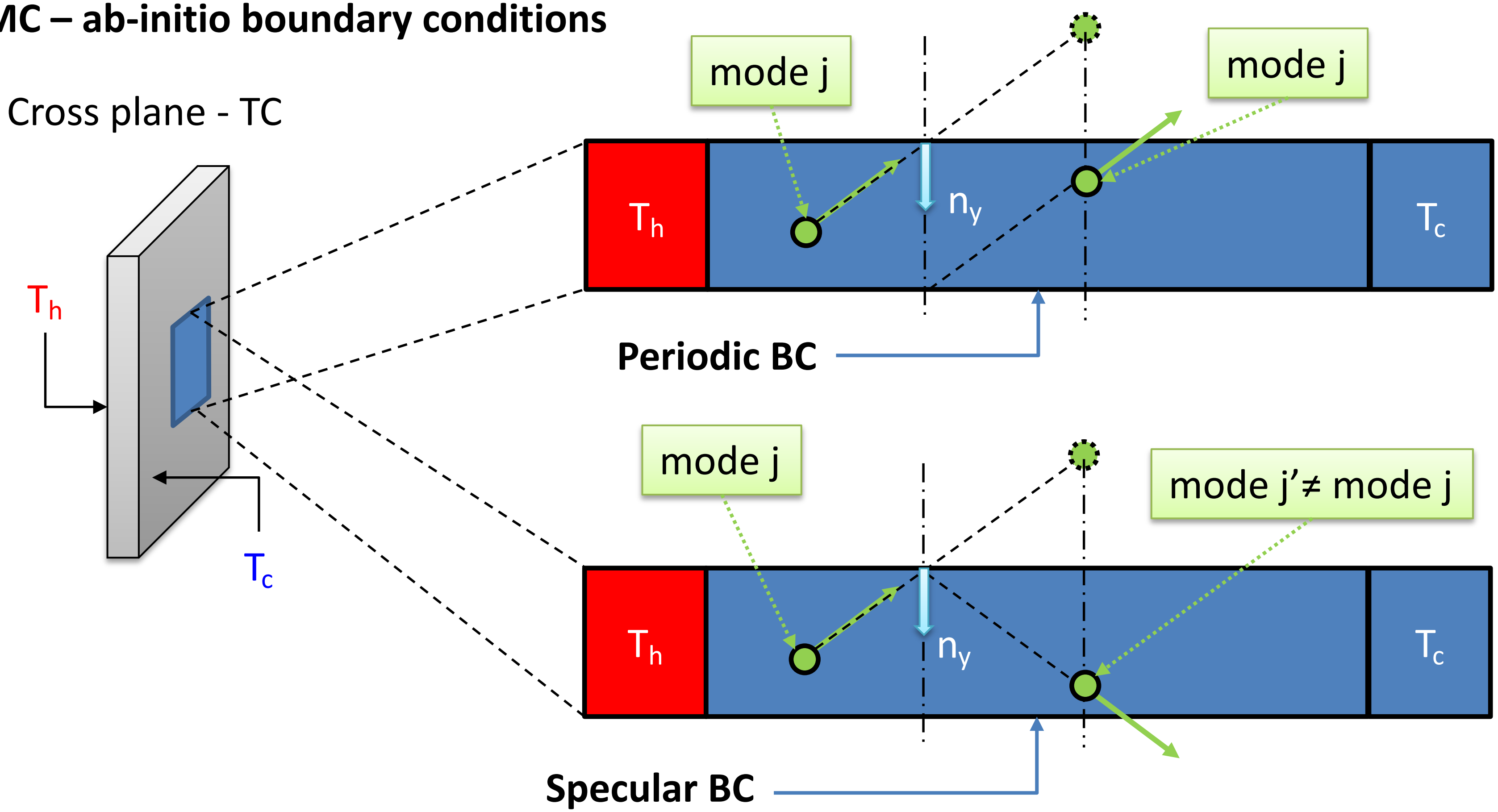
« E_{ref} » is the reference energy

« i » is the number of phonons per mode

« j » is the mode index

Monte Carlo simulations, ab-initio coupling 6

MC – ab-initio boundary conditions

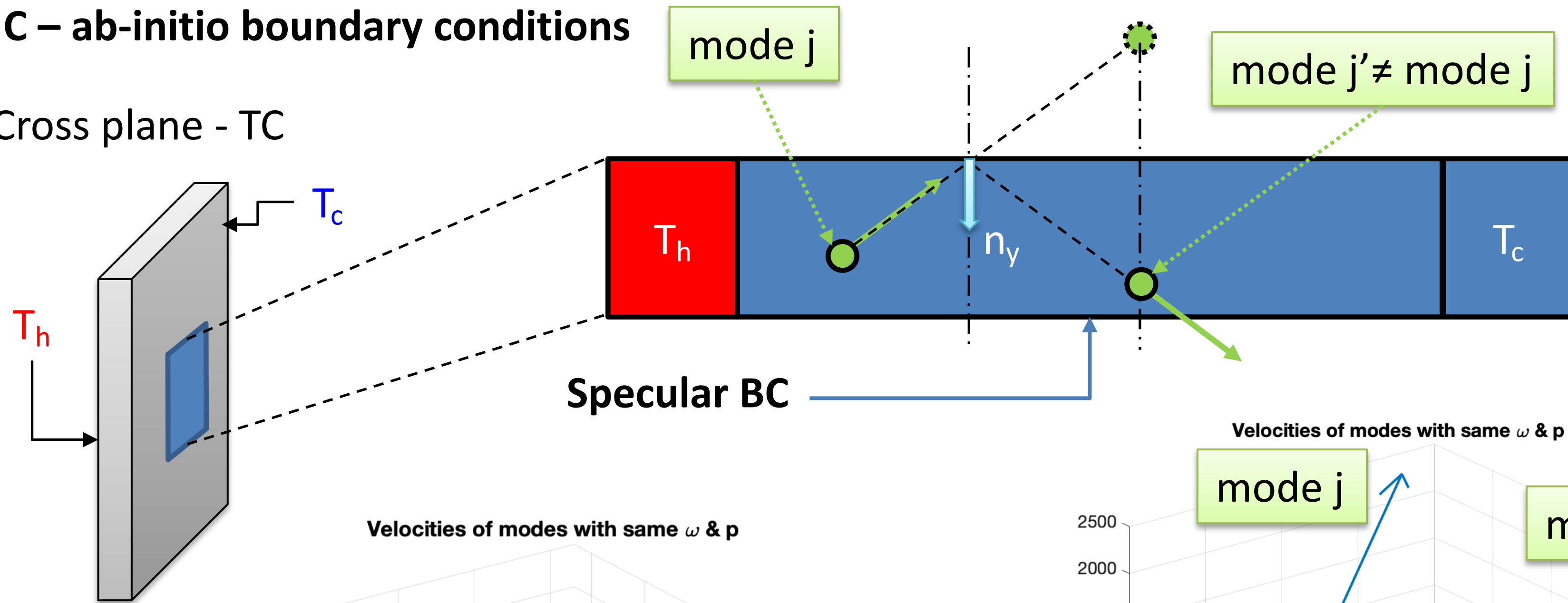


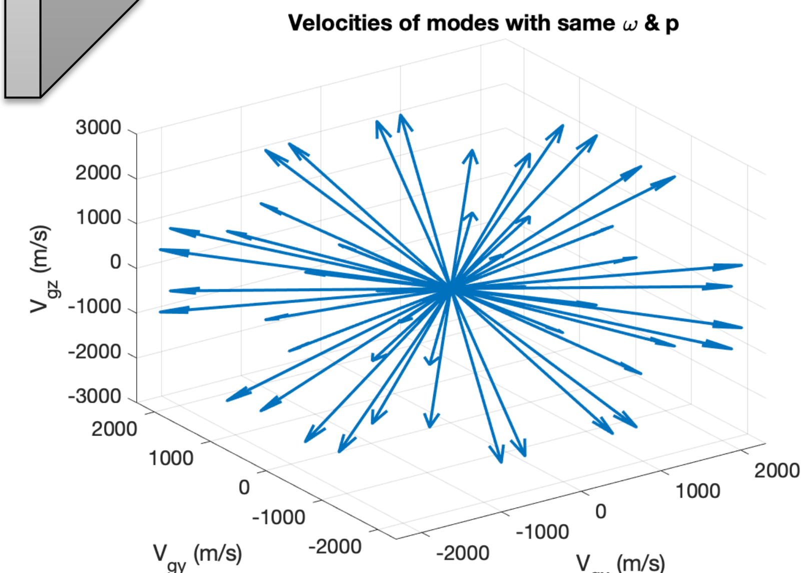
Problem with specular BC, we need to find the mode j' which has the same frequency and polarization $(\omega_{j'}, p_{j'}) = (\omega_j, p_j)$ but opposite velocity along "y" axis $v_{gy,j'} = -v_{gy,j}$

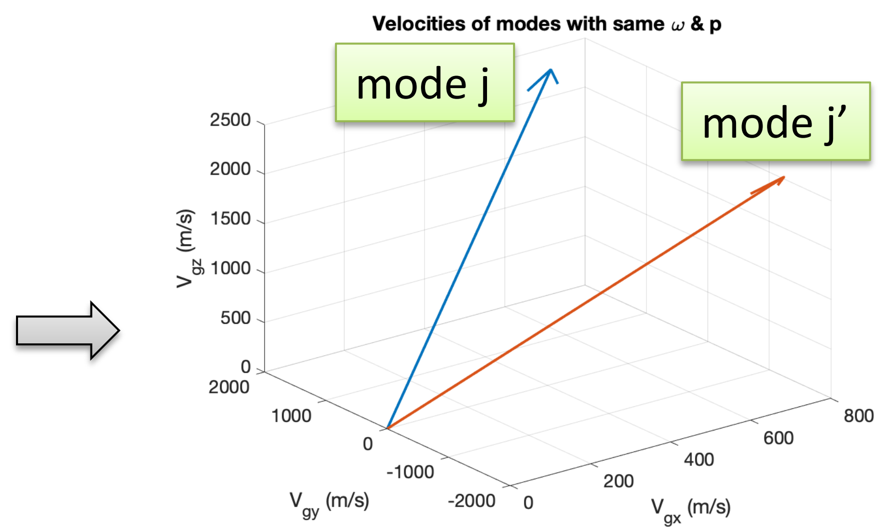
Monte Carlo simulations, ab-initio coupling 7

MC – ab-initio boundary conditions

Cross plane - TC





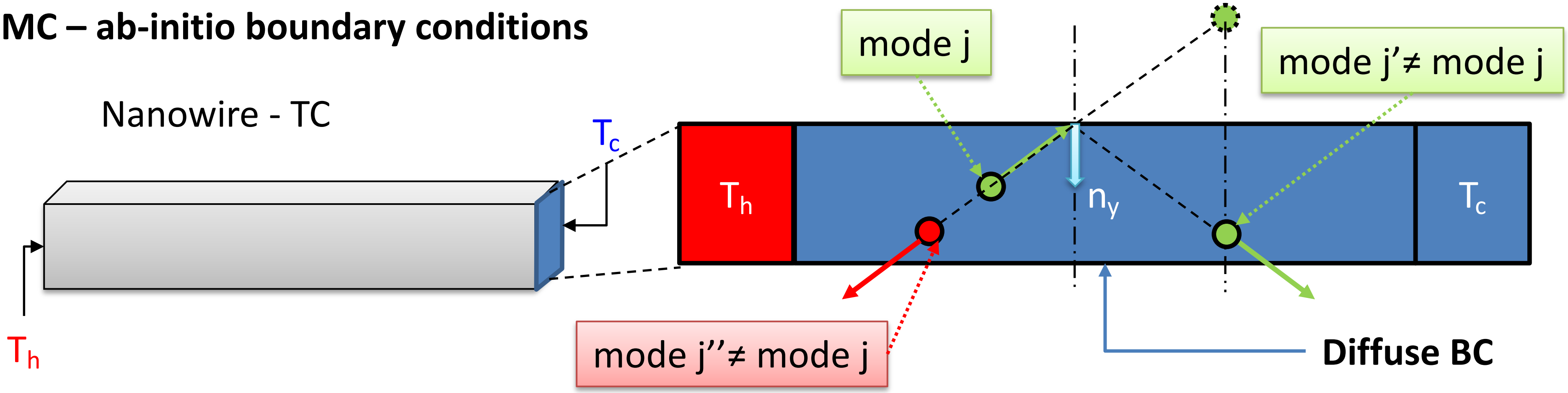


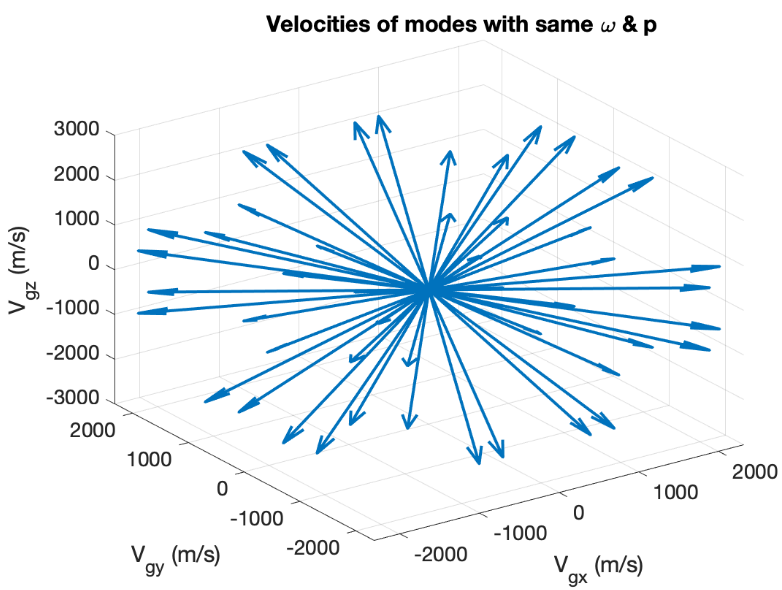
mode j : (6,14,21,1) ; ω_j=5.55 Thz

mode j' : (25,14,9,1) ; $\omega_{j'}$=5.55 Thz

Monte Carlo simulations, ab-initio coupling 8

MC – ab-initio boundary conditions





Phonon can be either :

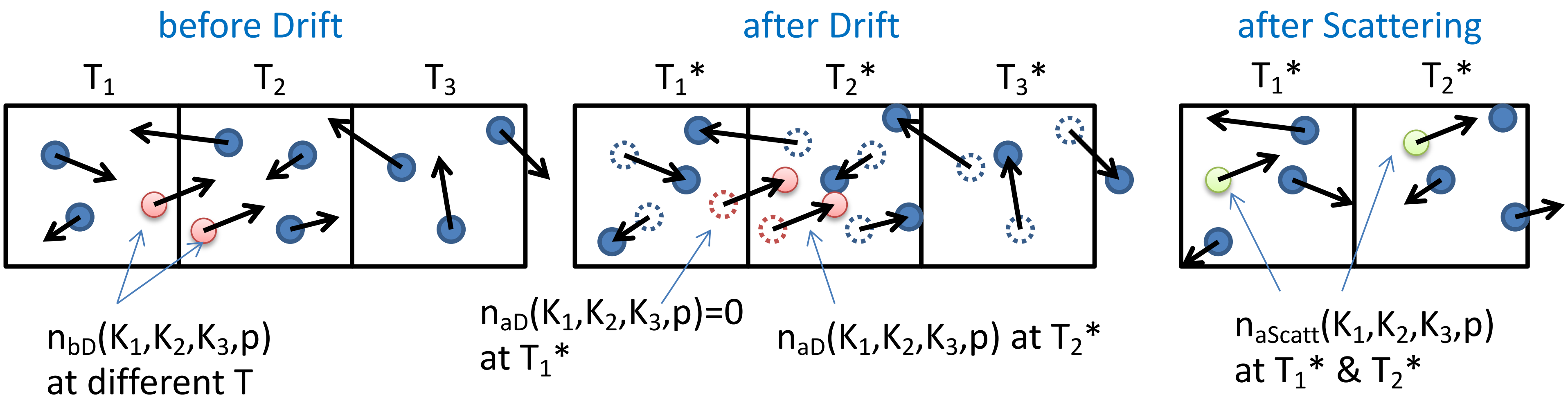
- Forward scattered (specular like)
- Back scattered (diffuse like)

Frequency and polarization are preserved (elastic scattering); forward or back scattering is randomly assessed from scattering parameter "p" (set or calculated from phonon wavelength and roughness)

Monte Carlo simulations, ab-initio coupling 9

Calculation of scattering term of the BTE

For each K point, a phonon is sampled in a cell and carries a given number of modes N.



Occupation number of each mode is corrected after each phonon displacement according to the local « pseudo » temperature T*

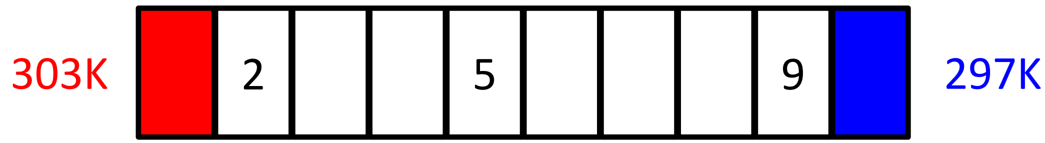
$$n_{aScatt} = n_{aD} + \frac{\delta t}{\tau(K_1,K_2,K_3,p)}\left[\Delta n_{BE}(T^*) - n_{aD}\right]$$

Once n_{aScatt} is know, new T and heat flux are calculated and next time step is considered

Monte Carlo simulations, ab-initio coupling 10

Calculation of T and Φ according to the local phonon distribution in the nanostructure

Si cross-plane TC



$$\Phi_z = \sum_{i=1}^{N} \frac{\hbar \omega_i V_{gz}}{V}$$

Silicon nanofilm

Lz = 2µm

δt = 0.5ps

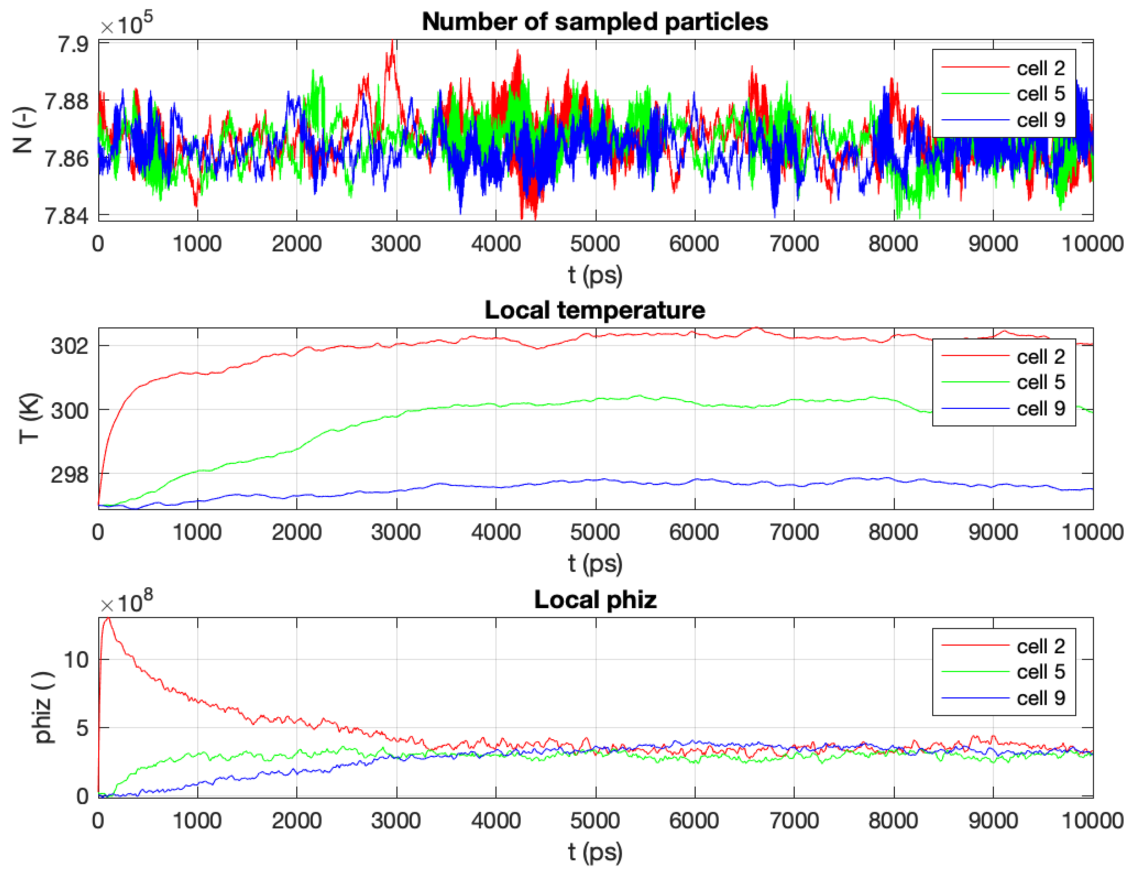
Nz = 10 cells

20 000 time steps

1787460 phonon modes

(31x31x31x6x10)

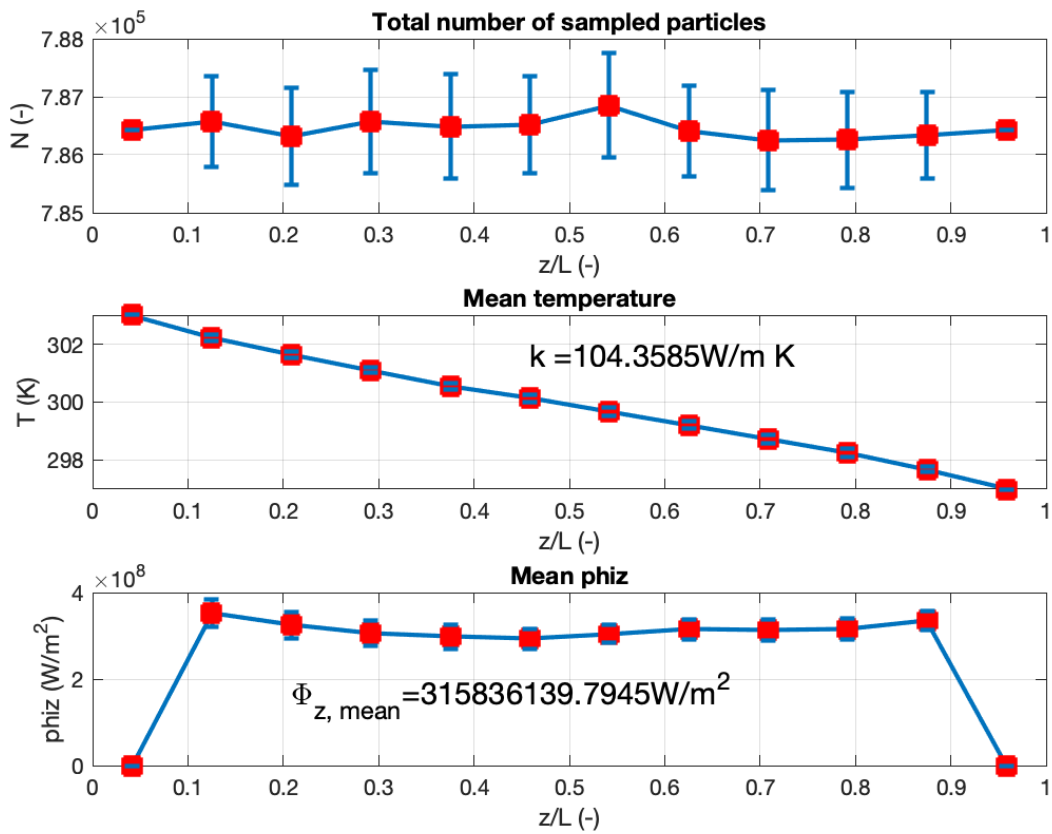
2 core / 8h



Monte Carlo simulations, ab-initio coupling 11

Calculation of T and Φ according to the local phonon distribution in the nanostructure

$$\Phi_z = \sum_{i=1}^{N} \frac{\hbar\omega_i V_{gz}}{V}$$



Silicon nanofilm
Lz = 2µm
δt = 05ps
Nz = 10 cells
20000 time steps
1787460 phonon modes
2 core / 8h
Cross plane TC
k = 104.36 +/-3.7 W/m K

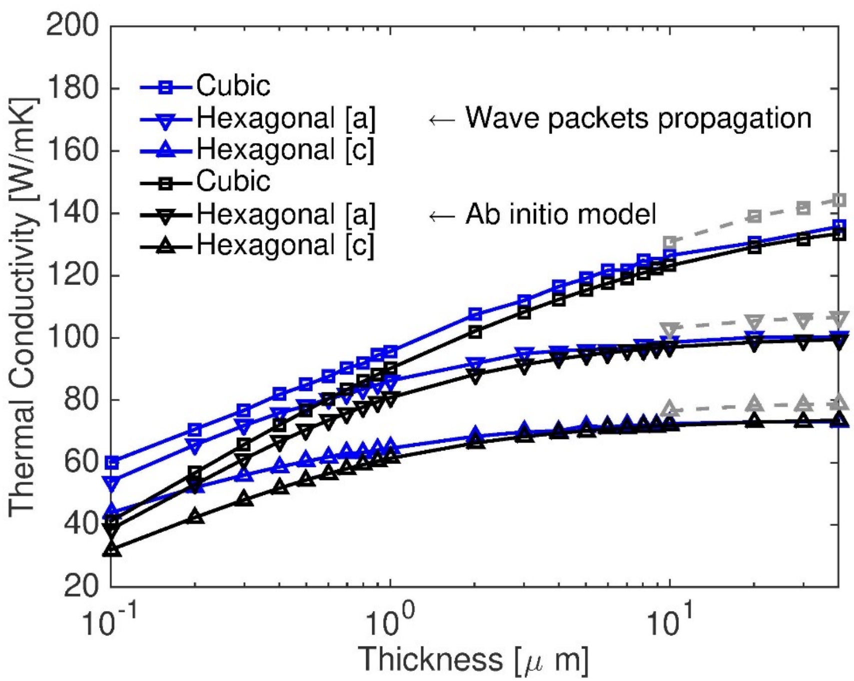
Holland's relaxation time : k = 128.7 W/m K (isotropic dispersions without optical modes)
Light Underestimation with the TC with MC-ab-initio for 2µm length

Monte Carlo & ab-initio - applications to thin films and nanowires

Monte Carlo & ab-initio - applications 1

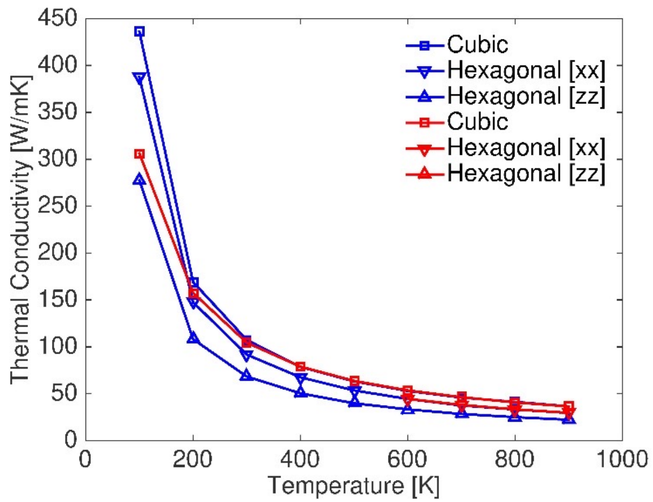
Diamond and Hexagonal phases studied

Cross-plane Thermal conductivity in Si film vs Lz

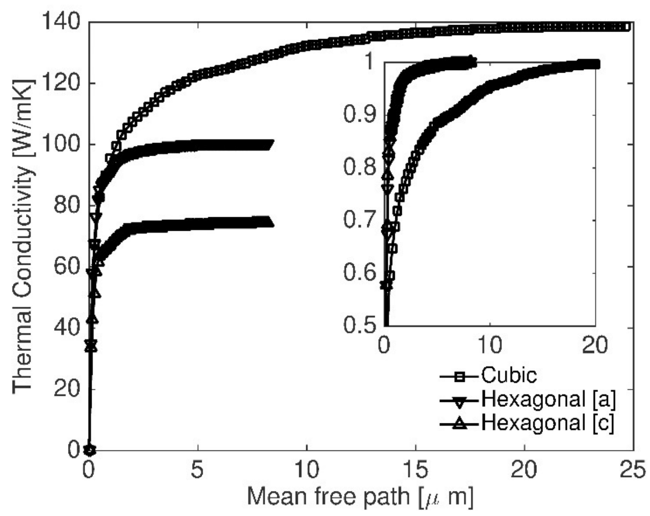


Applied Physics Letters, vol. 112, 033104

Thermal conductivity in Si vs T; Lz = 2μm



Thermal conductivity in Si vs mfp @ T=300K

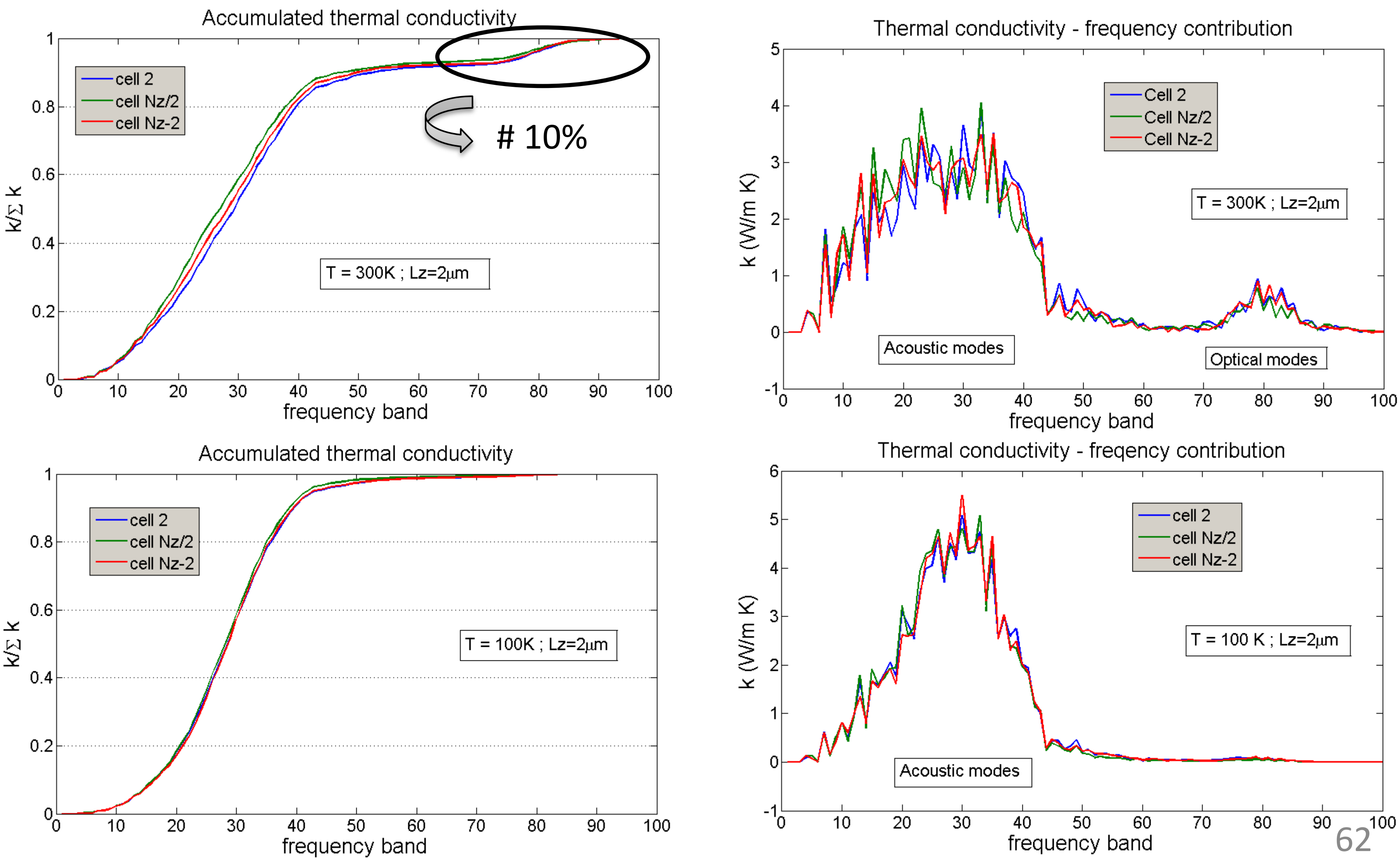


✓ Thermal conductivity variation with thickness well recovered

✓ Temperature dependence of thermal conductivity OK

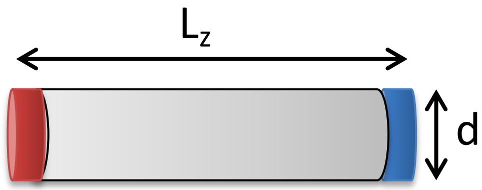
Monte Carlo & ab-initio - applications 2

Monte Carlo post-processing, mode contribution to Thermal Conductivity



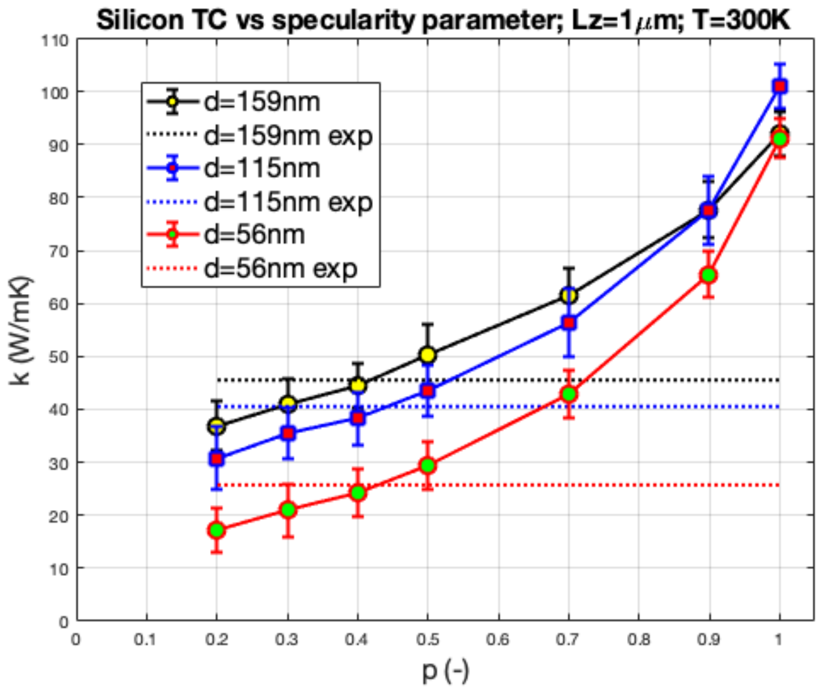
Monte Carlo & ab-initio - applications 3

Thermal Conductivity of nanowires

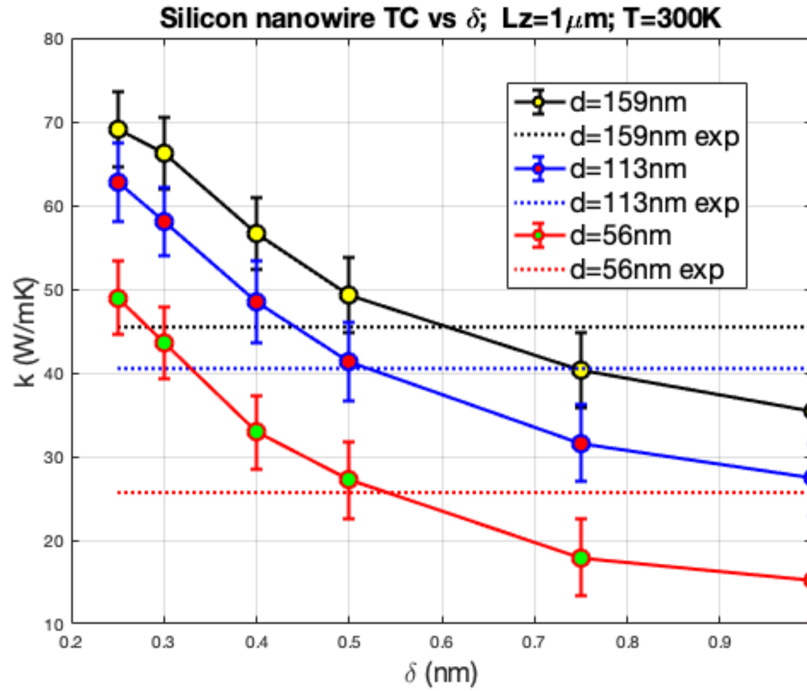


How phonon confinement in nanowires can be addressed ?

- Impose a global specularity parameter *p*,
- Compute the specularity parameter for all phonons that collide with boundaries (Ziman model) : $p = exp\left(\frac{-16\pi^2\delta^2}{\lambda^2}\right)$; with δ the average roughness and λ the phonon wavelength.



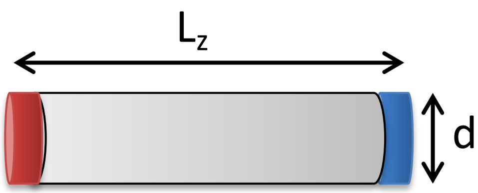
0.4 < *p* < 0.5



0.4nm < δ < 0.6nm

Monte Carlo & ab-initio - applications 4

Thermal Conductivity of nanowires

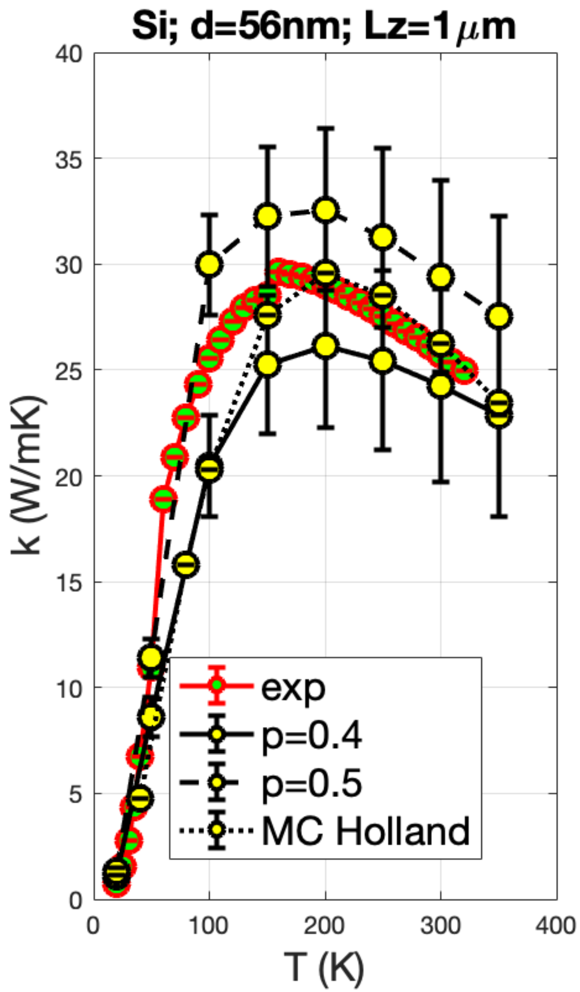


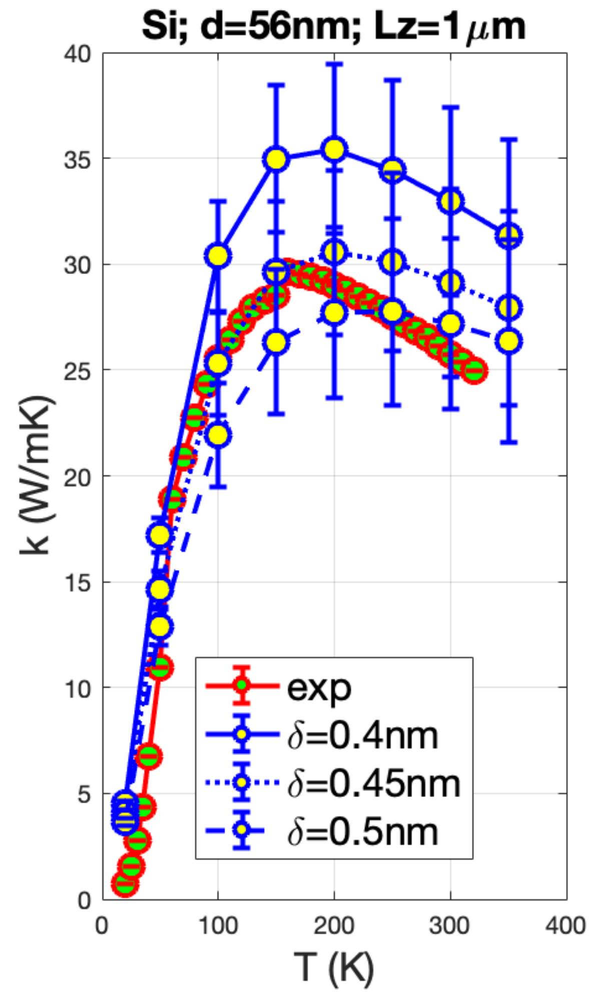
d = 56nm; Lz=1µm

0.4 < *p* < 0.5

0.4nm < δ < 0.5nm

silicon

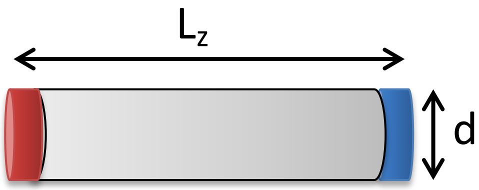




*D. Li, APL **83**, 2934*

Monte Carlo & ab-initio - applications 5

Thermal Conductivity of nanowires

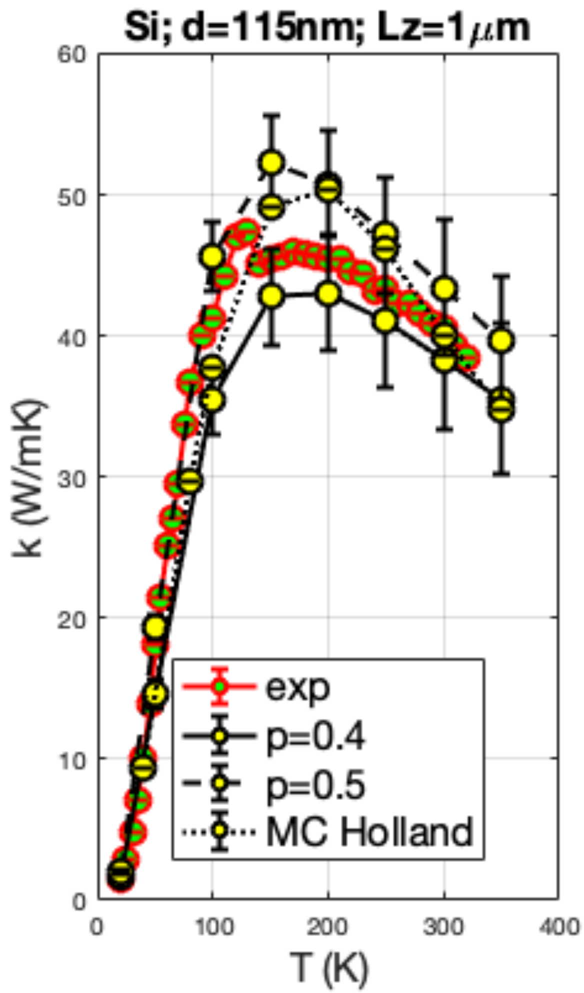


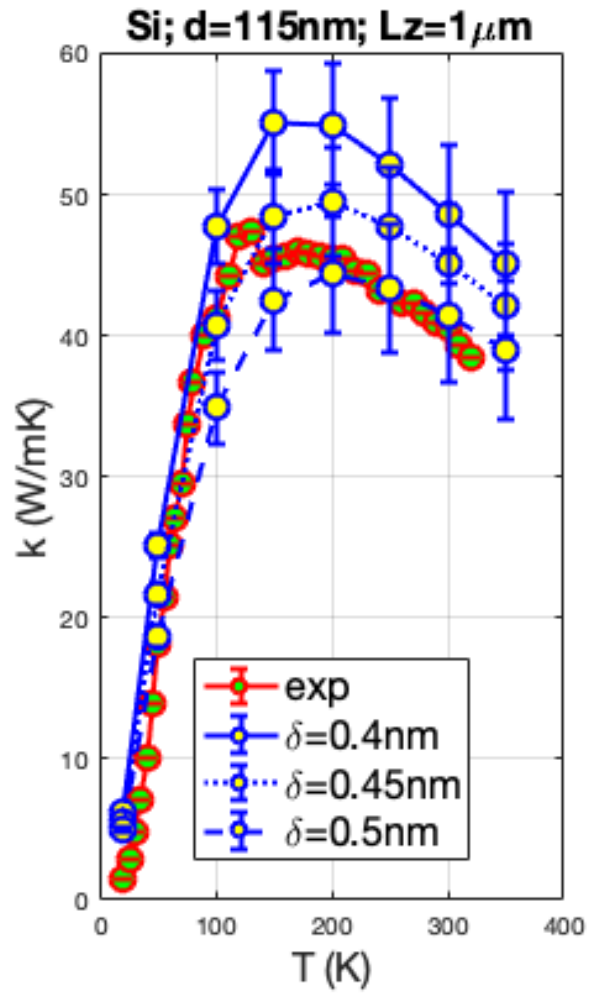
d = 115nm; Lz=1µm

0.4 < *p* < 0.5

0.4nm < δ < 0.5nm

silicon

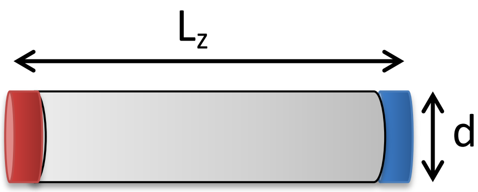




*D. Li, APL **83**, 2934*

Monte Carlo & ab-initio - applications 6

Thermal Conductivity of nanowires

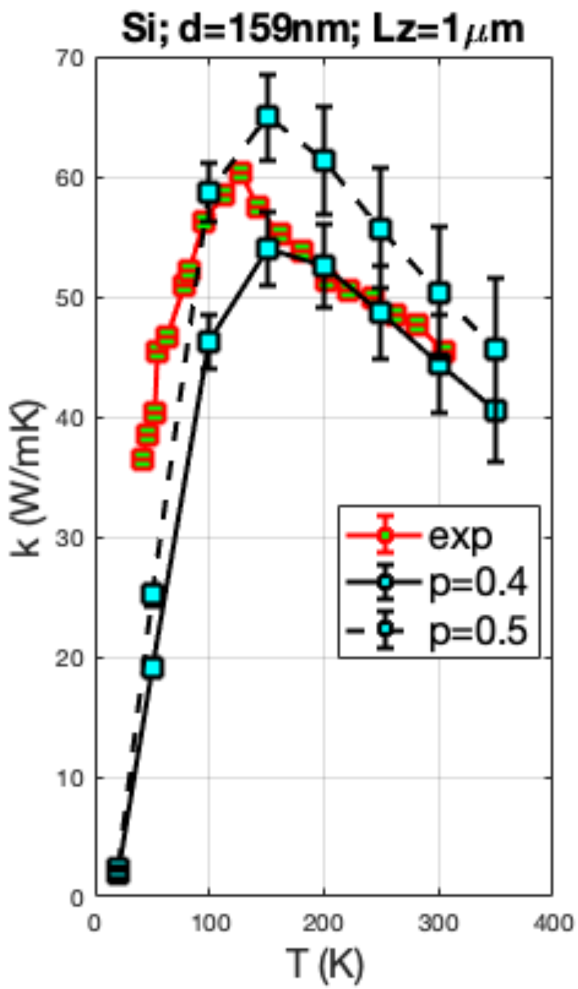


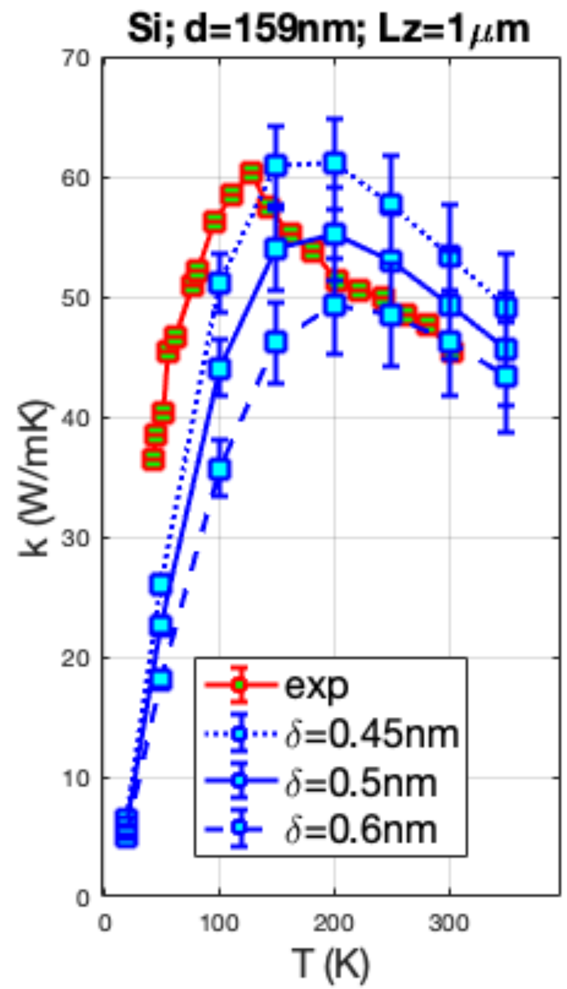
d = 159nm; Lz=1µm

0.4 < *p* < 0.5

0.4nm < δ < 0.6nm

silicon





A. Malhotra, Appl. Mat.&Int., ***14****, 1740*

Summary (Pros/Cons)

- Methodology that allows to use the real complexity of material characteristics through their detailed dispersion properties and the phonon lifetime
- All phonon modes are considered in the MC sampling ensuring better energy and momentum conservations
- Complex and large nanostructures can be handled

- Needs more memory to perform calculations, as compared to the previous MC model based on isotropic modelling and analytic relaxation times
- Boundary conditions (specular and diffuse) more complex to define
- DFT calculations with sufficiently dense K-grid to ensure accuracy

MC-BTE calculations of transport properties through autocorrelation

Autocorrelation & thermal conductivity

Project ANR: Spider-man

→ **Purpose: investigate ballistic-diffusive transition in semiconductors. Identify key parameters**

→ **Tools: Monte Carlo simulations of bulk and nanostructures**

- Mean square displacement of phonons
- Autocorrelation of heat flux → Thermal conductivity

Autocorrelation & thermal conductivity

Methodology

Phonon selection (initialization stage)

- Phonon's properties (frequency and polarization) are randomly sampled according a cumulative distribution function at a given temperature
- At the initial stage, particle position is evenly distributed in a initial domain (box) that can have boundary or not (bulk media modelling)

Phonon displacement

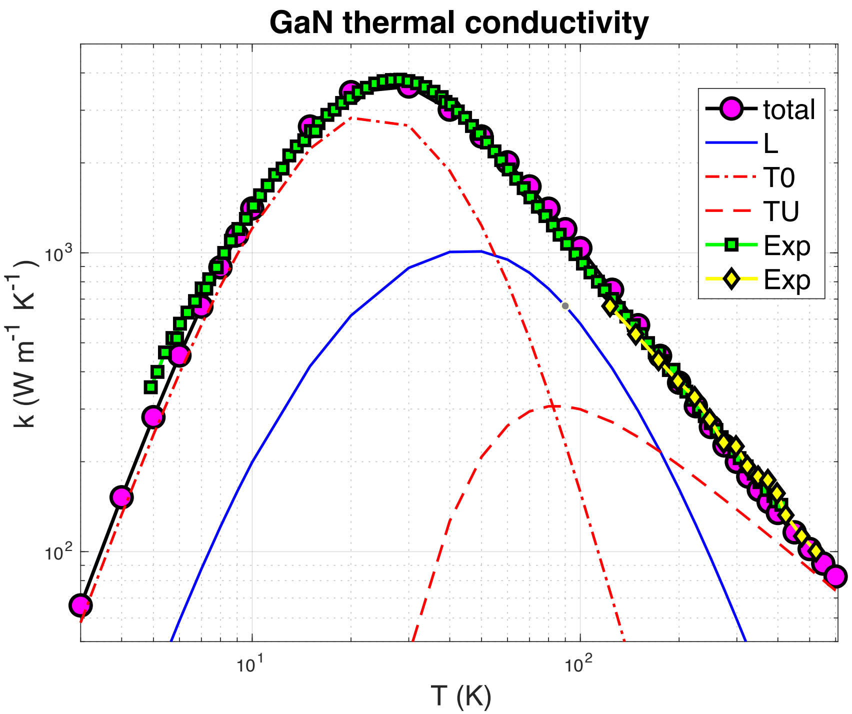
- Particles are displaced according to their group velocity and the time step
- Once displacement is achieved, a scattering collision probability is calculated, and the state of the particle is fully partially or not reset
- For each followed particle, heat flux at time t is computed
- Process is iterated until a fixed number of time steps

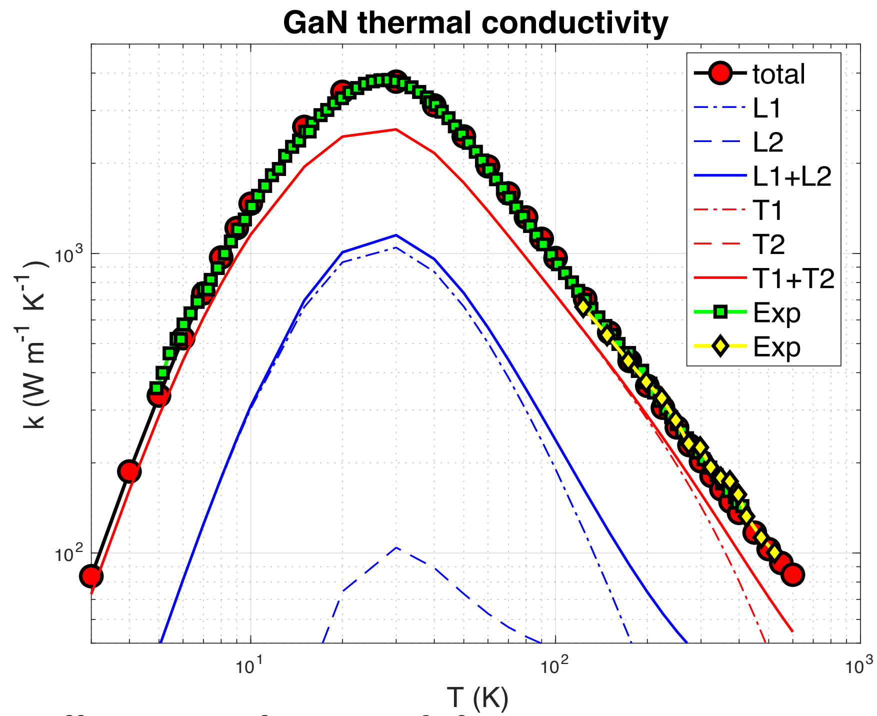
Heat flux autocorrelation

- Once all particle’s trajectories have been computed, the heat flux autocorrelation tensor is computed according to the Kubo formalism

Energy carriers transport properties

Gallium Nitride, bulk thermal conductivity





Holland model

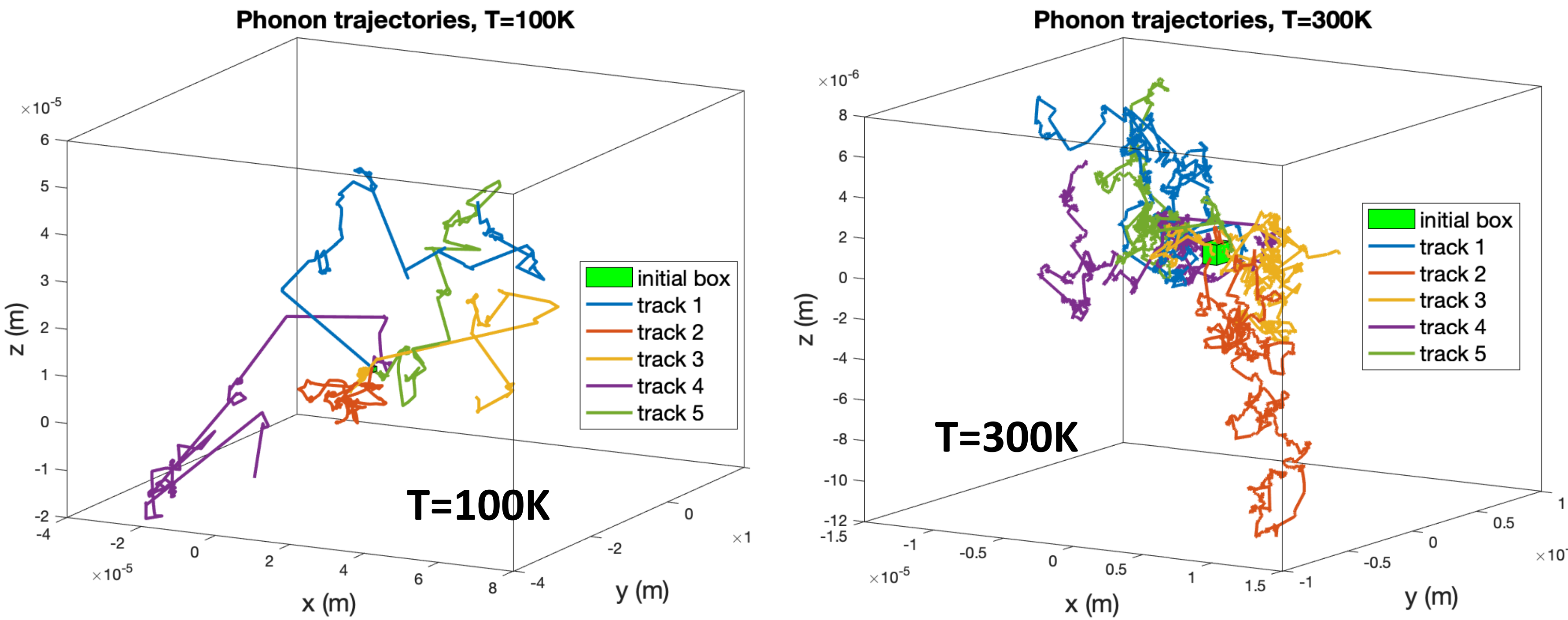
B_L = 8.0d-25 ; B_{TU} = 6.0d-18 ;
B_{TN} = 1.3d-12 ; B_I = 1.8d-45
L=1.7d-3 ; F=1

Callaway-Debye model

B_{NL} = 4.0d-24 ; B_{UL} = 1.1d-21 ;
B_{NT} = 1.0d-14 , B_{UT} = 5.0d-20 ;
V_{atom} = 46.943d-30 ; Γ = 8.0d-5

Phonon trajectories

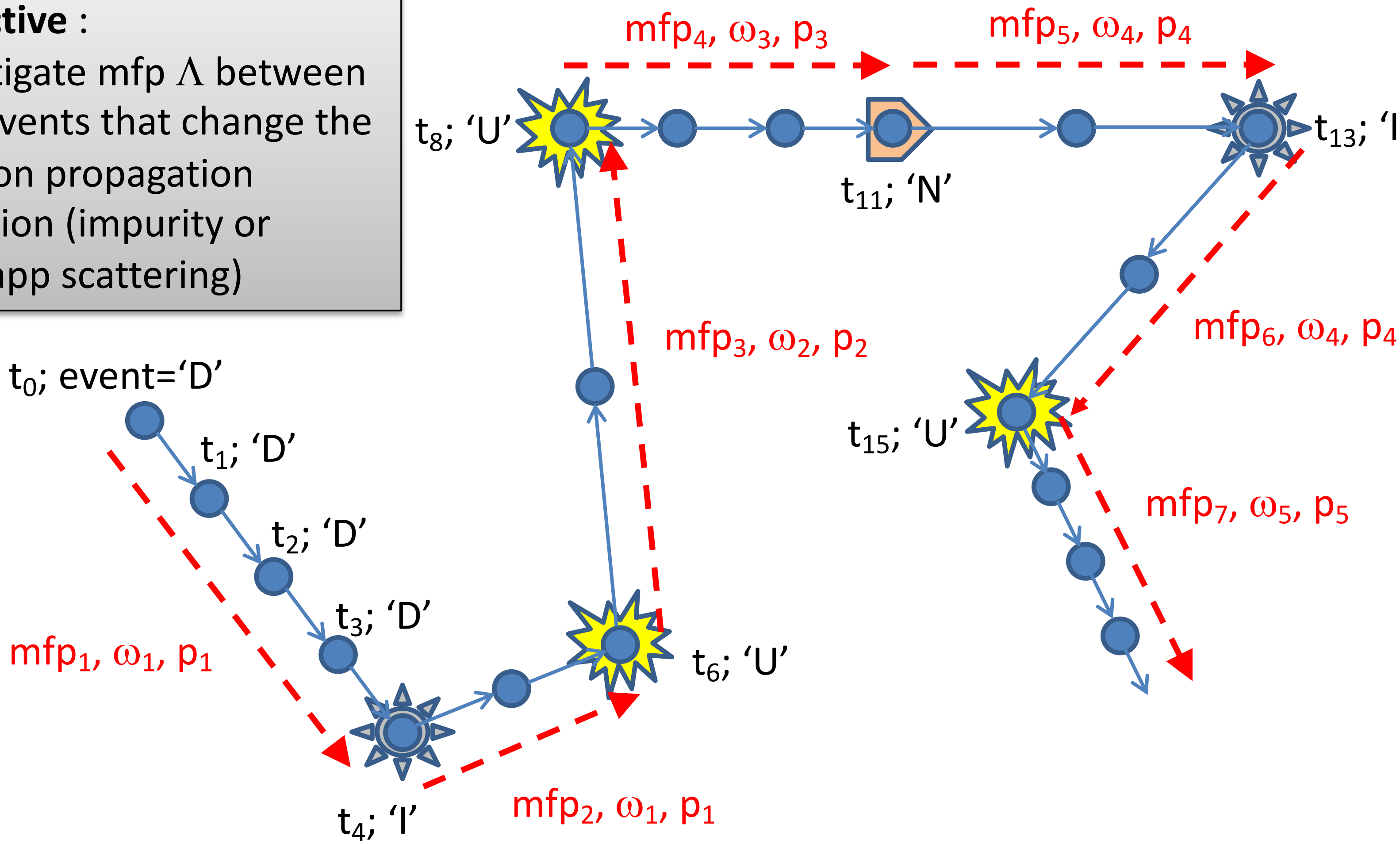
Phonon trajectories (5 phonons tracked) in bulk silicon



Phonon displacements are recorded during MC procedure at each time step (here 100 000 time steps of 1ps). The tracked phonons are at t=0 in a box of volume V=1x1x1 µm (green box)

Analysis of phonon mean free path 1

Objective :
Investigate mfp Λ between two events that change the phonon propagation direction (impurity or umklapp scattering)

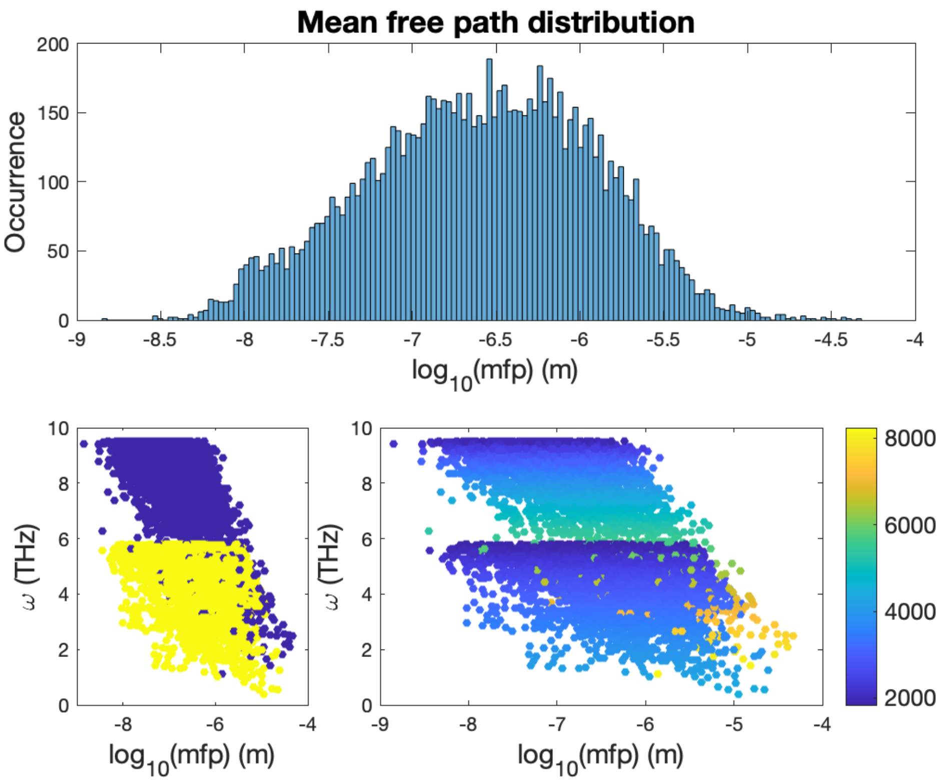


Scattering events are function of lifetime τ and time step δt

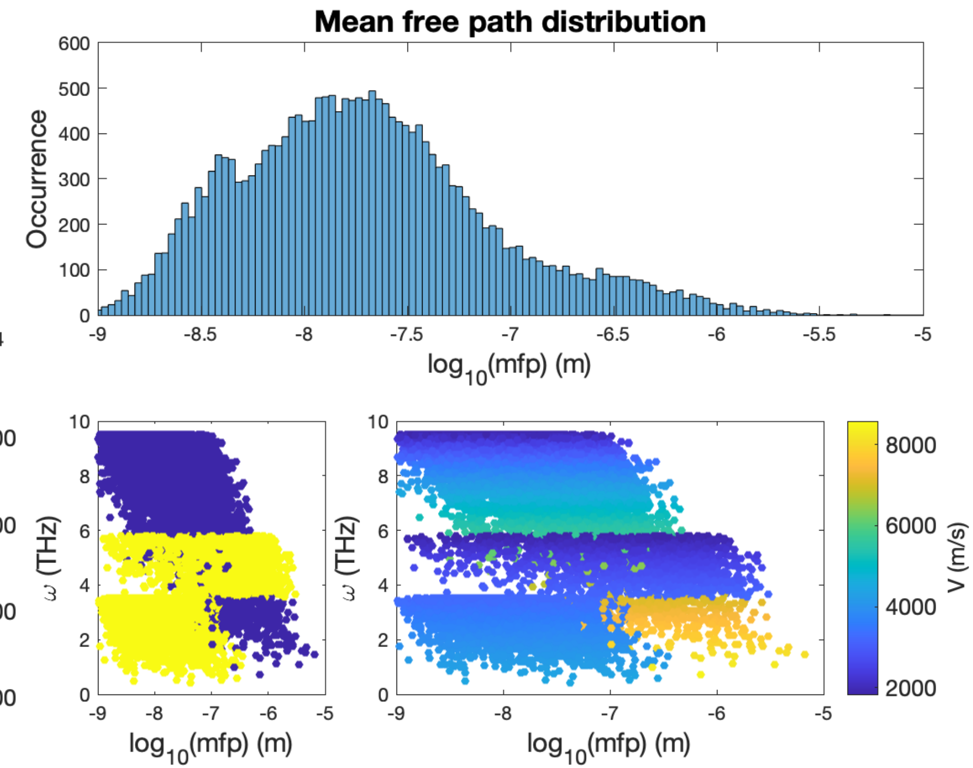
$$P_{scat} = 1 - \exp\left[\frac{-\delta t}{\tau(\omega, p, T)}\right]$$

Analysis of phonon mean free path 1

GaN @ 100K - Callaway-Debye model



GaN @ 300K - Callaway-Debye model



Lacroix, PRB, 104, 165202

Analysis of phonon mfp (over 100 000 time steps of five particle paths) as a function of frequency and polarization give some insights about scattering mechanisms and their evolution with temperature.

Heat flux autocorrelation of MC simulations 1

Using the MC methodology developed in the first section, at each time step we record the phonon state (ω, p) and propagation direction. From dispersions we have the group velocity, we can thus derive the instantaneous heat flux of particles "i" at time "t" : **q**(t,i)

$$\boldsymbol{q}(t,i) = \frac{1}{V} p(t,i)\hbar\omega(t,i)\boldsymbol{v}(t,i)\mathcal{W}(t)$$

$\mathcal{W}(t)$ is a weighting factor defined as the ratio of the theoretical energy of the system at T to the sampled energy by MC procedure

$$\mathcal{W}(t) = \frac{E^{th}(T)}{E^{MC}(t)}$$

$$E^{th}(T) = \int_0^{\omega_{max}} \sum_{p=LA,TA} \frac{1}{\left[exp\left({}^{\hbar\omega}/_{k_B T}\right) - 1\right]} \mathcal{D}(\omega) p\hbar\omega \, d\omega$$

$$E^{MC}(t) = \sum_{i=1}^{N_p} p(t,i)\hbar\omega(t,i)$$

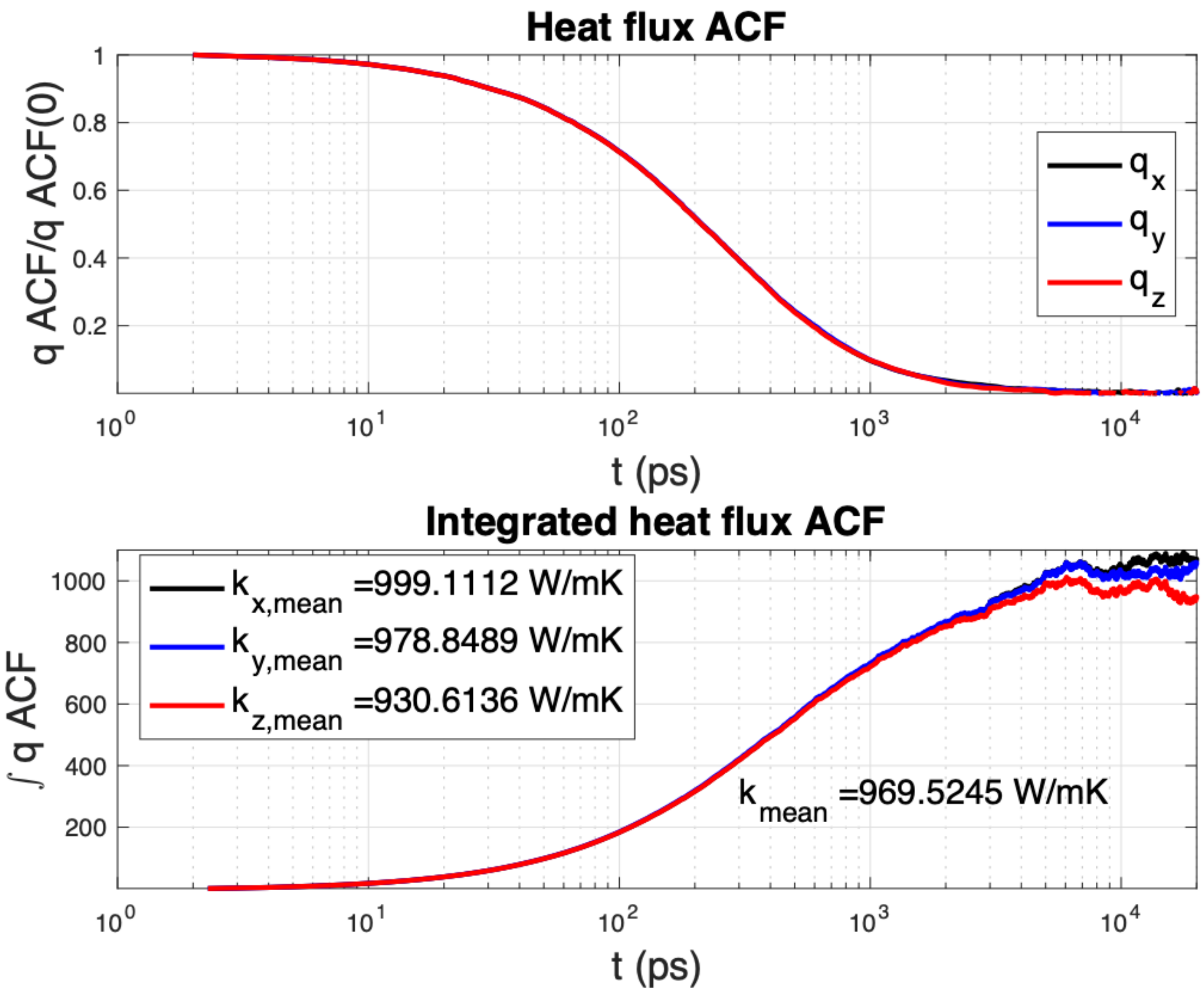
Green-Kubo formalism reads:

$$k_{\alpha,\beta} = \frac{V}{k_B T^2} \int_0^{\infty} \langle q_\alpha(0) q_\beta(t) \rangle dt \;\Rightarrow\; k_{x,y} = \frac{V}{k_B T^2} \frac{\delta t}{N_p} \sum_{i=1}^{N_p} \sum_{m=1}^{M} \frac{1}{N_t - m} \sum_{n=1}^{N_t - m} q_x(m+n)\, q_y(n)$$

With N_p the number of sampled particles, N_t the number of time steps and $M = \frac{N_t}{10}$

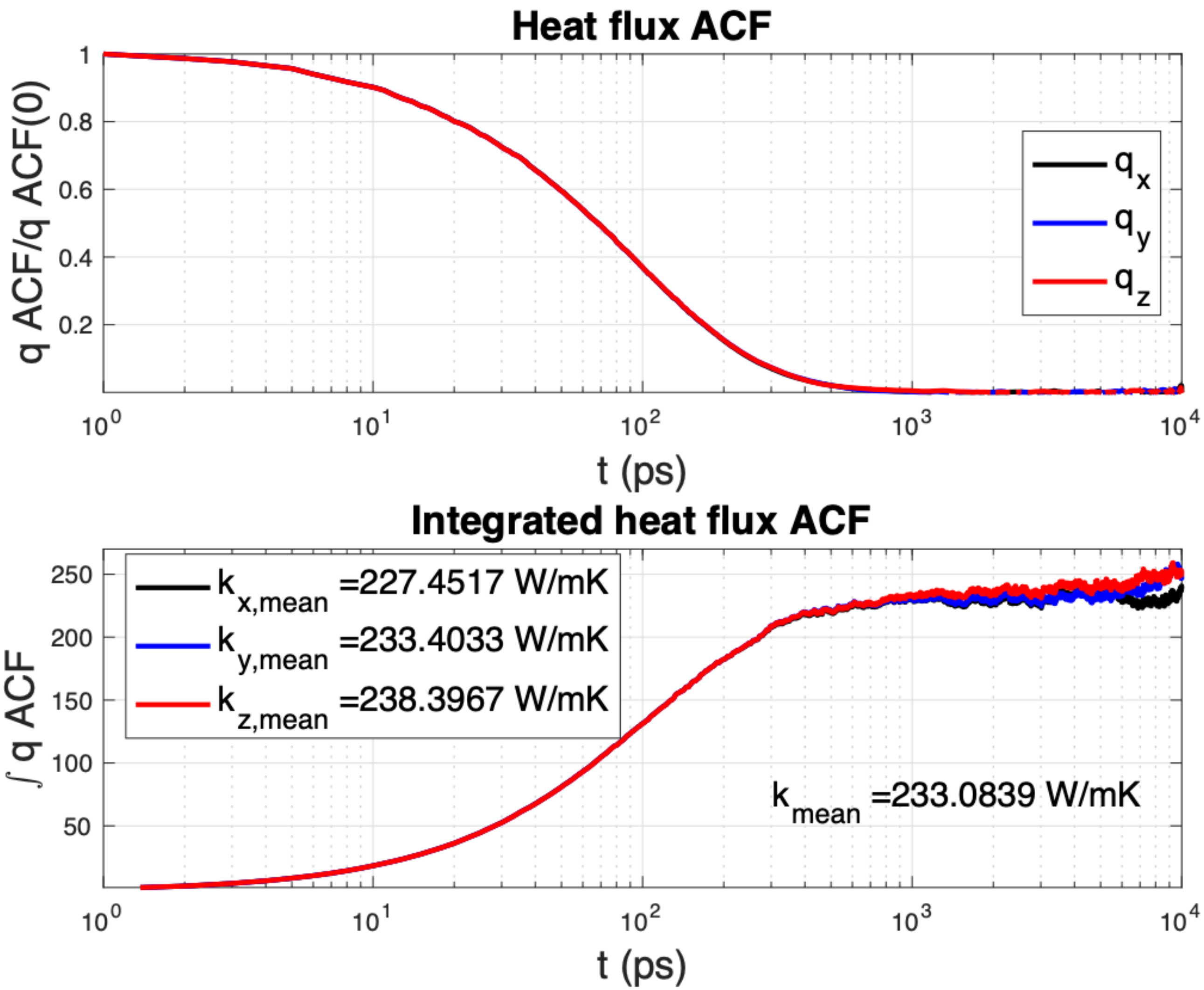
Heat flux autocorrelation of MC simulations 2

GaN @ 100K - Callaway-Debye model



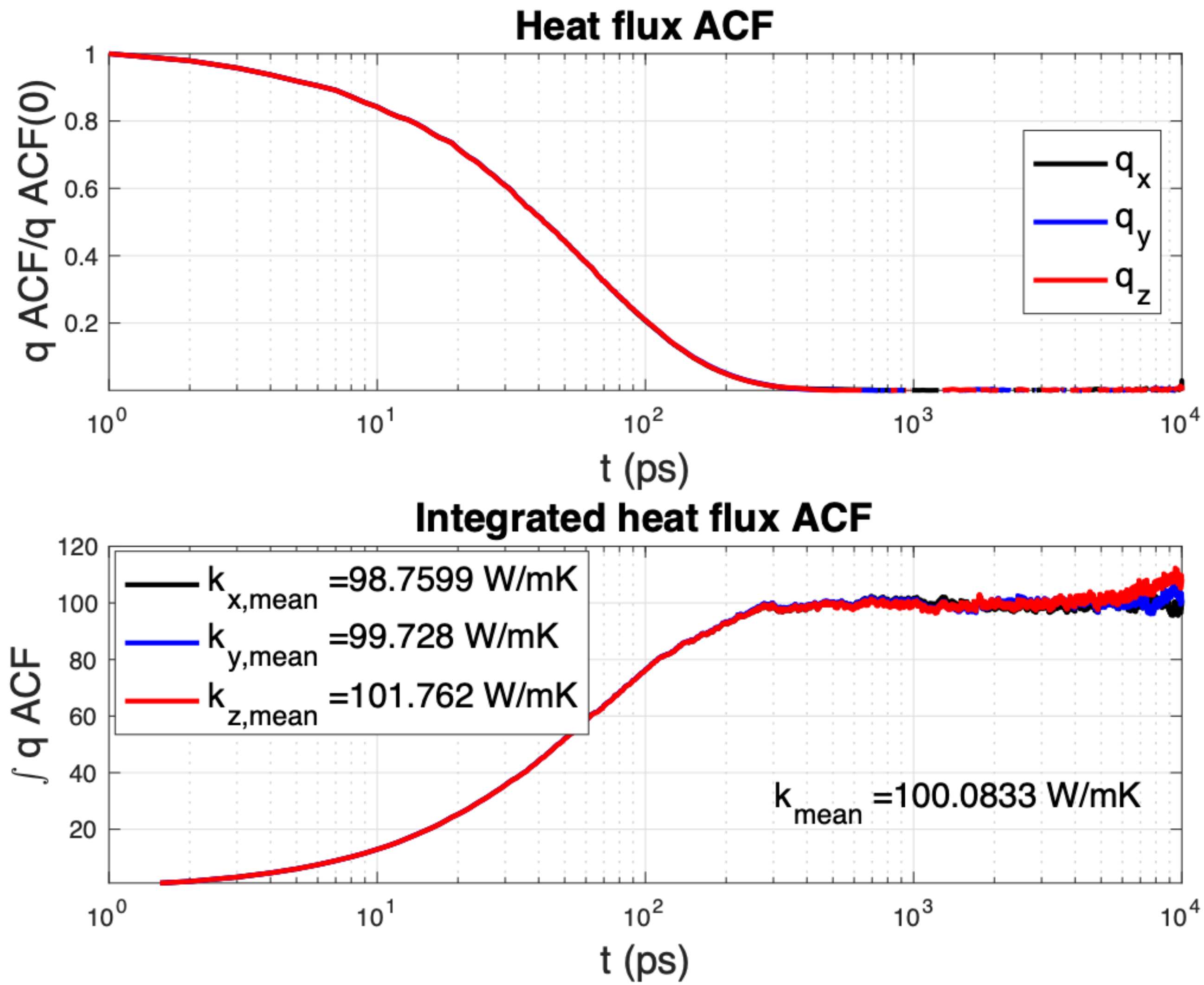
Heat flux autocorrelation of MC simulations 3

GaN @ 300K - Callaway-Debye model



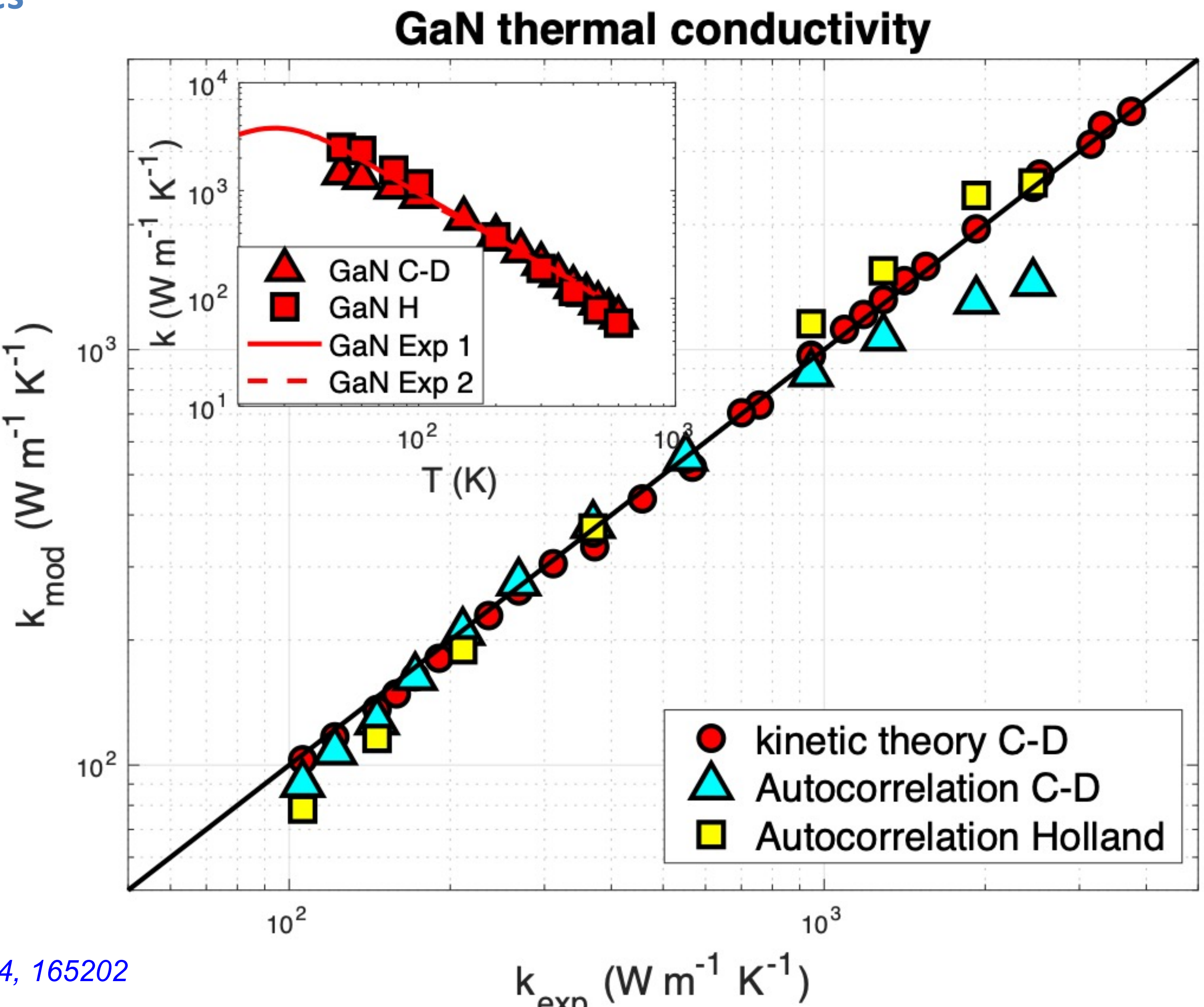
Heat flux autocorrelation of MC simulations 4

GaN @ 500K - Callaway-Debye model



TC from MC autocorrelation & KT simulations 1

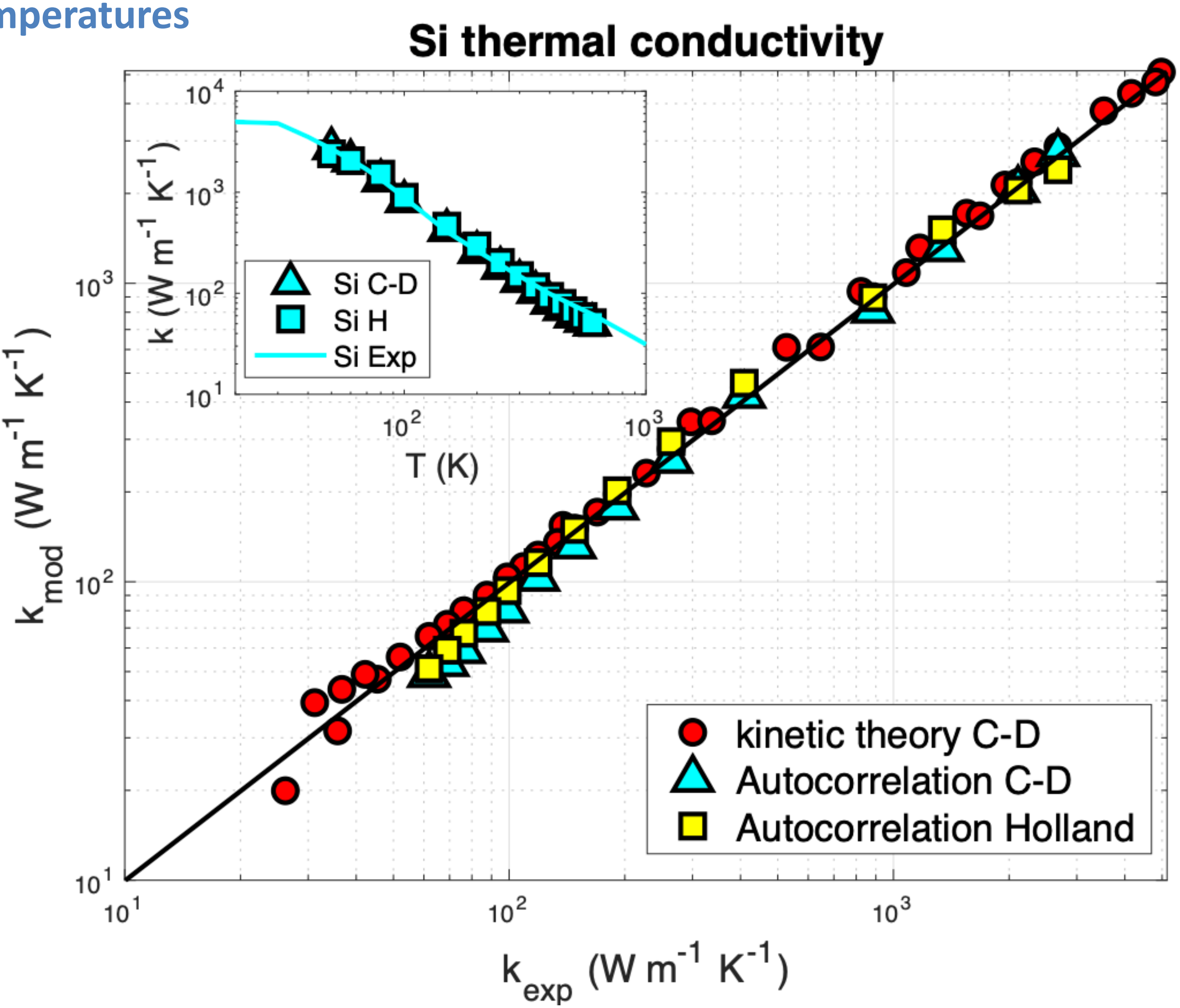
GaN : Comparison of kinetic and autocorrelation calculations to experimental data at different temperatures



Lacroix, PRB, 104, 165202

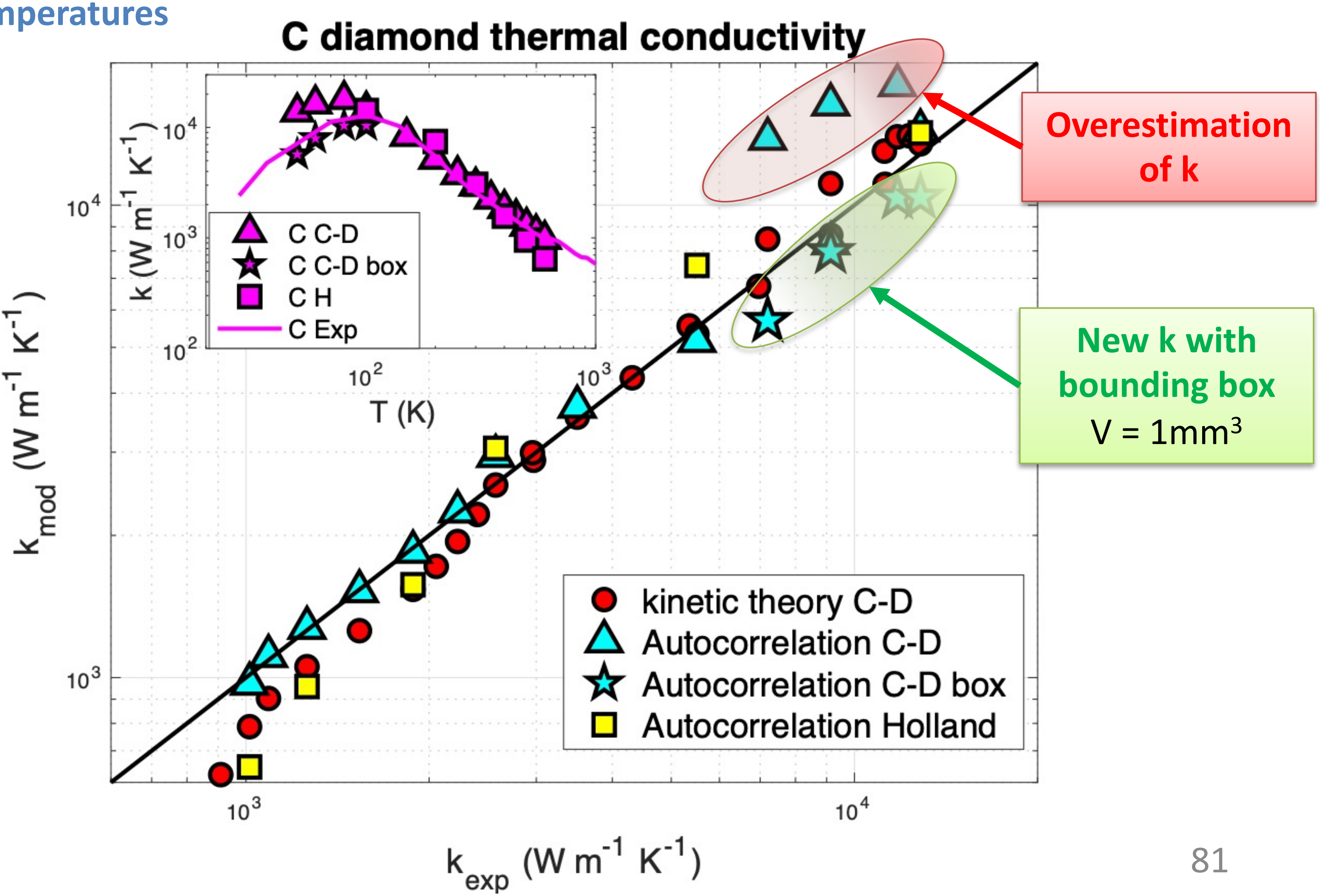
TC from MC autocorrelation & KT simulations 2

Silicon : Comparison of kinetic and autocorrelation calculations to experimental data at different temperatures



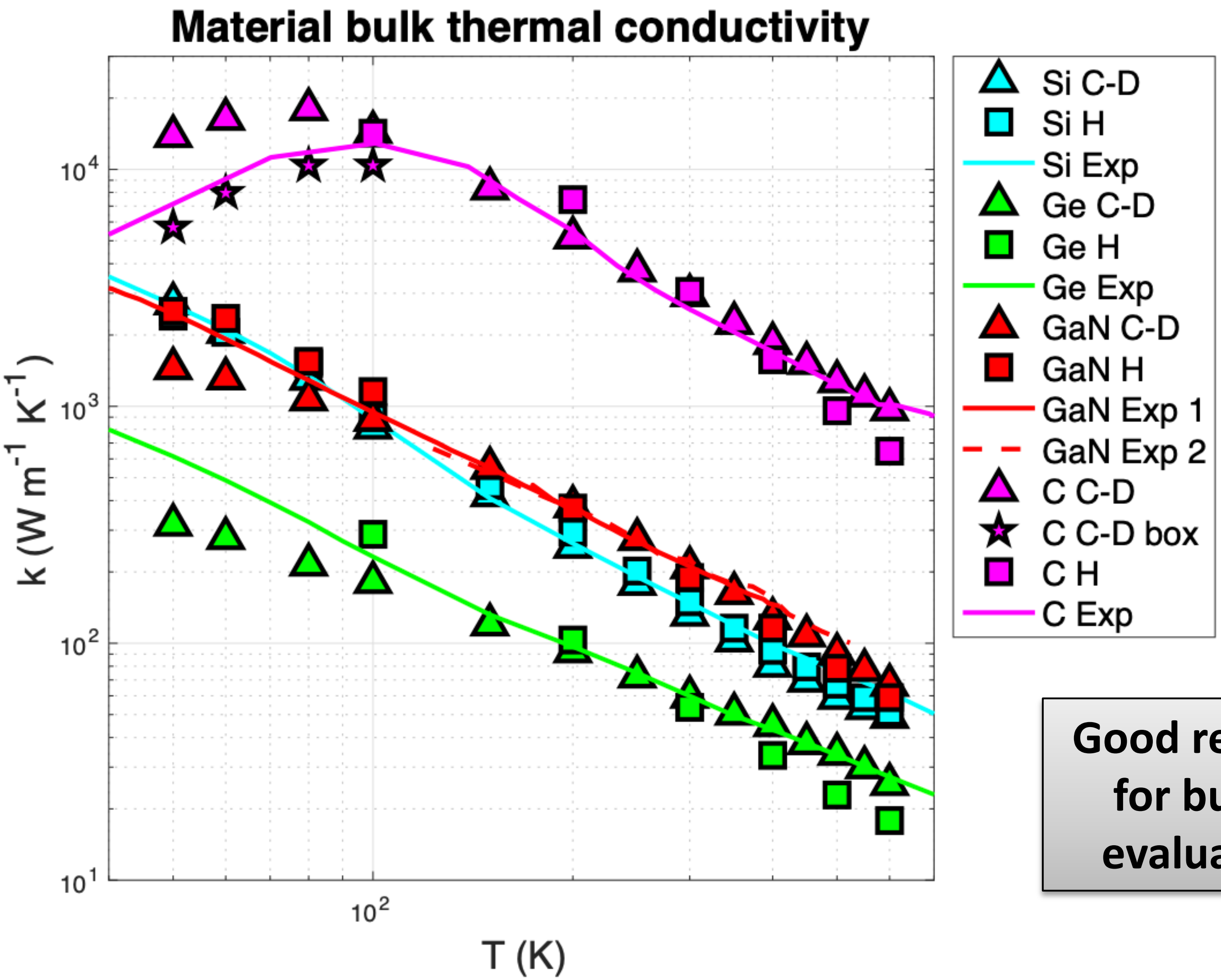
TC from MC autocorrelation & KT simulations 3

Diamond : Comparison of kinetic and autocorrelation calculations to experimental data at different temperatures



TC from MC autocorrelation & KT simulations 4

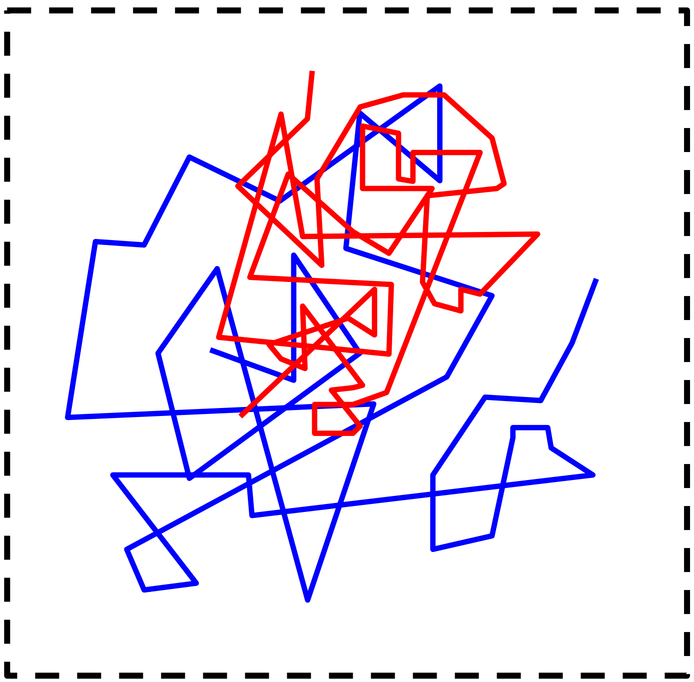
Results for : Si, Ge, GaN & Diamond



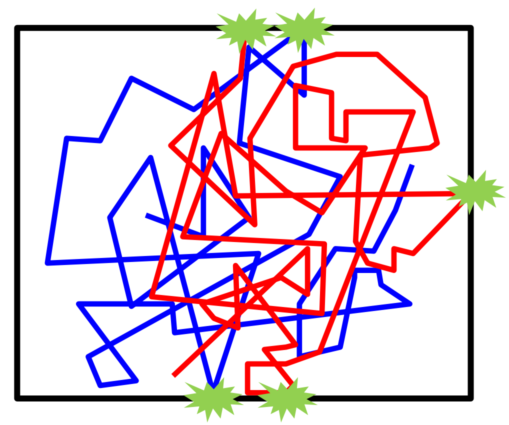
Good reliabilty for bulk TC evaluation !

Perspectives on MC autocorrelation simulations 1

First simulations were mostly done on “bulk materials” (except for C diamond), i.e., there is no boundary in the simulation domain and particles were free to move in an “infinite” structure. In other words, there is no boundary scattering.



Open domain : no boundaries

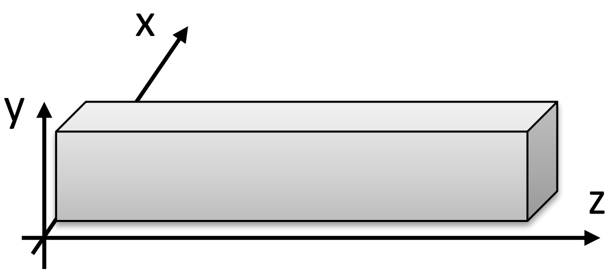


Closed domain : boundary scattering lowers phonon mfp

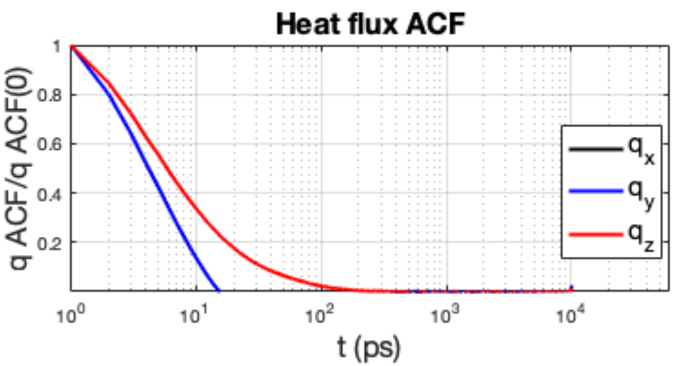
Nanowires, nanofilms, nanodots modelling possibilities ?

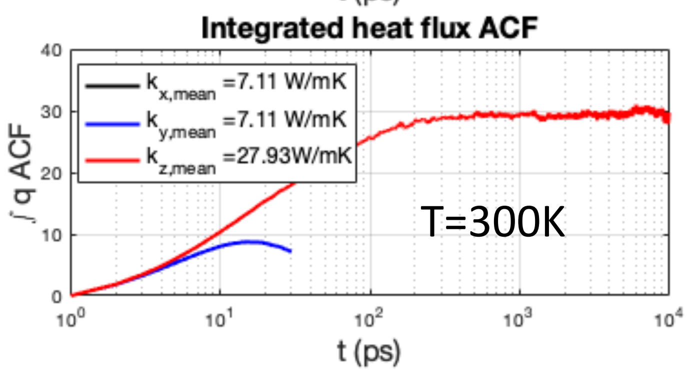
Perspectives on MC autocorrelation simulations 2

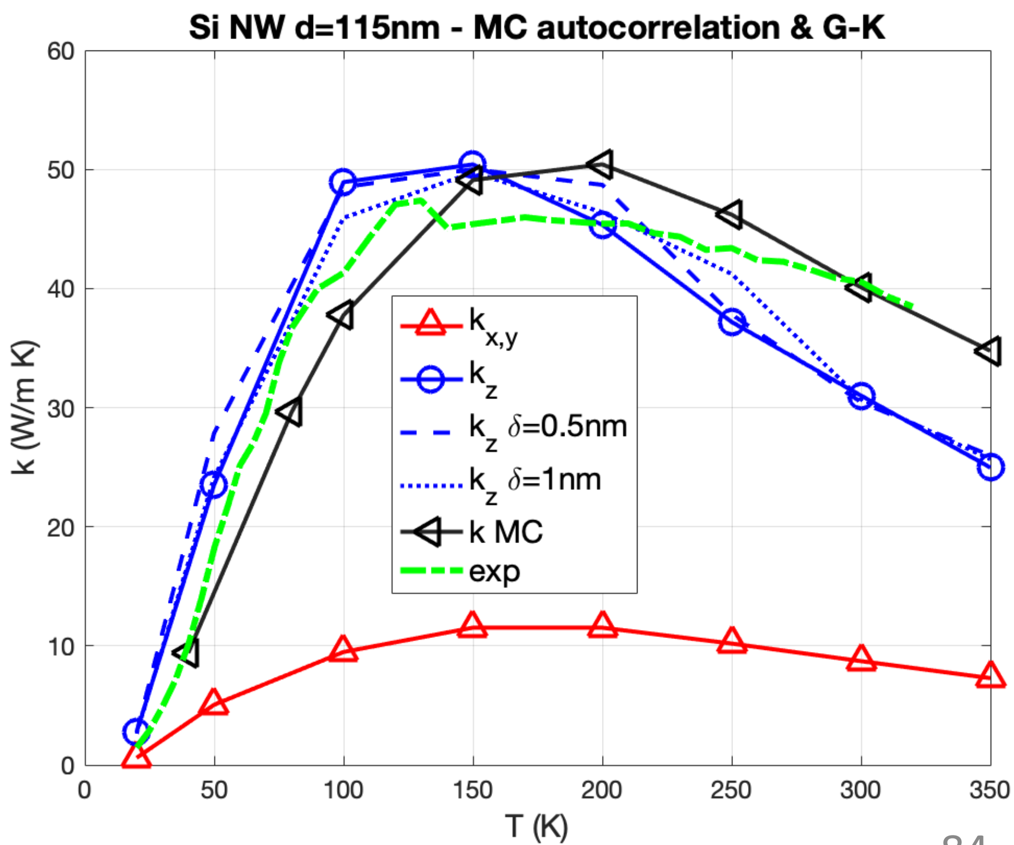
Nanowire modelling



- Isothermal system; L_x=L_y=102nm ; L_z=10µm
- Diffuse boundary scattering in x and y directions
- No boundary scattering in z direction



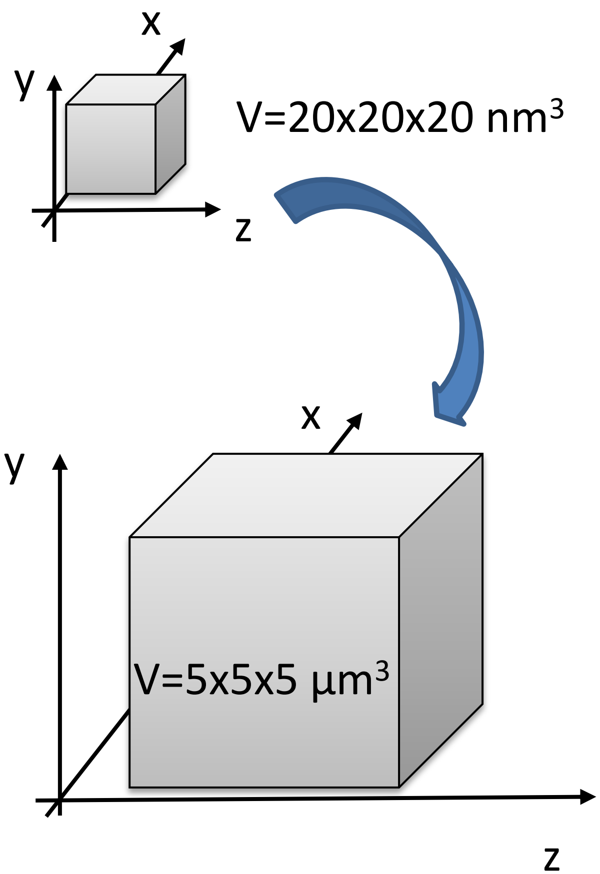


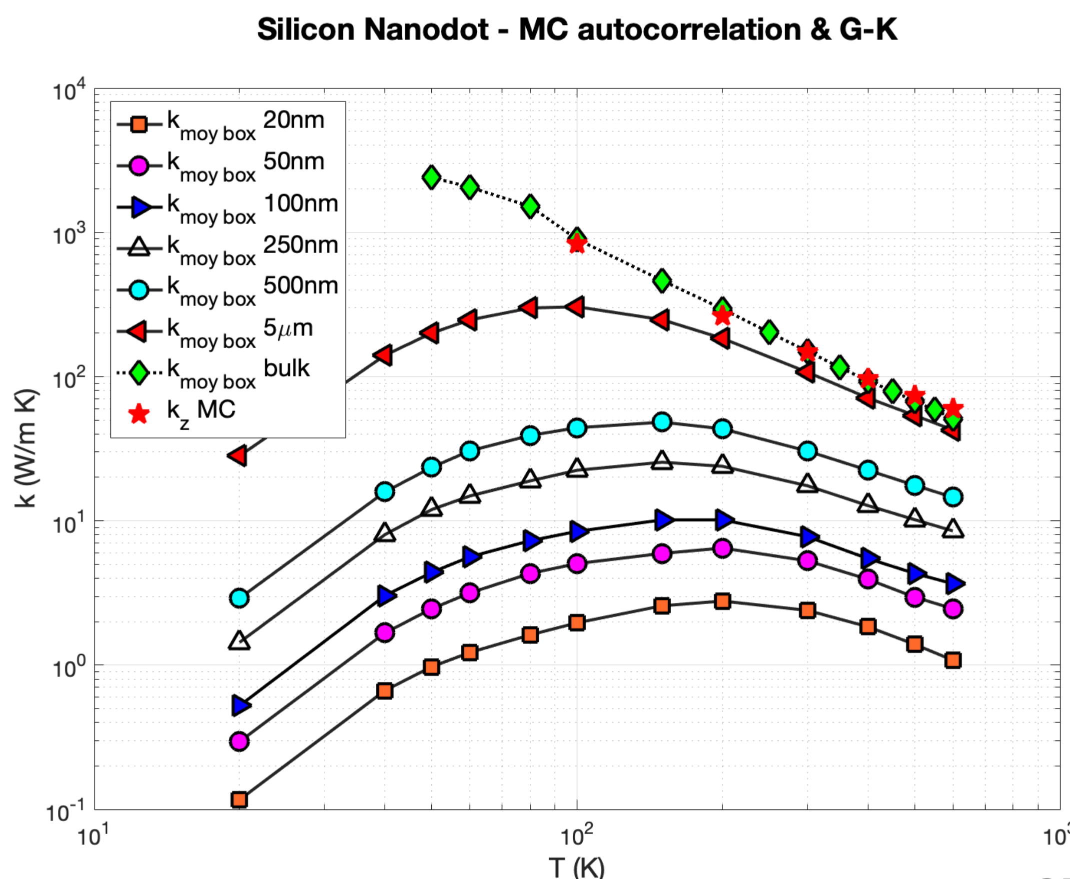


Perspectives on MC autocorrelation simulations 3

Nanodot modelling

- Isothermal system;
- Box size : 20nm < $L_x=L_y=L_z$ < 5µm
- Boundary scattering in x, y and z direction,





Summary (Pros/Cons)

- New methodology that combines MC and Green-Kubo formalism
- Efficient for high temperatures and/or strongly scattering nanostructures
- Isothermal simulations (no thermal gradient)
- Access to the conductivity tensor

- Needs more memory to perform calculations
- Improvement needed to recover other properties like thermal diffusivity
- Currently based on isotropic dispersion relations

General summary and future works

Summary

- MC solution of BTE offers a good flexibility to model heat transport in different kind of nanostructures close to the real ones, from ~10nm to ~10μm
- Computational cost is reasonable (some hours to max 1 week)
- Possibility to include real material dispersion properties (by DFT or through models)
- Gives transient information on heat transport
- Gives spectral information on phonon contribution to thermal properties
- Allows "multi-material" modelling (interfaces, inclusions, etc.)

Improvements, perspectives

- Coupling with other heat transport mode (radiative heating)
- Modelling of time modulated heating
- Coupling of MC methods for BTE solution to MD modeling (interfaces, inclusions)
- Coupling of MC methods to AI tools (optimization of nanostructured devices)
- Gives spectral information on phonon contribution to thermal properties
- Allows "multi-material" modelling (interfaces, inclusions, etc.)

Colleagues et collaborations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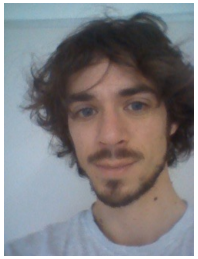
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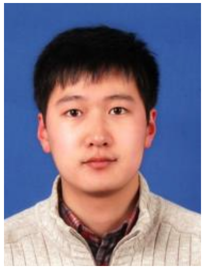
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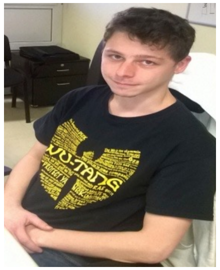
K. Termentzidis, DR, Cethil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Master students!

cnrs dépasser les frontières

Aristotle University of Thessaloniki

SiNaPS

iLM INSTITUT LUMIÈRE MATIÈRE

NÉEL institut

EM2C

inl

京都大学 KYOTO UNIVERSITY

cea

DEMOKRITOS NATIONAL CENTER FOR SCIENTIFIC RESEARCH

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IJL

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東京大学 THE UNIVERSITY OF TOKYO

ICN2

LOMA UMR5798 Laboratoire Ondes et Matière d'Aquitaine

Empa Materials Science and Technology

MC-BTE calculations for TE materials

Thermal conductivity of Bi_2Te_3 and SnSe using Debye-Callaway model and BTE

BTE

$$\frac{\partial f}{\partial t} + \nabla_k \omega \cdot \nabla_{\mathbf{r}} f + \mathbf{F} \cdot \nabla_p f = \left(\frac{\partial f}{\partial t}\right)_{scat}$$

f is the phonon distribution function

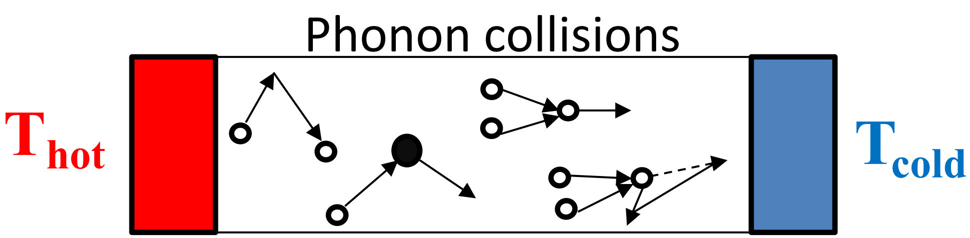
Relaxation Time Approximation

$$\left(\frac{\partial f}{\partial t}\right)_{scat} = \frac{f_0 - f}{\tau(\omega)}$$

$\tau(\omega)$ → Relaxation time

Data can be found in the literature for bulk materials but few ones exist for thin films and complex geometries

Collision probability

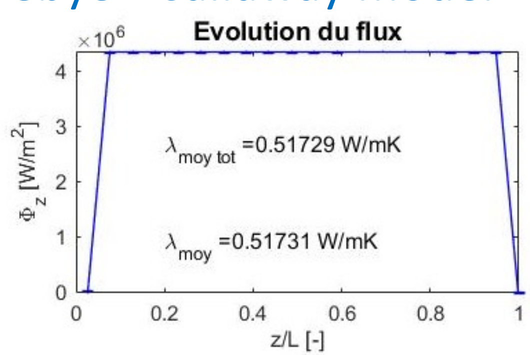


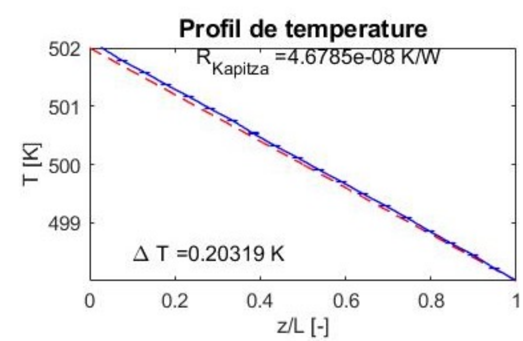
$$P_{scat} = 1 - \exp\left[\frac{-\delta t}{\tau(\omega,p,T)}\right]$$

$$\tau(\omega,p,T)^{-1} = \sum_{process} \tau_{process}(\omega,p,T)^{-1}$$

Heat flux evaluation using Debye - Callaway model

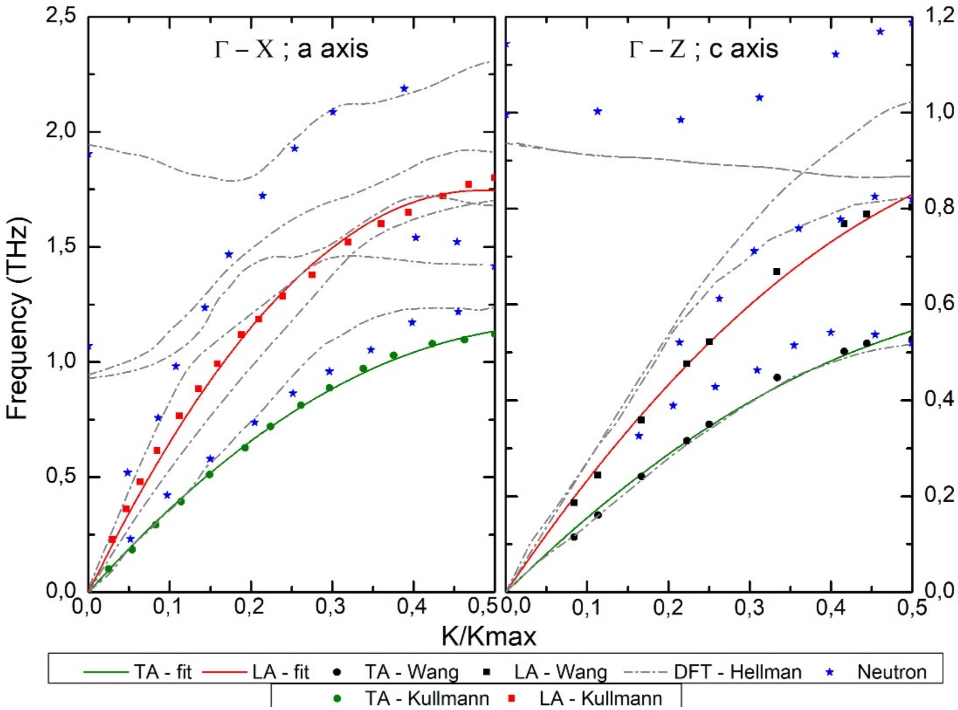
$$\Phi_z = \sum_{i=1}^{N} \frac{\hbar \omega_i \mathrm{V}_{gz}}{V}$$



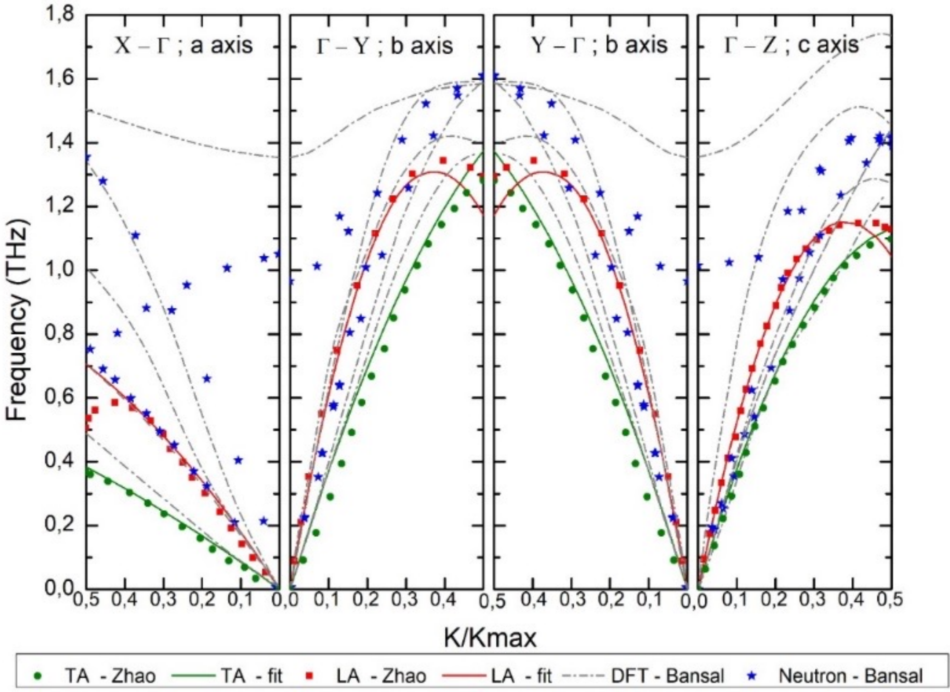


Phonon dispersions in Bi_2Te_3 and SnSe

Phonon dispersions in Bi_2Te_3 – fit a, and c axis



Phonon dispersions in SnSe – fit a, b, and c axis



Frequencies, quadratic fit

$$\omega_{TA} = c_{TA}K + v_{TA}K^2$$

$$\omega_{LA} = c_{LA}K + v_{LA}K^2$$

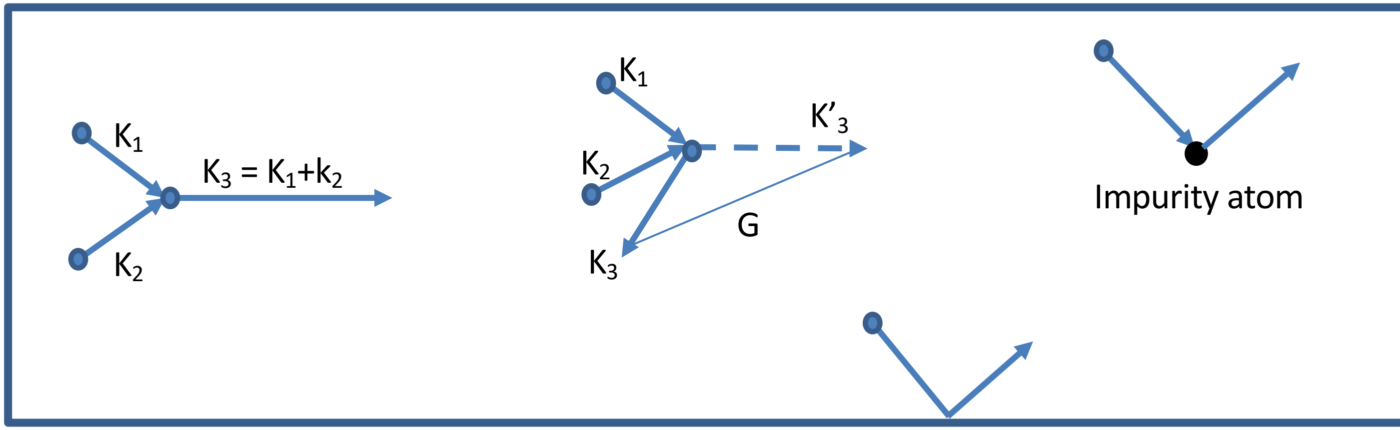
Group velocity

$v_g = d\omega/dk$

Scattering lifetimes and Relaxation time parameters

Phonon scattering mechanisms

Normal scattering B_N Umklapp scattering B_U Impurity scattering B_I



Phonon-boundary scattering

Intrinsic to MC solution of BTE

$$\tau = cte \times f(\omega, T)$$

$$B_N^L \approx \frac{k_B^3 \gamma_L^2 V}{M \hbar^2 v_L^5}$$

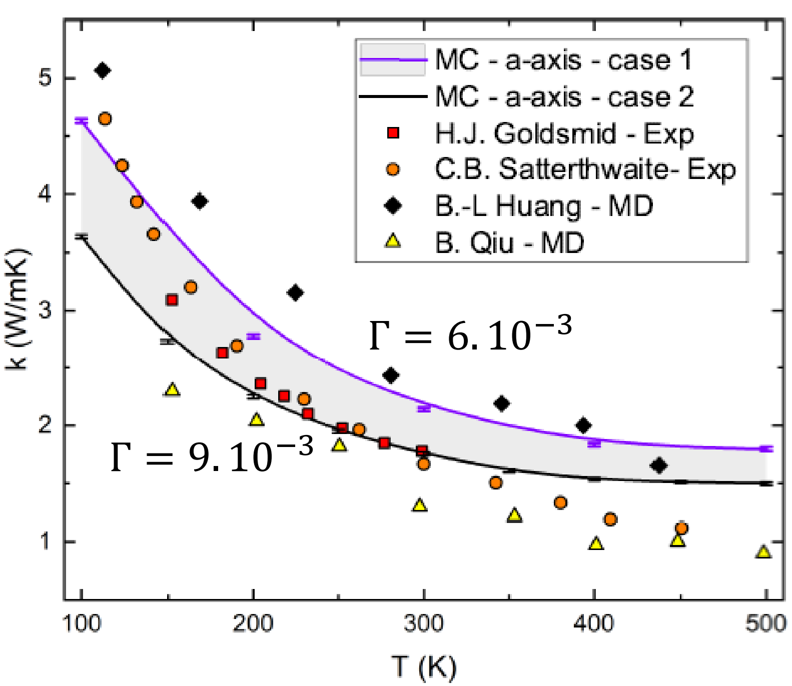
$$B_U \approx \frac{\hbar \gamma^2}{M v^2 \theta}$$

$$B_N^T \approx \frac{k_B^4 \gamma_T^2 V}{M \hbar^3 v_T^5}$$

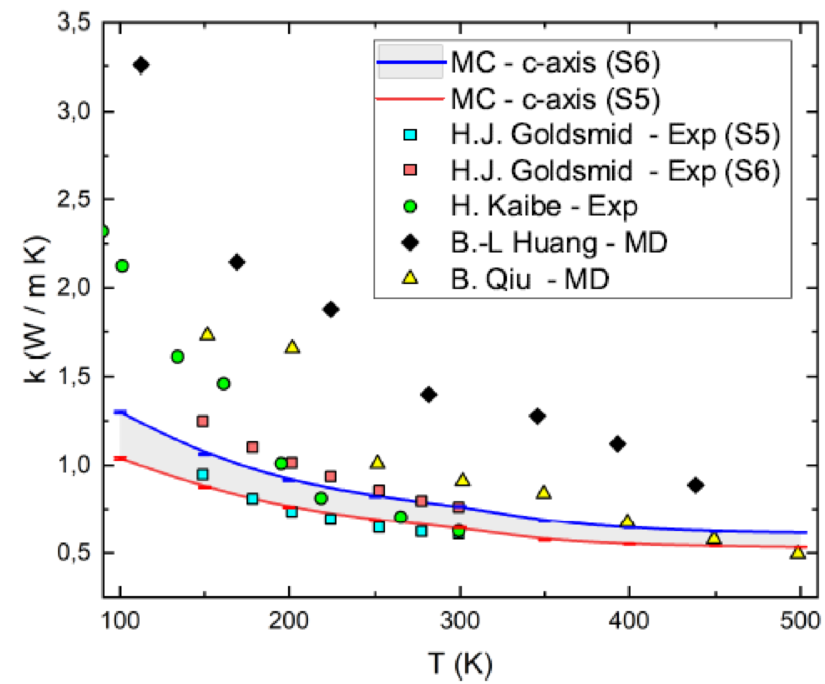
$$B_I \approx \frac{\Gamma V}{4 \pi v^3} + A$$

Thermal conductivity of Bi_2Te_3 along a and c directions versus temperature

Bi_2Te_3 Γ- X a-axis (cross-plane)



Bi_2Te_3 Γ- Z c-axis (cross-plane)



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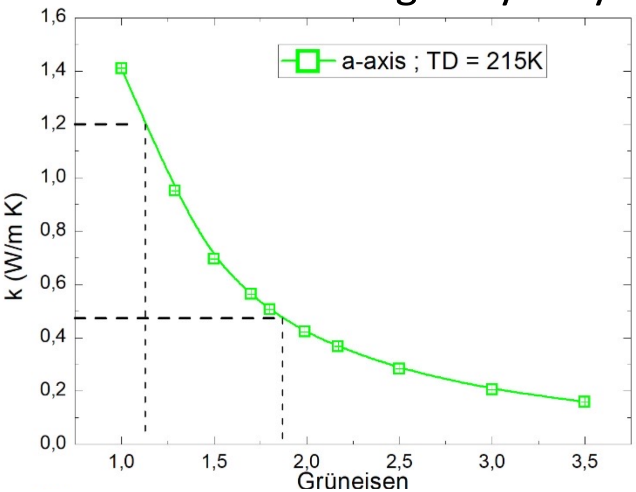
Increasing Γ decreases the thermal conductivity with a weaker effect at high temperatures

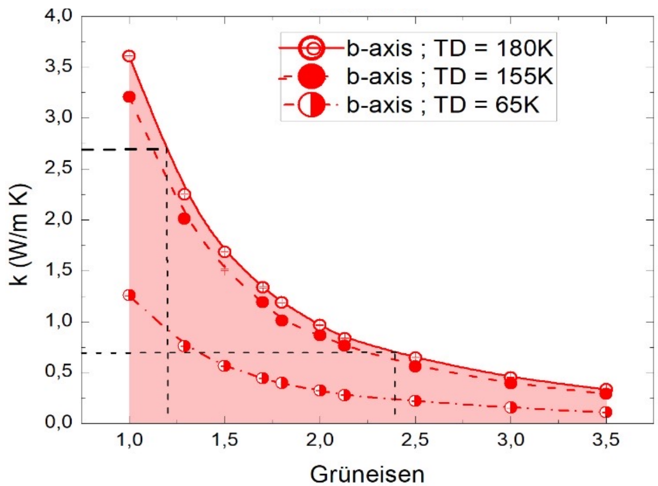
In the Γ- Z direction the thermal conductivity is lower than along Γ- X direction

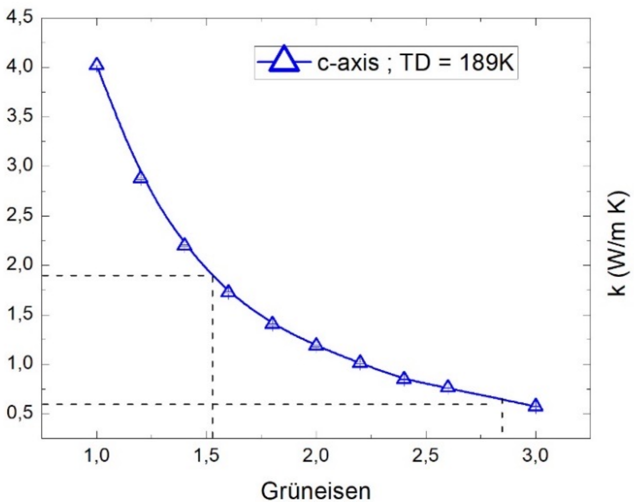
Thermal conductivity of SnSe along a and c directions versus temperature

Study of Grüneisen parameter ϒ effect on TC

γ → Related to the vibrational frequencies of atoms that changes by varying the volume of a solid







Macroscopic thermodynamic definition

Volume thermal expansion coefficient

Bulk modulus

$$\gamma = \frac{1}{\rho}\frac{\alpha K}{C_p}$$

Density

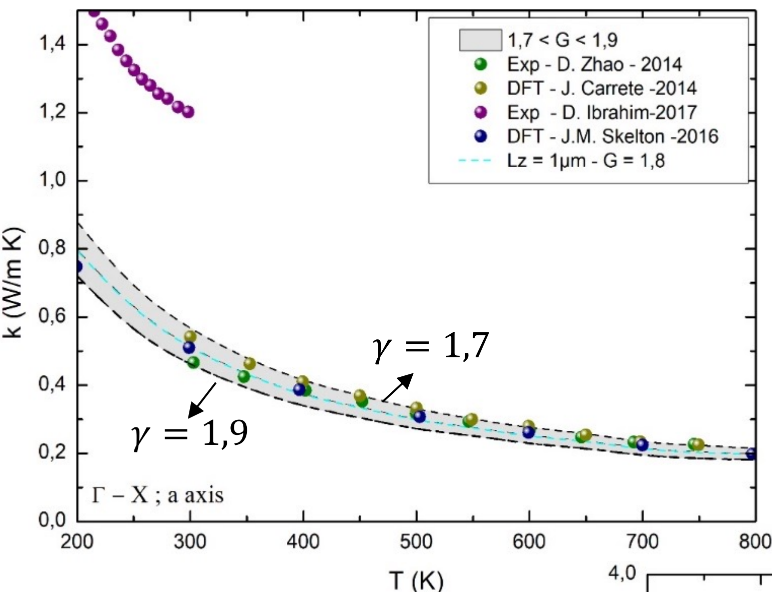
T = 300 K

k @ 300 K	a-axis	b-axis	c-axis
D. Zhao - Exp	0,466	0,7	0,676
D. Ibrahim - Exp	1,202	2,335	1,683
R. Guo - DFT	0,8	2	1,7
J.M. Skelton - DFT	0,52	1,43	1,88
J. Carrete - DFT	0,53	1,8	0,91
Grüneisen min	1,1	1,2	1,5
Grüneisen max	1,9	2,4	2,8

Recover TC obtained from DFT and experiments

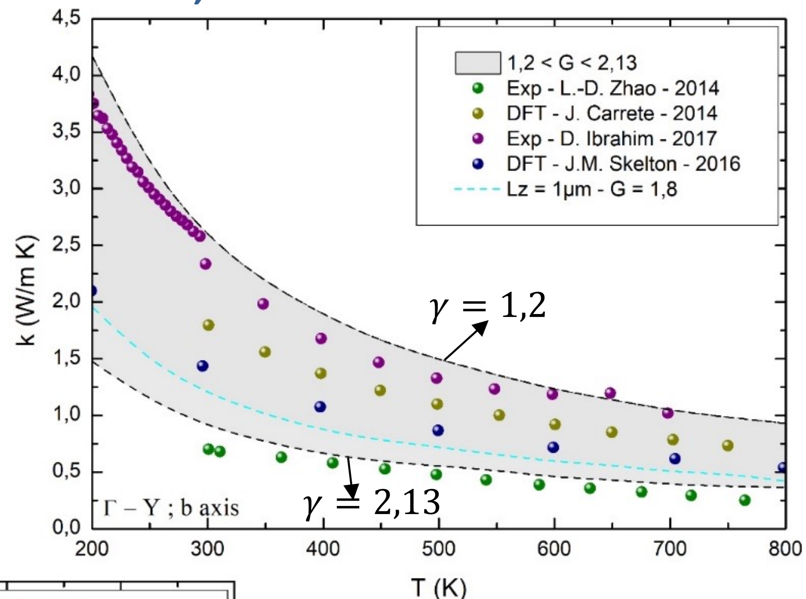
Thermal conductivity of SnSe along a and c directions versus temperature

SnSe, a-axis

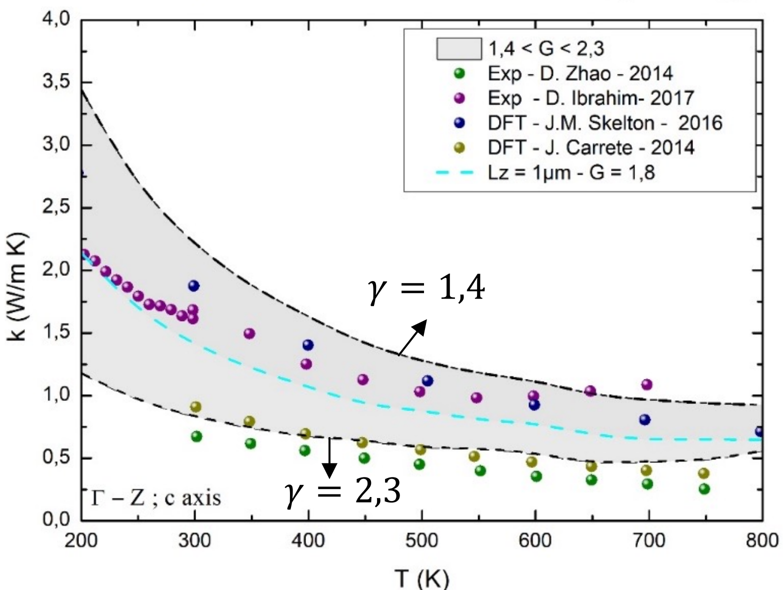


Extra low TC verified by samples with lower densities

SnSe, b-axis



SnSe, c-axis



Bulk SnSe, Lz = 1µm

The variation of γ allows to recover TC of bulk SnSe on extended temperature range with good agreement with the literature

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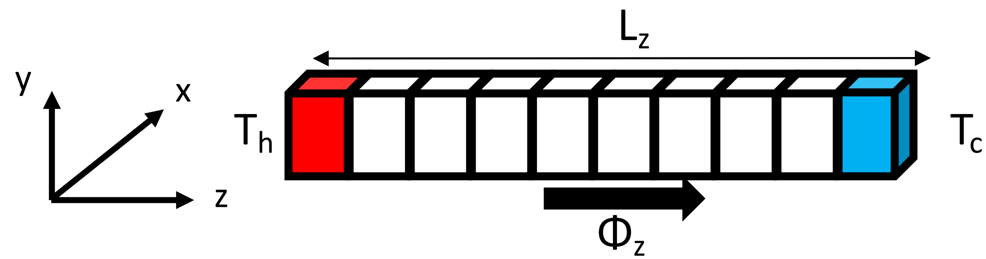
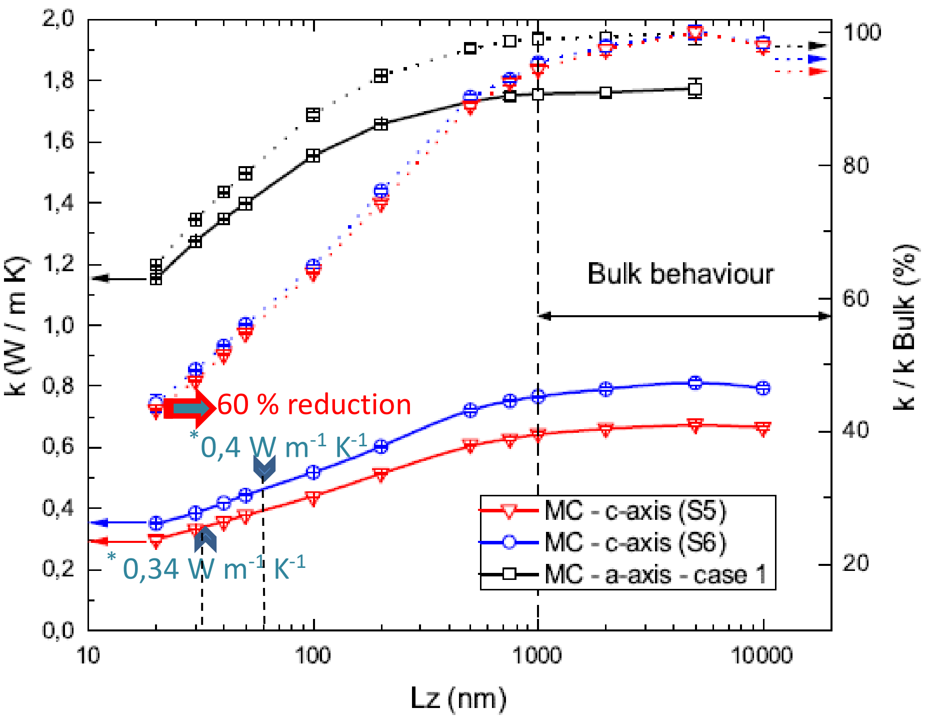
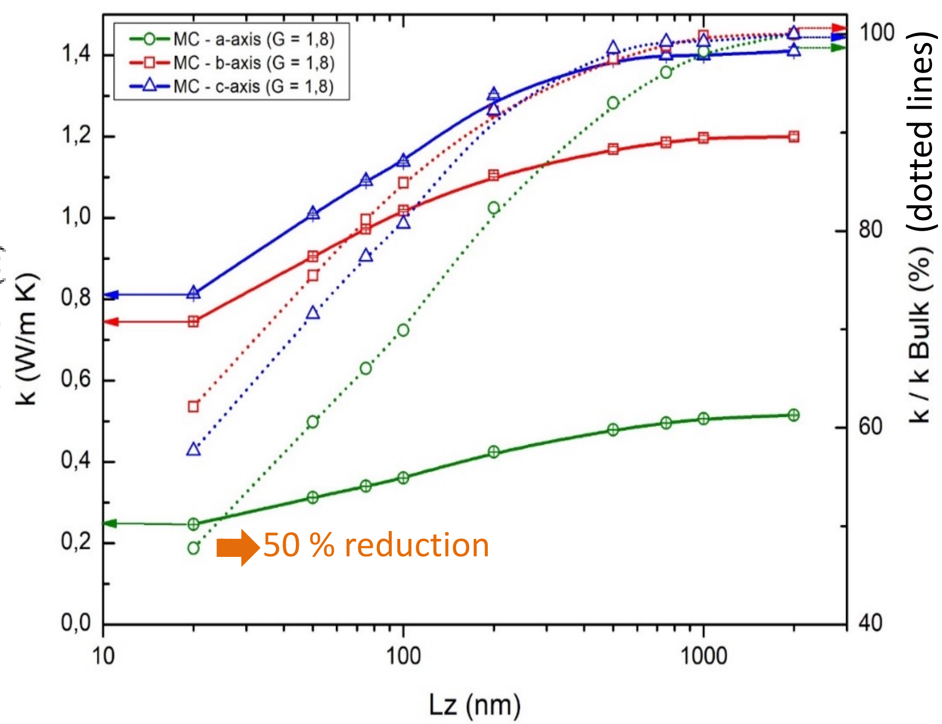
Film cross plane thermal conductivity versus thickness for Bi_2Te_3 and SnSe



Bi_2Te_3 thin film, 20 nm ≤ Lz ≤ 10 000 nm



SnSe thin film, 20 nm ≤ Lz ≤ 2000 nm



Lack of data for comparison in the literature

* M. Takashiri *et al.*, J. Appl. Phys., 104 (8), 2008

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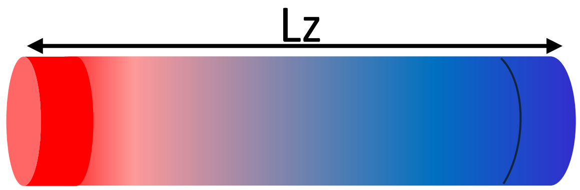
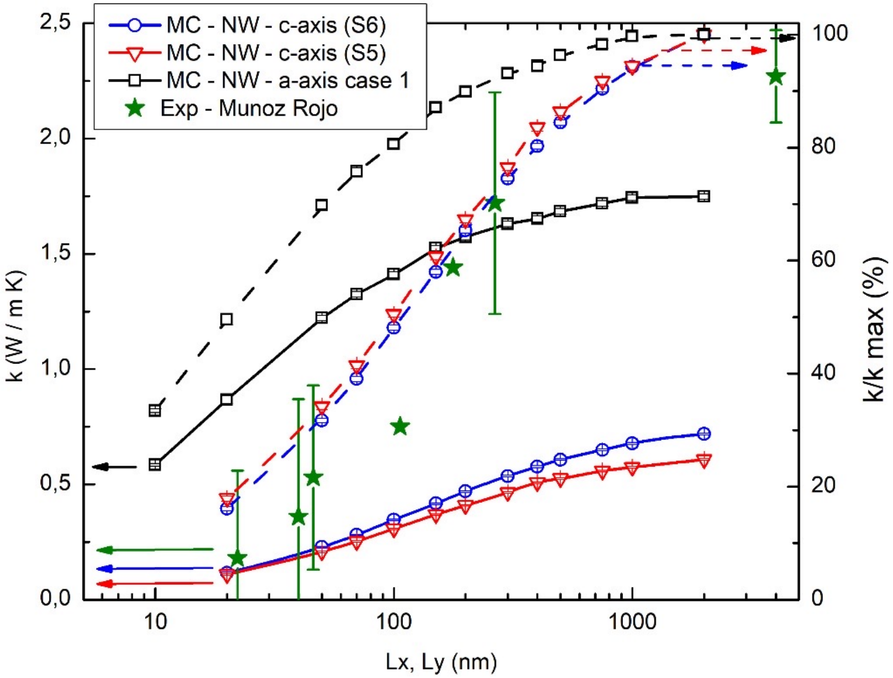
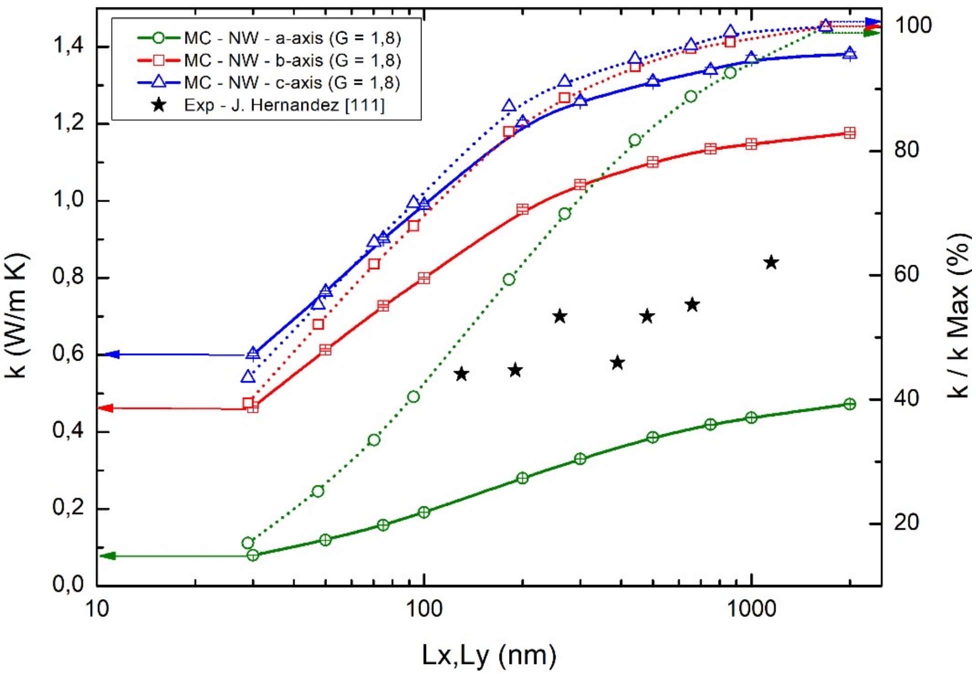
Nanowire thermal conductivity versus side length for Bi_2Te_3 and SnSe



NW Bi_2Te_3, Lz = 1000 nm



NW SnSe, Lz = 1000 nm



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Nanowire thermal conductivity versus side length for Bi_2Te_3 and SnSe

Polycrystalline model: Composed of large number of grains where the orientation of the atoms is different for each grain

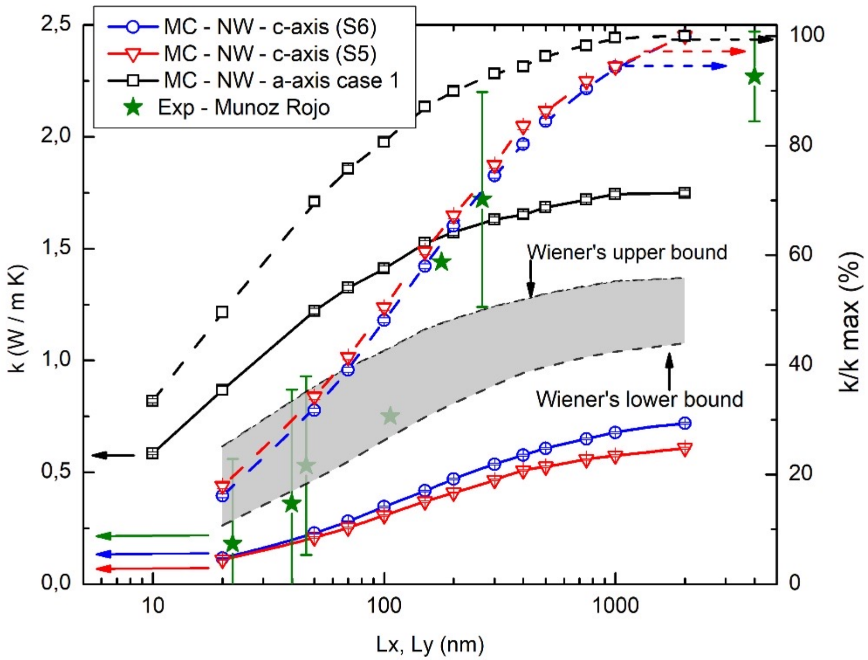
Lower bound, Harmonic mean

$$\frac{1}{k_{HM}} = \frac{1}{3}\left(\frac{1}{k_x} + \frac{1}{k_y} + \frac{1}{k_z}\right)$$

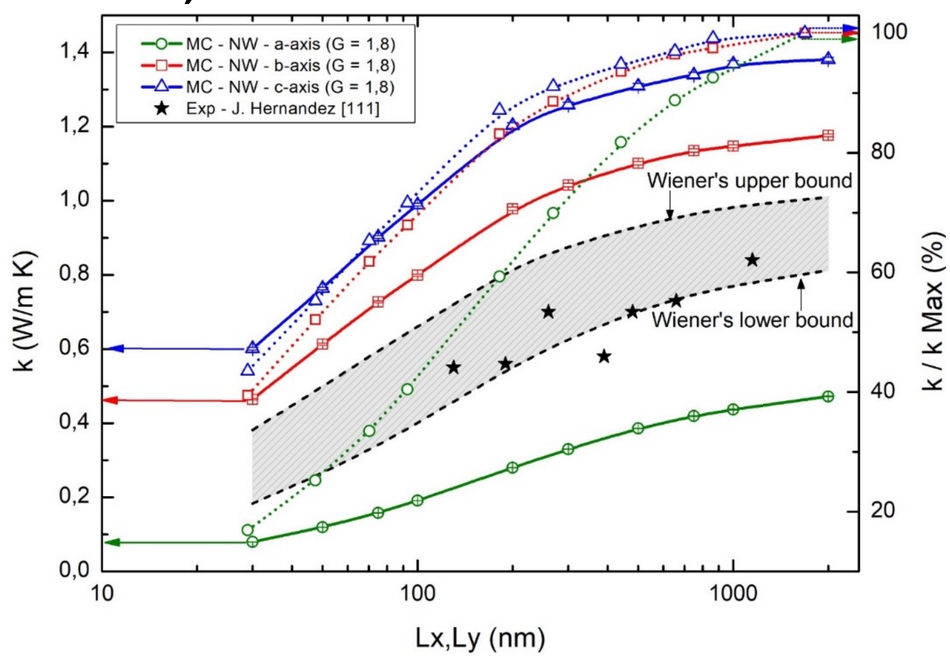
Upper bound, Arithmetic mean

$$k_{AM} = \frac{1}{3}(k_x + k_y + k_z)$$

Bi_2Te_3, Lz = 1000 nm



SnSe, Lz = 1000 nm



Obvious reduction in TC due to phonon confinement in good agreements with experimental data