Nanoscale interfacial heat transfer: insights from molecular dynamics

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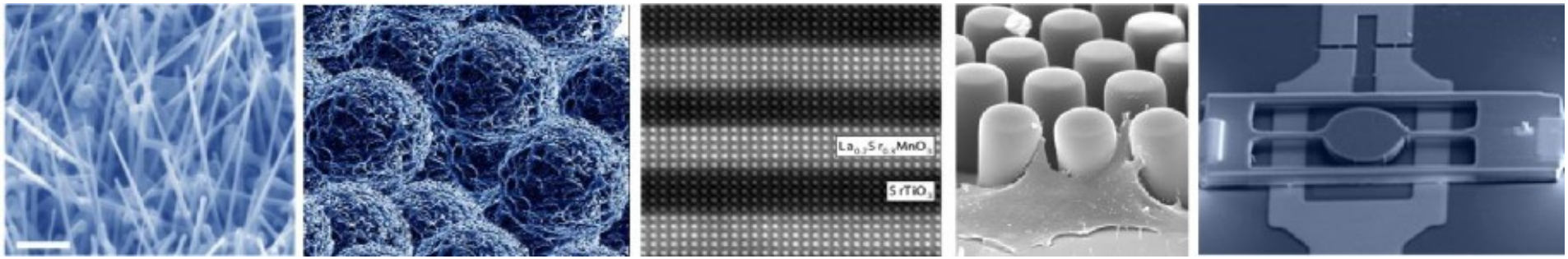
SFB-TRR 75
Tropfendynamische Prozesse unter extremen Umgebungsbedingungen

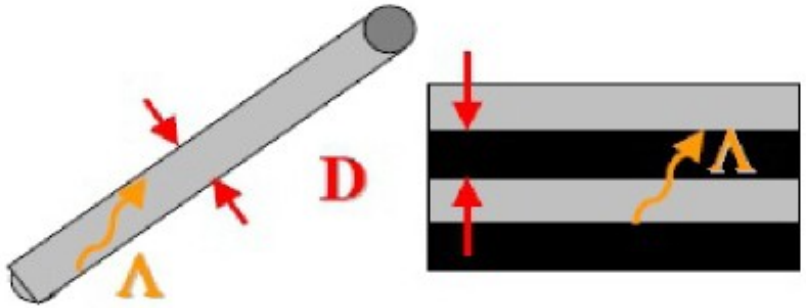
TECHNISCHE UNIVERSITÄT DARMSTADT

H. Han, F. Müller-Plathe
Technische Universität Darmstadt, Germany

CECAM LAMMPS workshop
June 26th, 2018 Lyon

Nanostructured materials





$D >> \Lambda$, Diffusive regime

$D \approx \Lambda$, Balistic regime

Si @300 K : $\Lambda > 300\,nm$

Fourier

$$\vec{J} = -\lambda \vec{\nabla} T$$

Thermal conductivity

Thermal conductivity

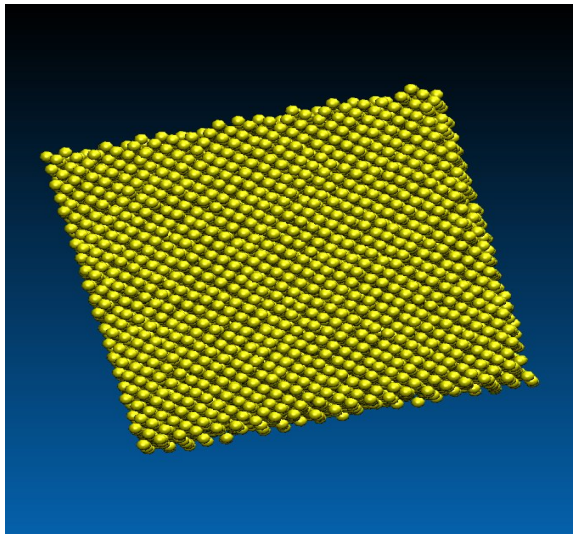
Essentially, two methods :

1. the « direct » method

Apply a temperature gradient or energy flux
and calculate the conductivity with Fourier law

2. equilibrium method

Probe the fluctuations around equilibrium
of the energy flux vector

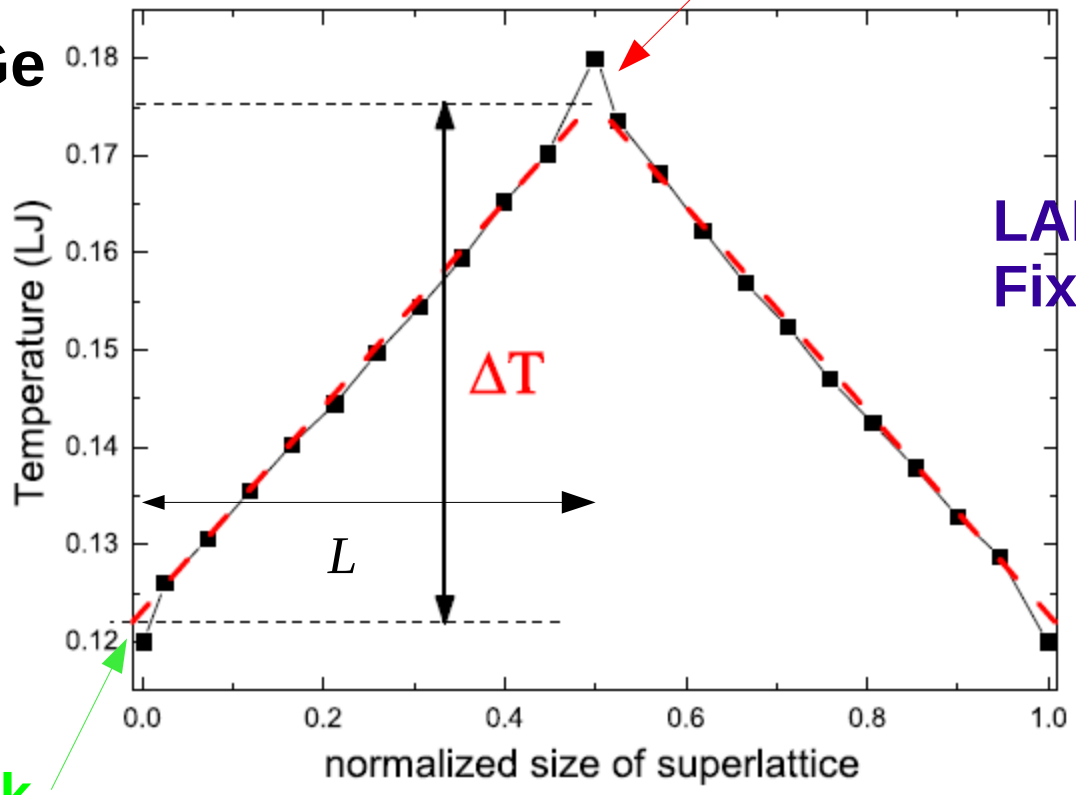


Thermal conductivity : the direct method

Steady state temperature profile

Heat source

Example Si/Ge



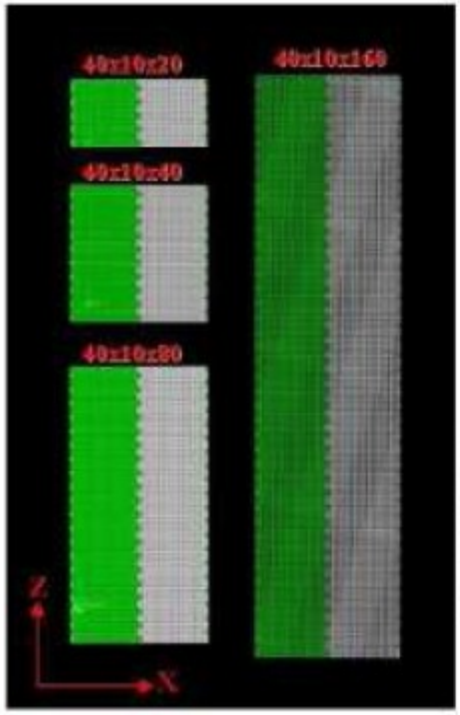
LAMMPS command= Fix temp/rescale

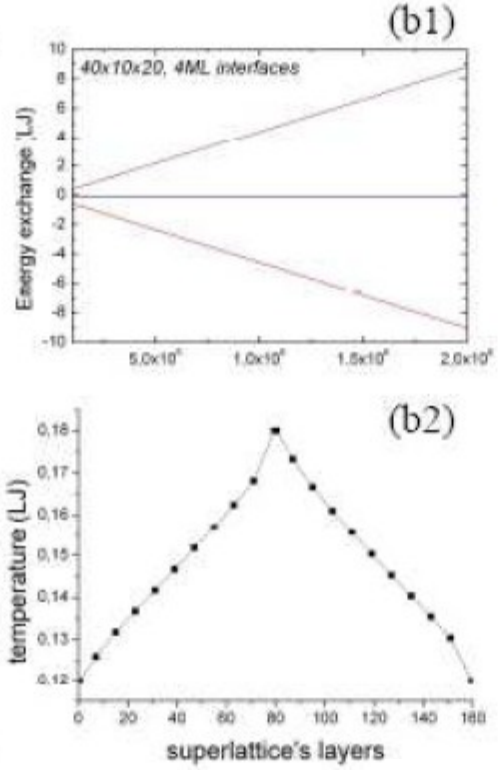
Heat sink

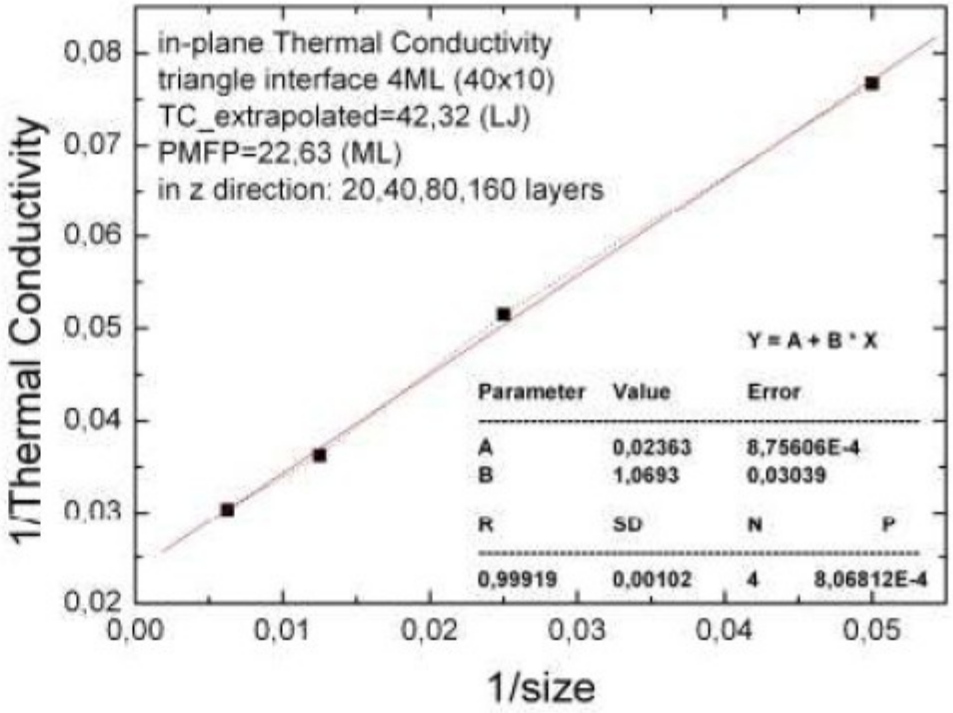
Fourier law : $$J = -\lambda \frac{\Delta T}{L}$$

Thermal conductivity : the direct method

Finite size effect analysis







« Bulk » thermal conductivity $1/\Lambda(L) = 2/L + 1/\Lambda(L \to \infty)$

Thermal conductivity : direct method

Advantages : - relatively easy to implement using open sources codes (LAMMPS)
-may be used also to compute the thermal boundary resistance

Inconvenients : -need to check if we are in the linear regime
=> analyze different heat fluxes
-severe finite size effects !
=> analyze different system sizes to properly extrapolate a « bulk » conductivity

Thermal conductivity : Green-Kubo equilibrium simulations

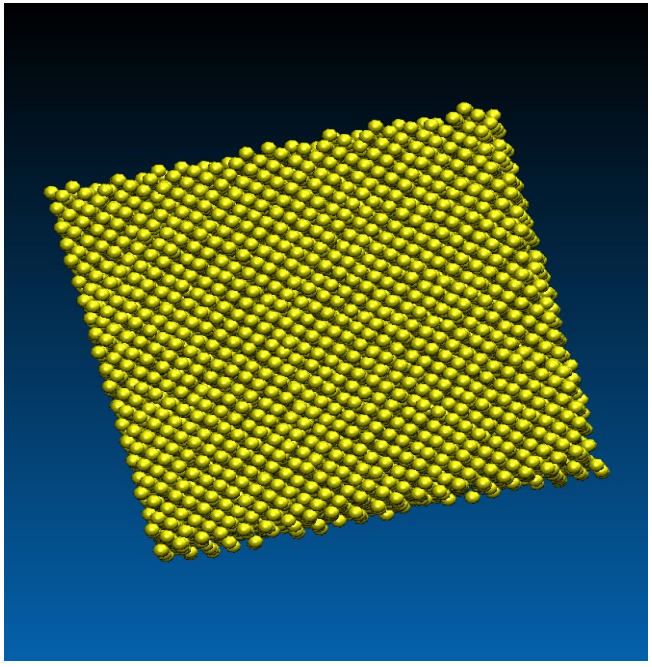
Green-Kubo formula :

$$\lambda_{\alpha,\beta} = \frac{1}{V k_B T^2} \int_0^{+\infty} \langle J_\alpha(t) J_\beta(0) \rangle \, dt$$

Heat flux vector : $\vec{J} = \frac{d}{dt}\left(\sum_i E_i \vec{r}_i\right)$

$$\vec{J} = \sum_i E_i \vec{v}_i + \frac{1}{2} \sum_{i \neq j} \vec{F}_{ij} \cdot \left(\vec{v}_i + \vec{v}_j\right)$$

In practice, run in NVE ensemble
LAMMPS command = compute heat/flux



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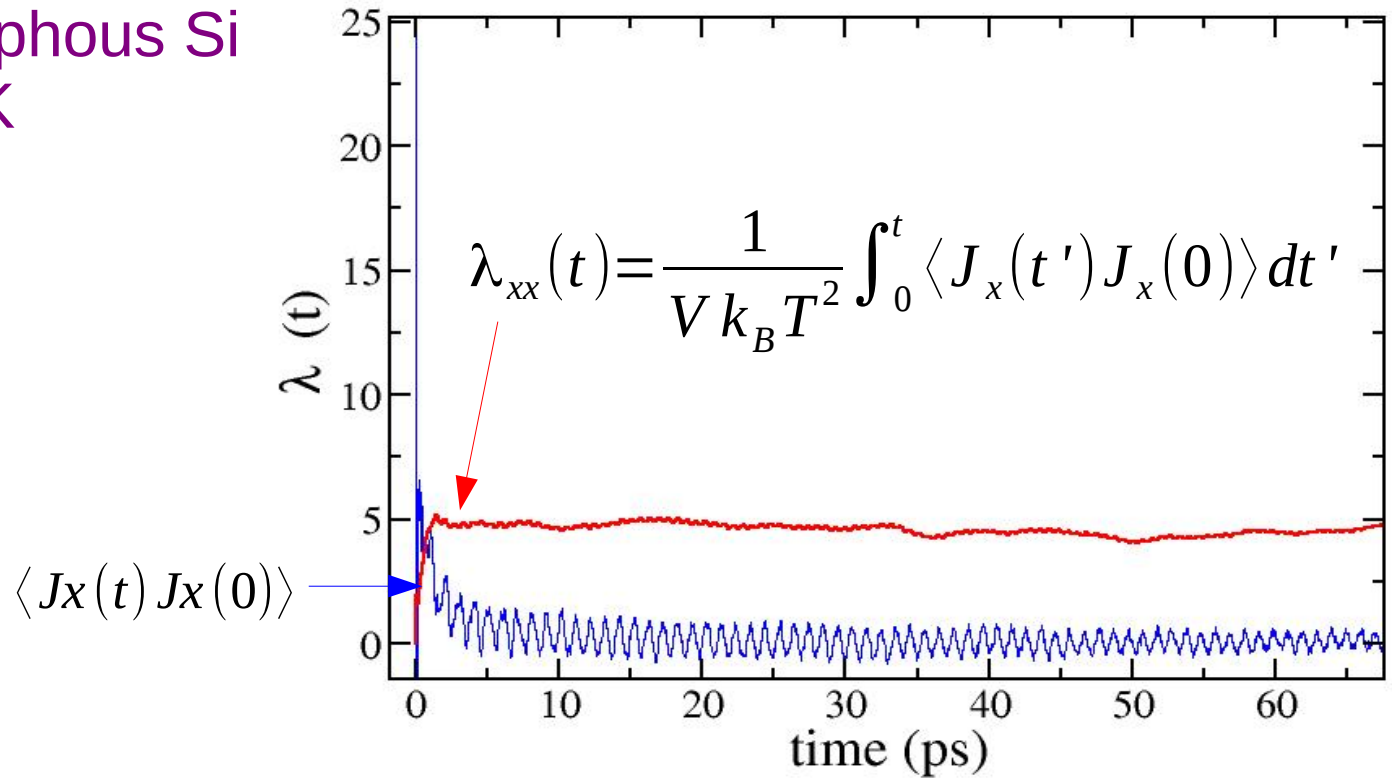
Example amorphous Si
300 K



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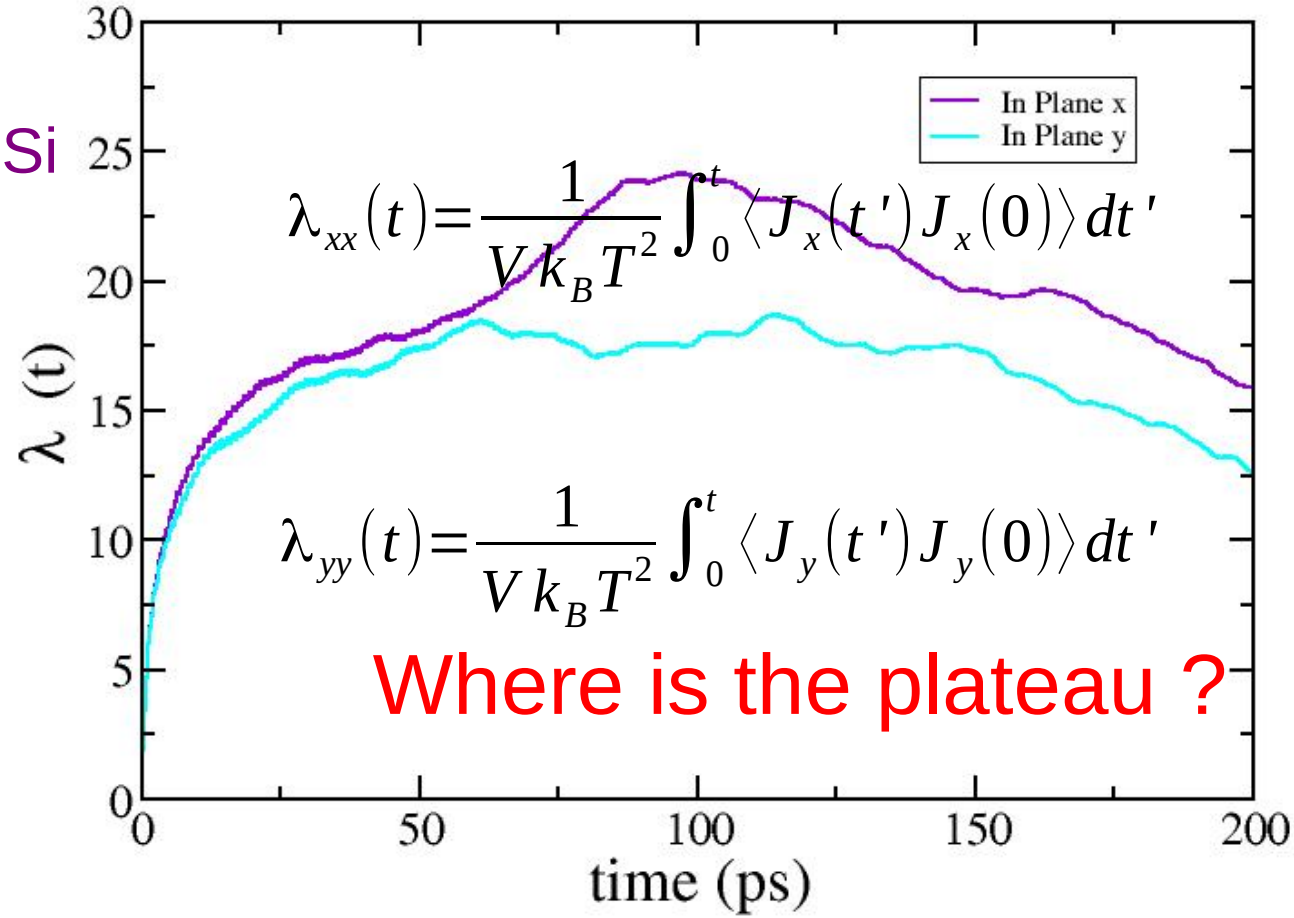
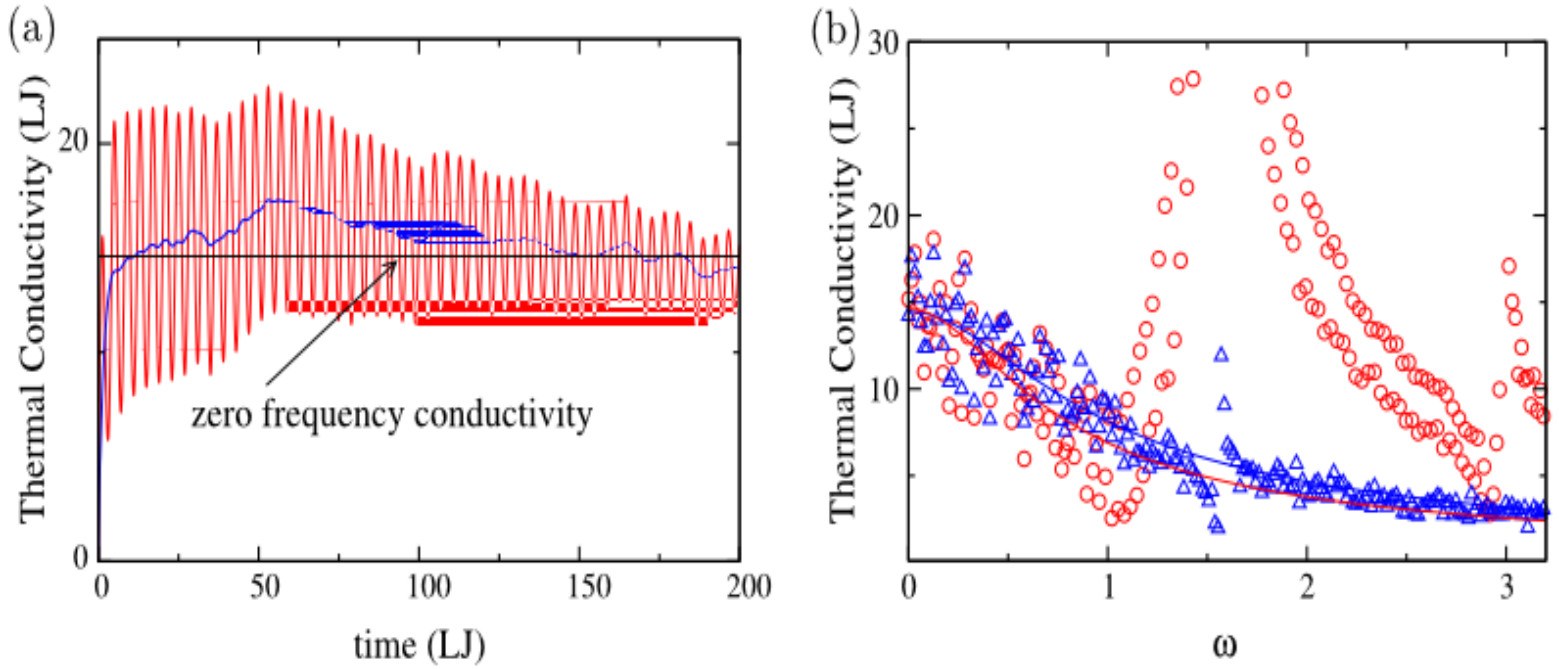


Optical modes



$$\vec{J} = \sum_i E_i \vec{v}_i + \frac{1}{2} \sum_{i \neq j} \vec{F}_{ij} \cdot (\vec{v}_i + \vec{v}_j)$$

Replaced by :

$$\vec{J} = \sum_i E_i^0 \vec{v}_i + \frac{1}{2} \sum_{i \neq j} \vec{F}_{ij}^0 \cdot (\vec{v}_i + \vec{v}_j)$$

Equilibrium positions

$$\lambda(\omega) = \frac{1}{V k_B T^2} \int_0^\infty \langle J(t) J(0) \rangle \exp(i \omega t) dt$$

Termentzidis, SM, Chantrenne IJHMT 2011

Not implemented in LAMMPS

Thermal conductivity : Green-Kubo equilibrium simulations

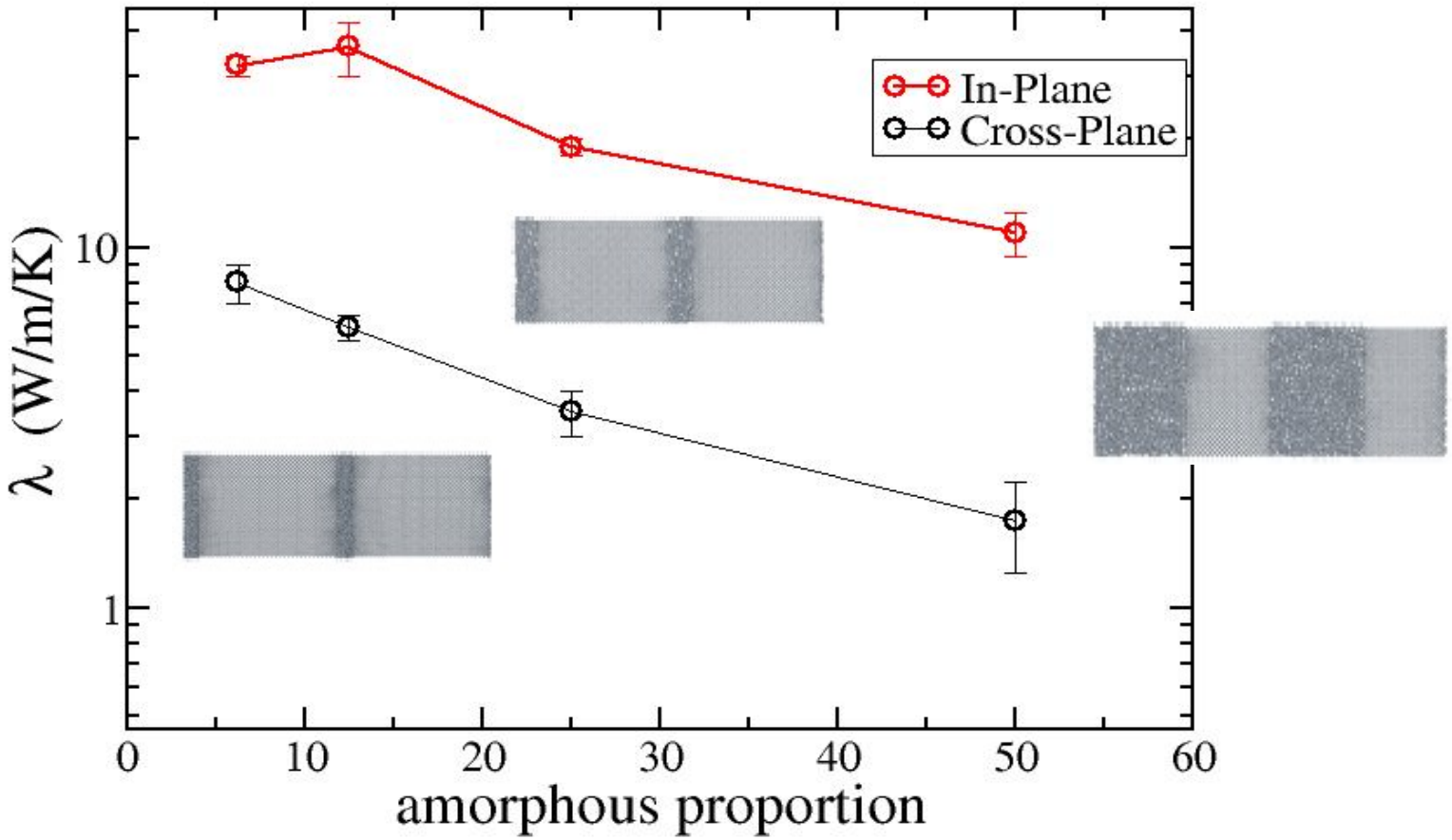
Advantages : - less severe finite size effects

- access to the full thermal conductivity tensor in a single simulation (anisotropic materials, superlattices)

Inconvenients : -need to run several independent simulations (usually 10 to 20)

-the plateau is sometimes difficult to identity (in principle, in a finite system the Green-Kubo formula should give a vanishing conductivity ...)

Thermal anisotropy

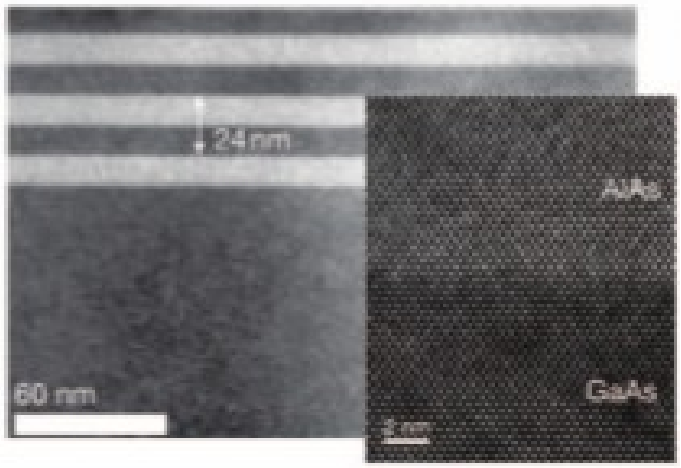


A.F. Lannord, SM, T. Albaret, D. Lacroix, K. Termentzidis, 2014

Thermal boundary resistance

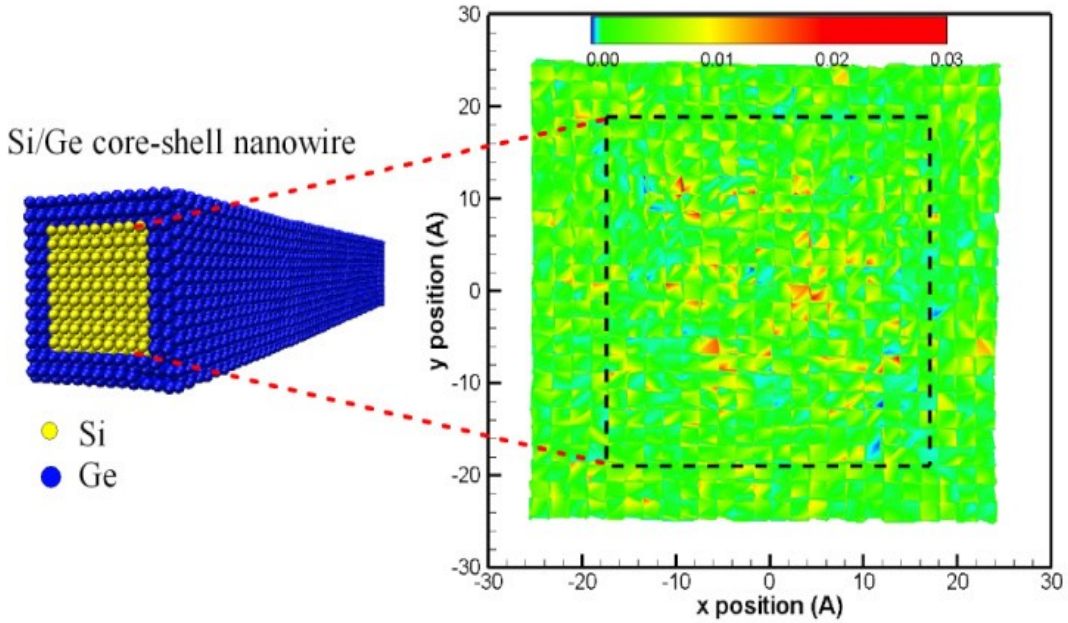
Heat Transfer at the nanoscale

Superlattices



Dresselhaus, Chen, Science 2012

Nanocomposites-nanowires

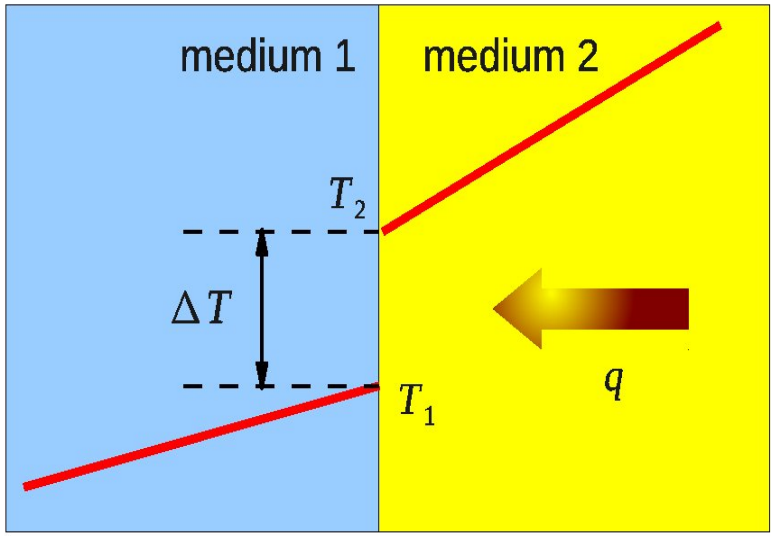


Poulikakos, NanoLetters 2011

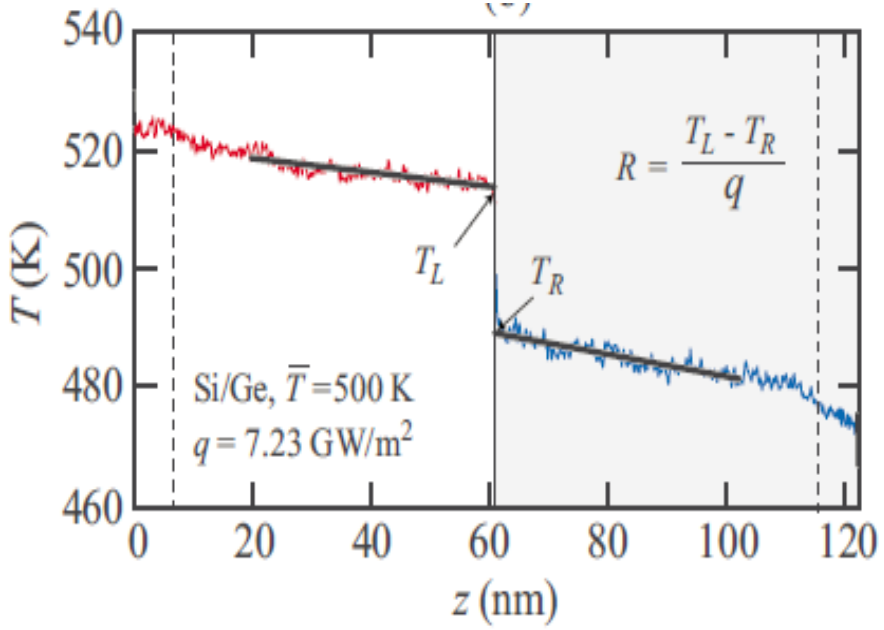
-Deviations from Fourier's law (dimensions < phonon mean free path)

-Thermal boundary resistance

Thermal boundary (Kapitza) resistance



Molecular dynamics Si/Ge



McGaughey, PRB 2009

$$G = 1/R = \int C_v(\omega) v_g(\omega) t_{12}(\omega) d\omega$$

Energy transmission coefficient

$$G \simeq 1 - 1000\, MW/m^2/K$$

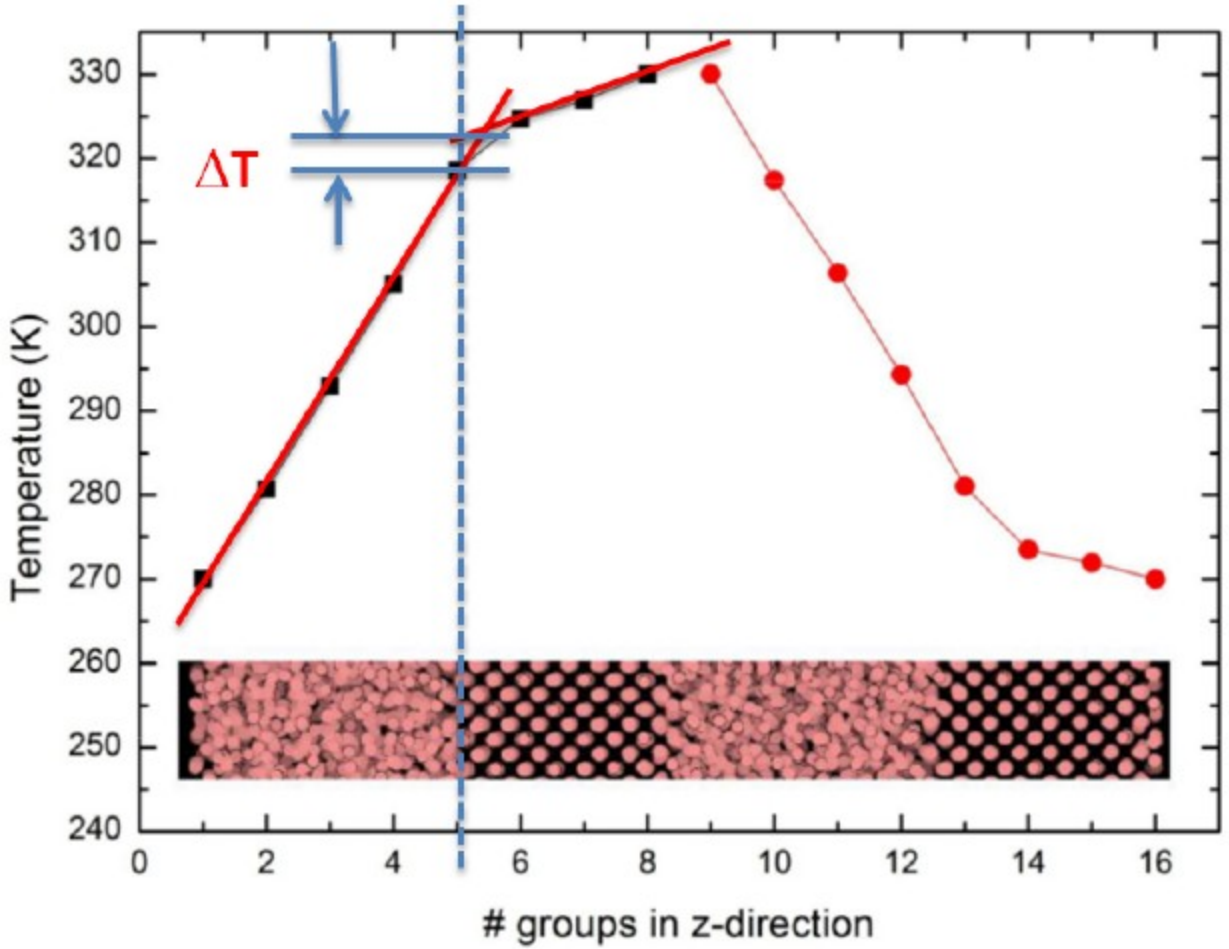
Non-equilibrium simulations

Amorphous Si/
Crystalline Si

A. France Lanord et al.,
J. Phys. Cond. Mat. 2014

Fourier law :

$$J = -\lambda \frac{\partial T}{\partial z}$$

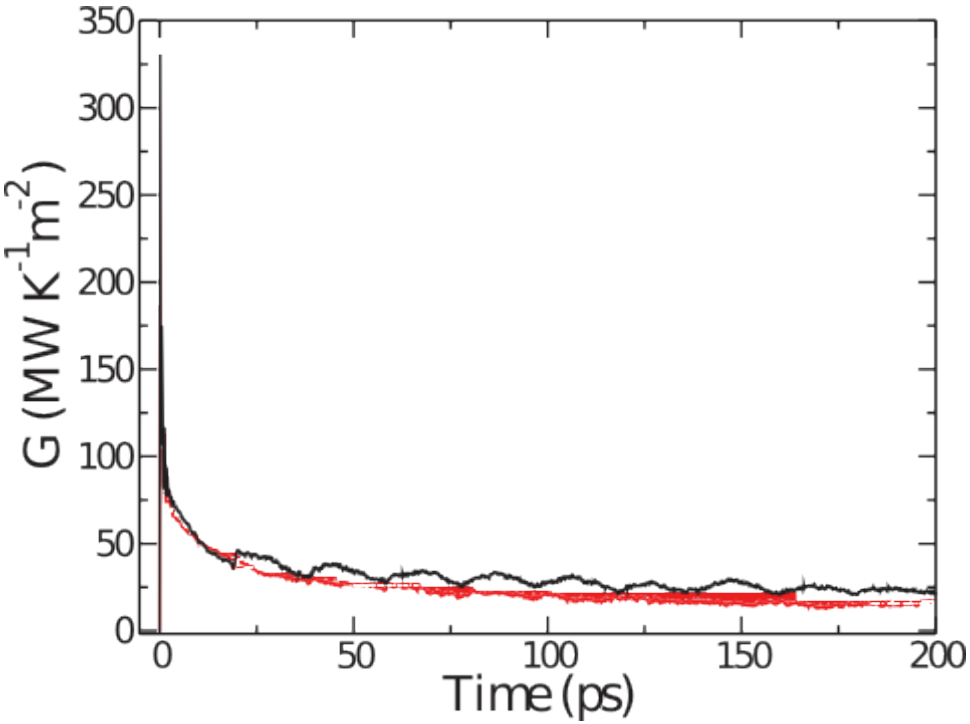


Thermal boundary resistance : $R = \Delta T / J$

Equilibrium simulations

Puech' s formula

$$G = \frac{1}{A\,k_B T^2} \int_0^{+\infty} \langle q(t) \cdot q(0) \rangle \, dt$$



A interfacial area

Analogous to the Green-Kubo formula for the thermal conductivity

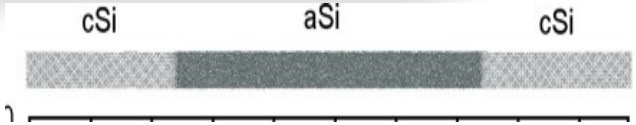
Interfacial heat flux :

$$q = \Sigma_{i \in 1,\, j \in 2} \vec{F}_{ij} \frac{\left(\vec{v}_i + \vec{v}_j\right)}{2}$$

Not computed in LAMMPS !
Postprocessing !

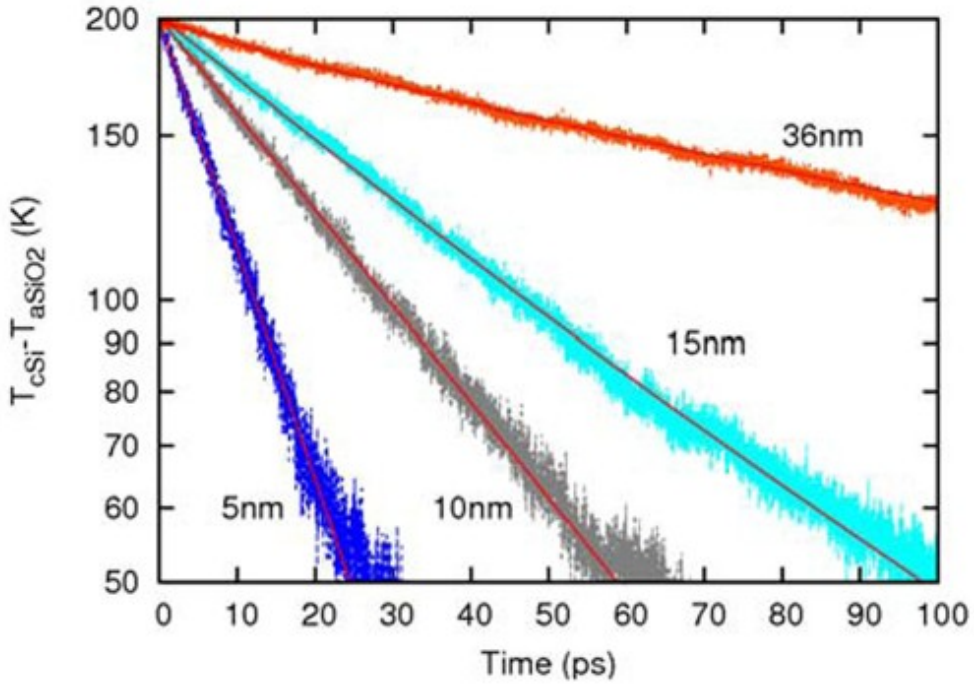
Barrat and Chiaruttini, *Mol. Phys.* 2003
SM and Termentzidis, *PRB* 2012

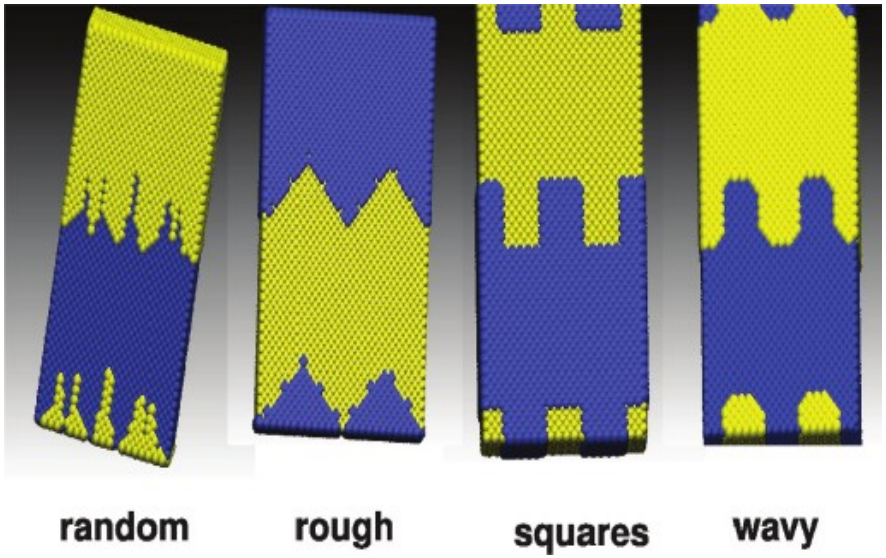
« Approach to equilibrium » or « Thermal relaxation »



Temperature relaxation

Well adapted to imperfect interfaces !





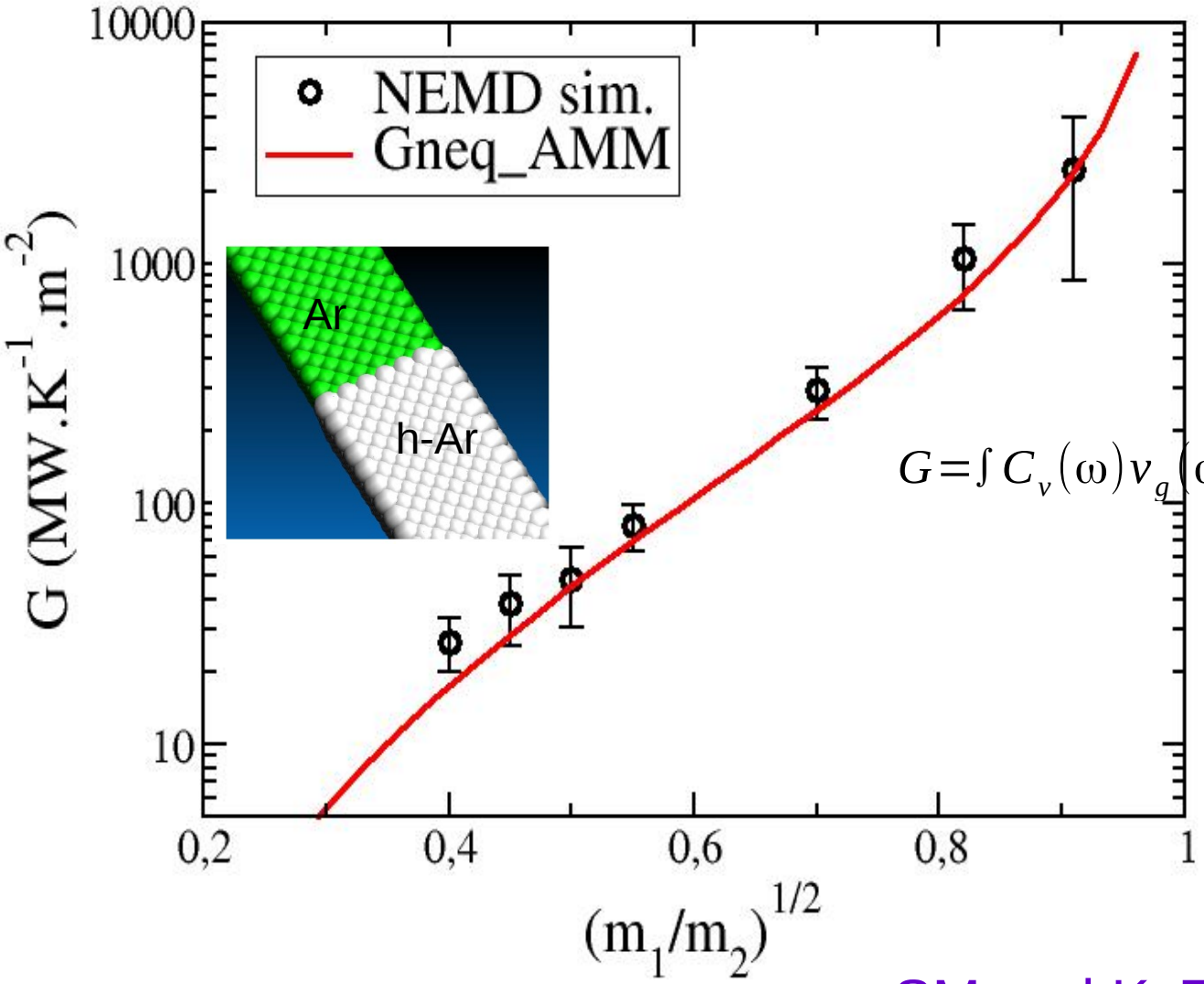
$$\Delta T(t) \propto \exp(-t/\tau)$$

$$G = C_v/(A\tau)$$

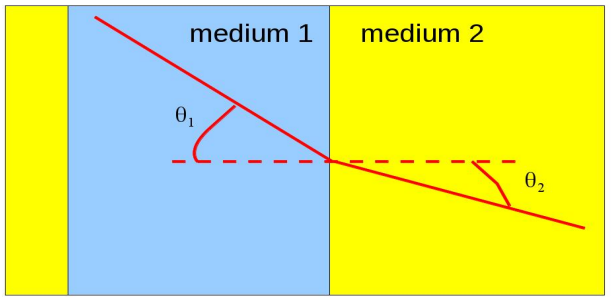
E. Lampin et al., *APL* 2012
S. Merabia, Termentzidis 2014

Easy to implement in LAMMPS !

Acoustic description of interfacial heat transfer



Acoustic model



$$G = \int C_v(\omega) v_g(\omega) \int t_{12}(\cos\theta_1, \cos\theta_2) d\cos\theta_1 d\omega$$

$$t_{12} = \frac{4 Z_1 Z_2 \cos\theta_1 \cos\theta_2}{(Z_1 \cos\theta_1 + Z_2 \cos\theta_2)^2}$$

Acoustic impedances :

$$Z_i = \rho_{m,i} c_i$$

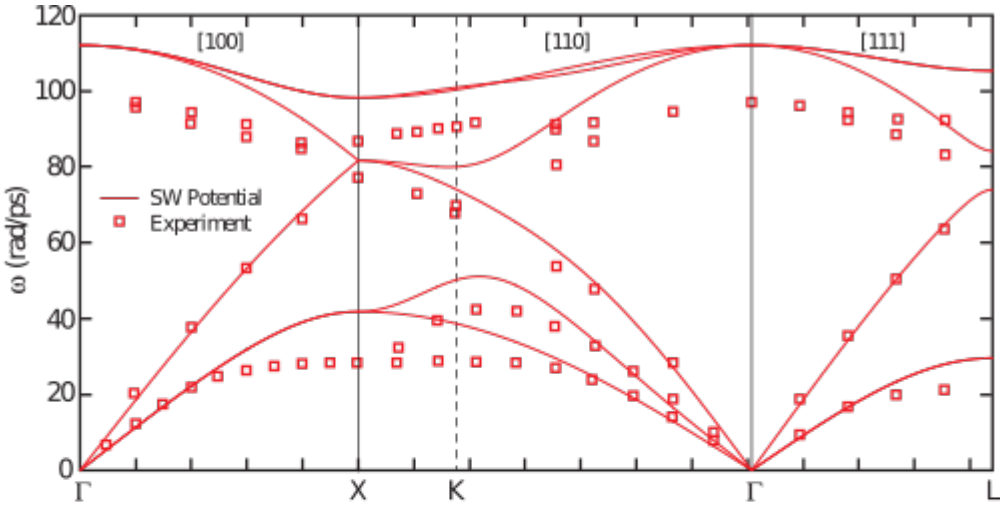
SM and K. Termentzidis, PRB 2012

Challenges

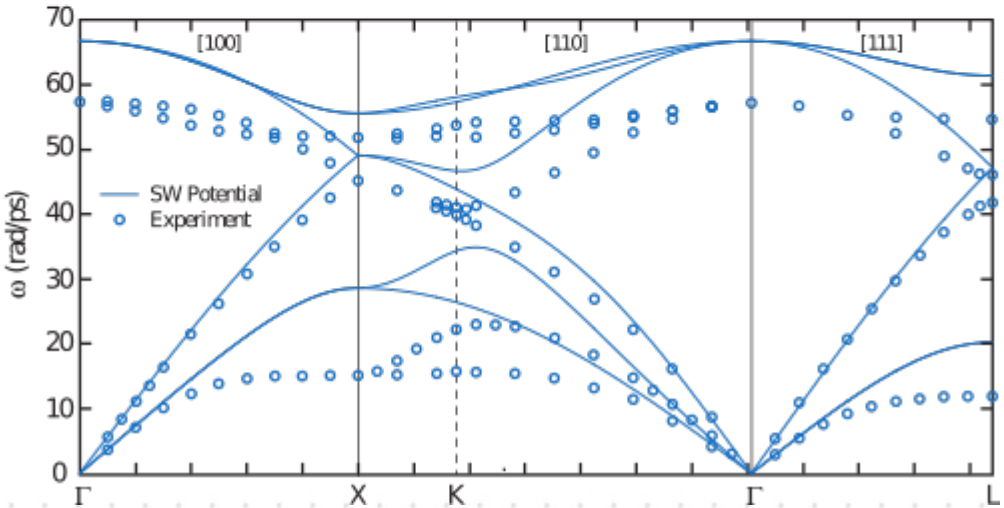
Interatomic force constants

Stillinger-Weber potential

(a) Si

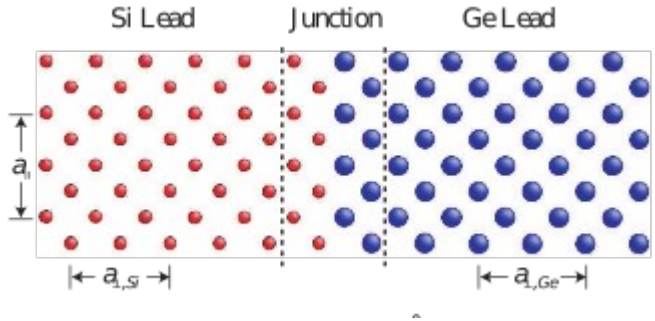


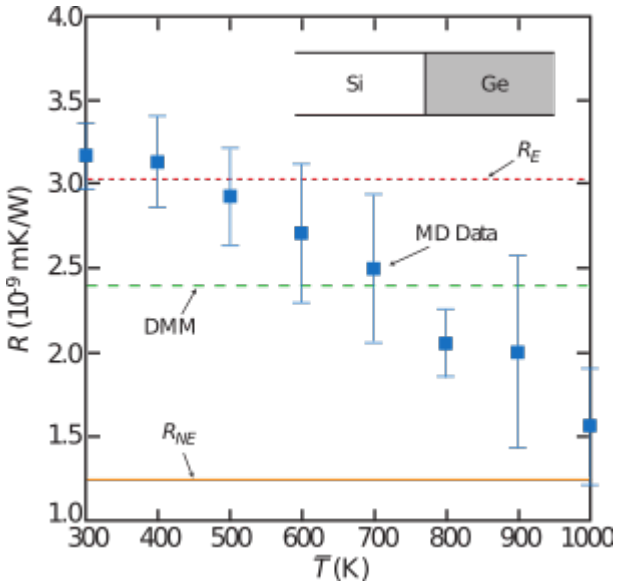
(b) Ge



Landry, phD thesis 2009

(b)





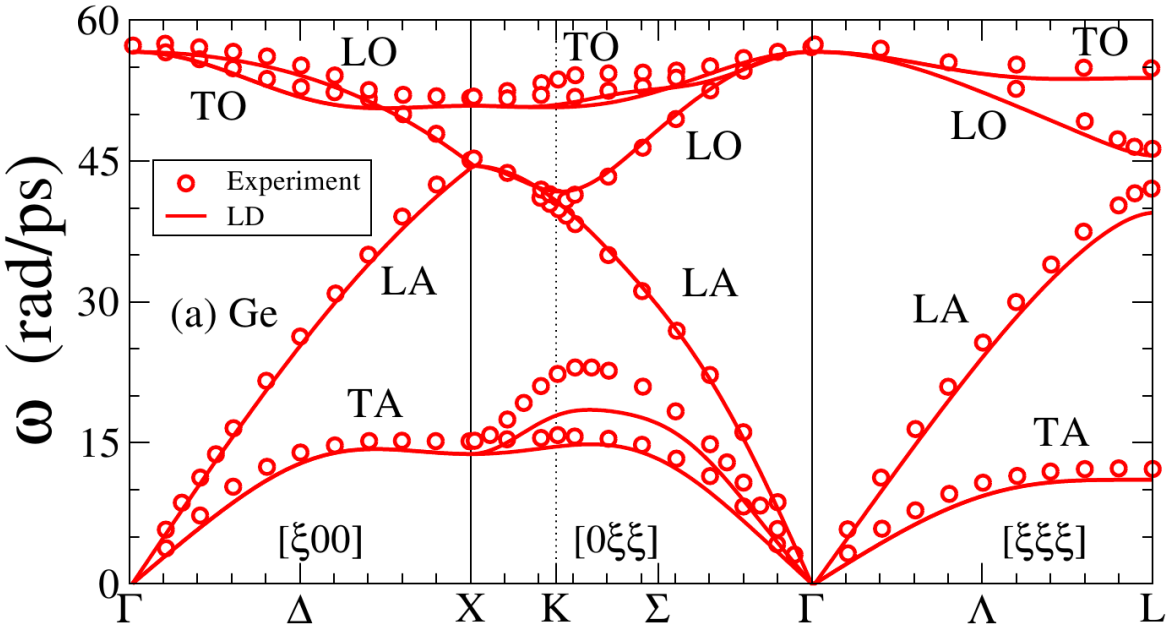
MD : $G \simeq 320\ MW/m^2/K$

Exp. : $G \simeq 200\ MW/m^2/K$

Landry, McGaughey PRB2009

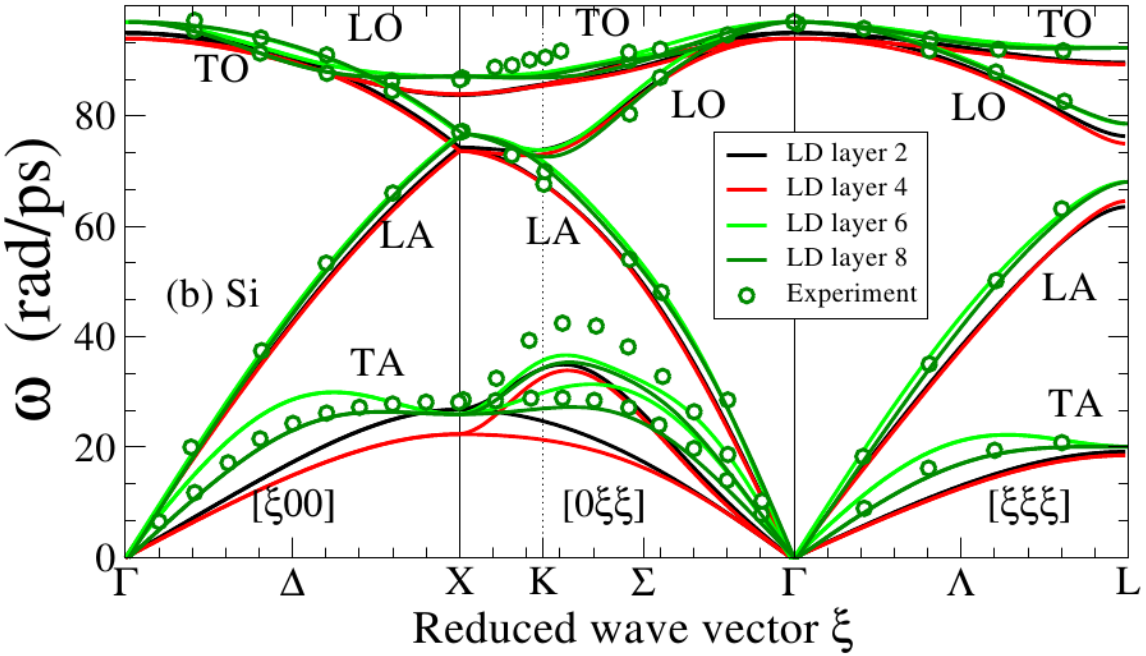
Ab-initio Interatomic force constants

Dispersion curves of Si and Ge calculated using LD with ab initio IFC up to 4th unit cell.



Ge

Si



Necessity of going up to 4th unit cell (8th neighbour) to have a good agreement.

Ab initio interatomic force constants from M. Aouissi *et al Phys. Rev. B* **74**, 054302 (2006)

Theoretical Models: *Ab Initio* Lattice Dynamics

In bulk :

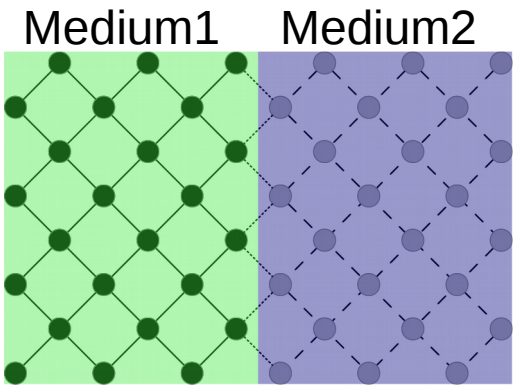
from *ab initio*

$$m_i \frac{d^2 u_{i,\alpha}}{dt^2} = -\sum_{j,\beta} \Phi_{\alpha,\beta}(i,j) u_{j,\beta}$$

$$u_{i,\alpha}(t) = \sum_{\vec{k}} \frac{A(\vec{k})}{m_i} e_\alpha(\vec{k}) \exp(i(\vec{k} \cdot \vec{r}_i^{\,0} - \omega(\vec{k})t))$$

$$D_{\alpha,\beta}(\vec{k}) = \sum_{j \text{ neighb i}} \frac{\Phi_{\alpha,\beta}(i,j)}{\sqrt{m_i m_j}} \exp(i(\vec{k} \cdot (\vec{r}_j^{\,0} - \vec{r}_i^{\,0}))$$

$$D_{\alpha,\beta}(\vec{k})\vec{e}_\beta(\vec{k}) = \omega^2(\vec{k})\vec{e}_\alpha(\vec{k})$$



n atom / unit cell leads to:

- 3n equations in medium 1
- 3n equations in medium 2
- 2 x 3 x n equations at the interface in 3 dimensions.

Zhao, H., and J. B. Freund. *J. Appl. Phys.* **97**, 024903 (2005).
D.A. Young and H.J. Maris, *Phys. Rev. B* **40** 3685 (1989)

Ab initio interatomic force constants are from:
M. Aouissi *et al Phys. Rev. B* **74**, 054302 (2006)

Theoretical Models: *Ab Initio* Lattice Dynamics

from *ab initio calculations*

At interface :

$$m_j \ddot{\vec{u}}(\vec{r}_j) = -\sum_i \Phi^L(r_{ij}) u^L(\vec{r}_{ij}) - \sum_l \Phi^C(r_{lj}) u^C(\vec{r}_{lj}) - \sum_k \Phi^R(r_{kj}) u^R(\vec{r}_{kj})$$

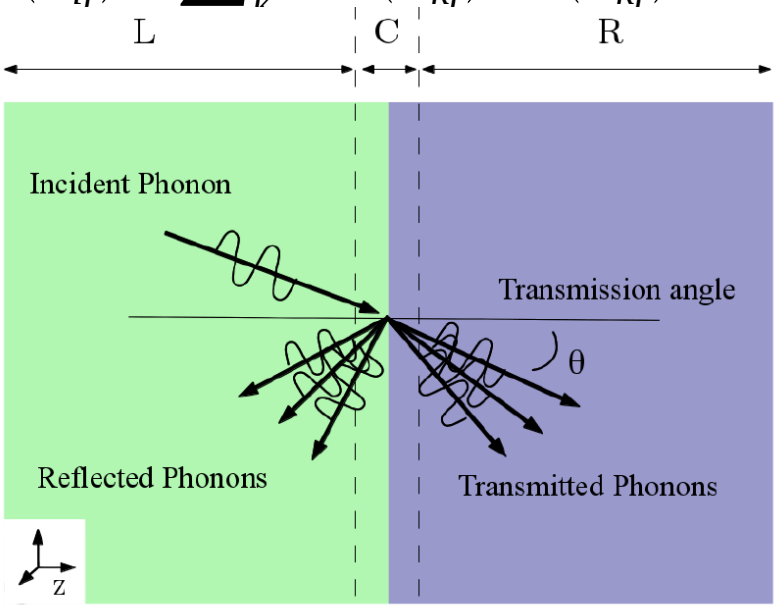
$$\vec{u}(\vec{r}) = \sum_{\vec{k}} A(\vec{k}) \vec{e}(\vec{k}) \exp(i \vec{k} . \vec{r})$$

$$\omega(\vec{k}_{inc}) = \omega(\vec{k}_{tra}) = \omega(\vec{k}_{ref})$$

$$k^x_{inc} = k^x_{tra} = k^x_{ref} , \quad k^y_{inc} = k^y_{tra} = k^y_{ref}$$

$$[\boldsymbol{D}^L(\vec{k}) + \boldsymbol{D}^C(\vec{k}) + \boldsymbol{D}^R(\vec{k})] \vec{e}(\vec{k}) = \omega^2(\vec{k}) \vec{e}(\vec{k})$$

$$\mathcal{T}_{1\to 2} = \frac{\rho_{m,2}}{\rho_{m,1}} \sum_{q=4}^{6} \frac{v^z_{g,q} \cdot |A_q|^2}{v^z_{g,0} \cdot |A_0|^2}$$



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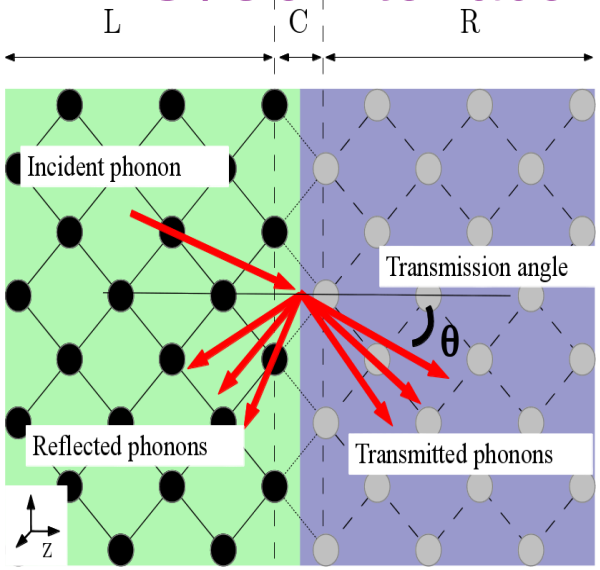
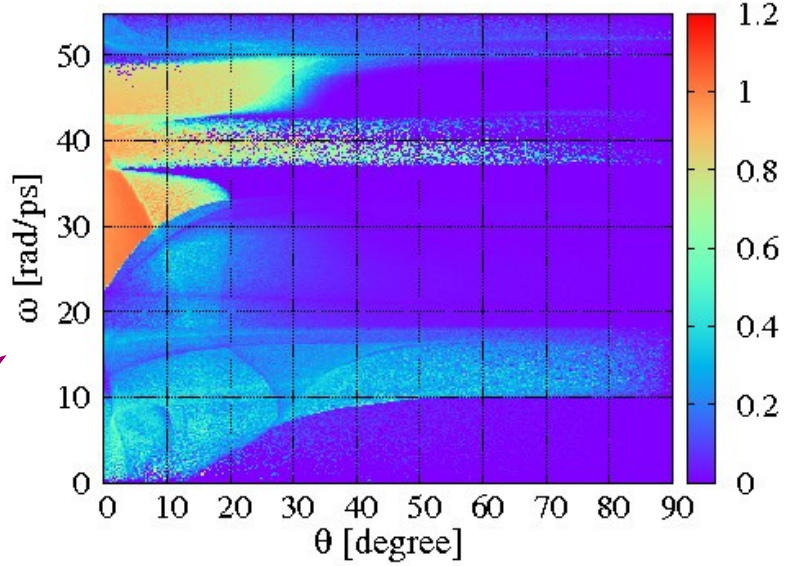
Zhao, H., and J. B. Freund. *J. Appl. Phys.* **97**, 024903 (2005). D.A. Young and H.J. Maris, *Phys. Rev. B* **40** 3685 (1989)

Phonon transmission coefficient

$$t_{1\to 2} = \frac{\rho_{m,2}}{\rho_{m,1}} \sum_{q=4}^{6} \frac{v_{g,q}^{z} \cdot |A_q|^2}{v_{g,0}^{z} \cdot |A_0|^2}$$

Si/Ge interface





transmission

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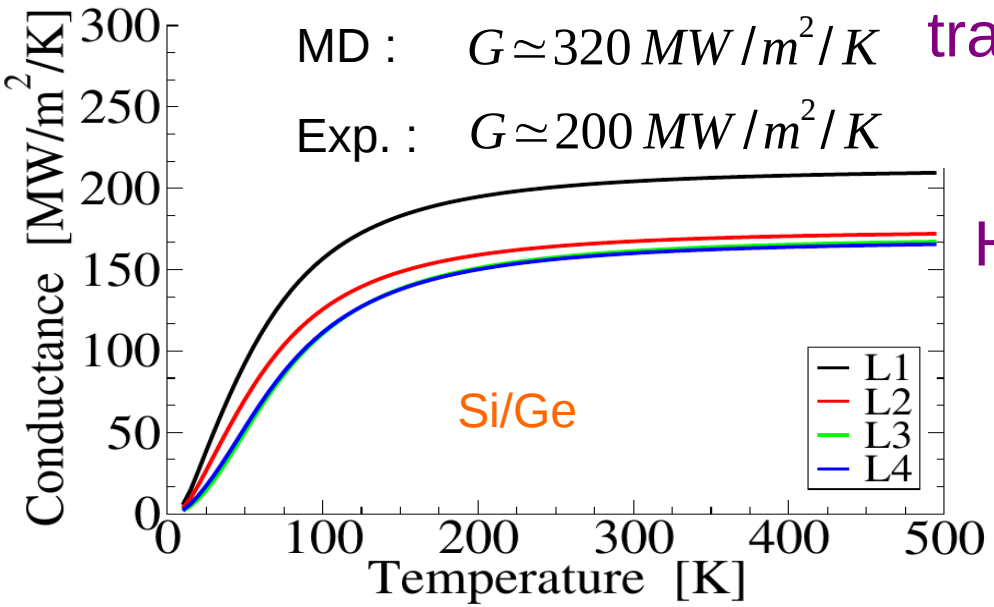
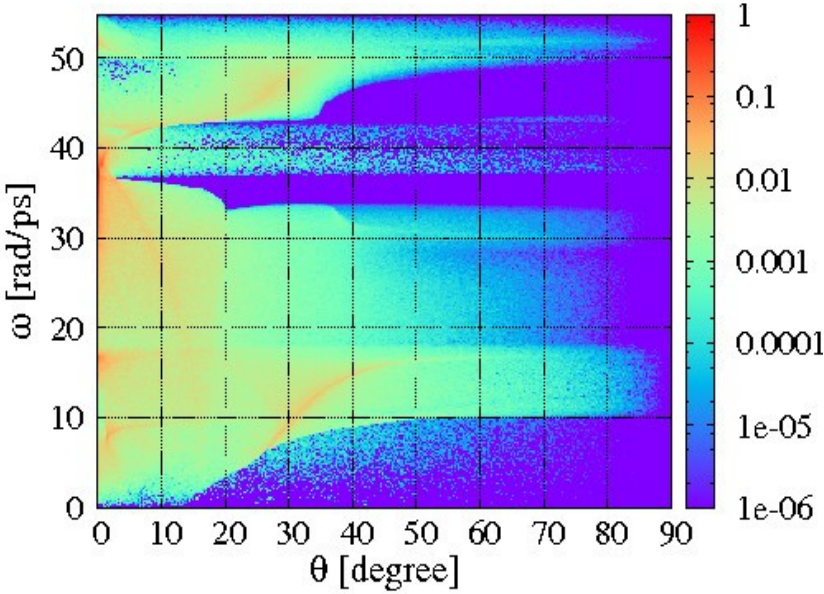
Exp. : $G \simeq 200\ MW/m^2/K$



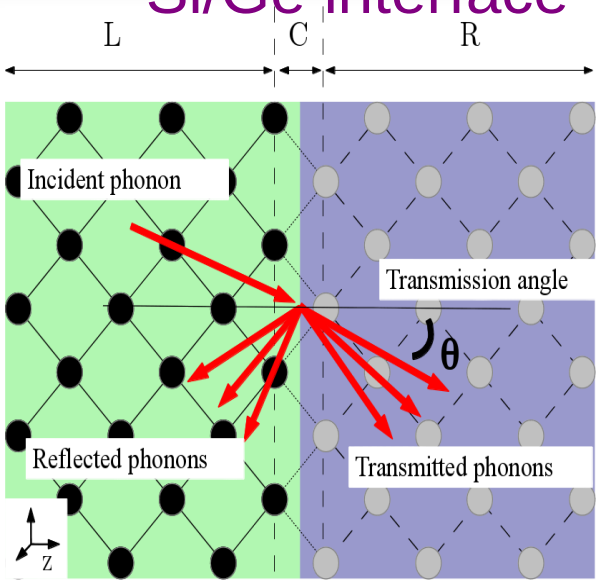
Heat flux

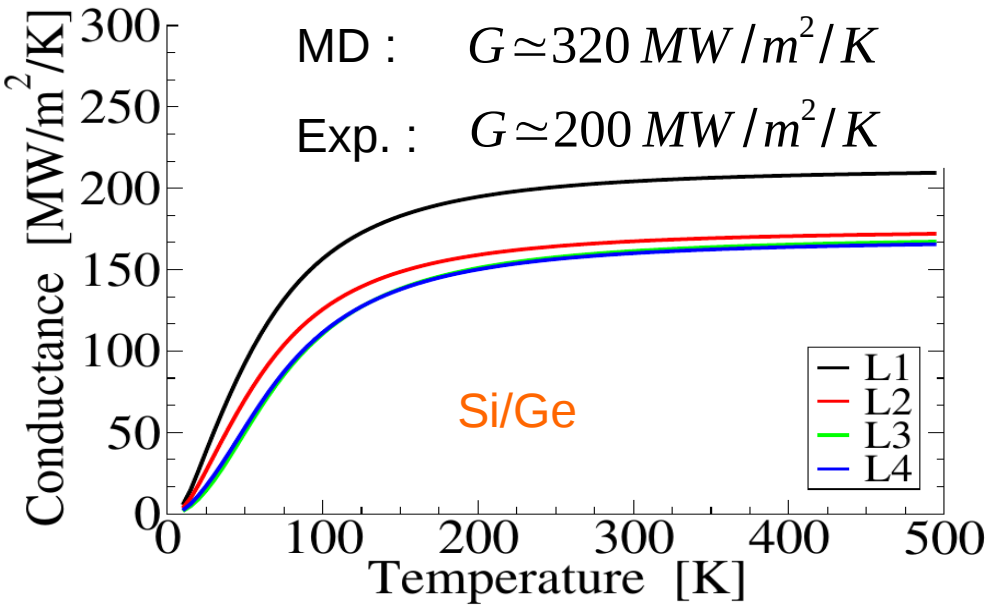


Alkurdi, Pailhès, Merabia APL 2017

Phonon transmission coefficient

Si/Ge interface





Alkurdi, Pailhès, Merabia APL 2017

Difference between calculations and experiments :

-Anharmonic effects

$$H_0 = \frac{1}{2} \sum_{i,j,\alpha,\beta} \Phi_{ij}^{\alpha,\beta} u_{i,\alpha} u_{j,\beta}$$

$$H' = \frac{1}{6} \sum_{i,j,k,\alpha,\beta,\gamma} X_{ijk}^{\alpha,\beta,\gamma} u_{i,\alpha} u_{j,\beta} u_{k,\gamma}$$

-Need to couple of MD

Challenge in LAMMPS :

-build interatomic potentials deriving from ab-initio calculations

-accurate description of interfacial heat transfer

-thermal transmission

Electron-phonon couplings

Two temperature model

$$c_e\,\partial_t T_e = k_e\,\partial^2_{xx} T_e - G(T_e - T_p),$$

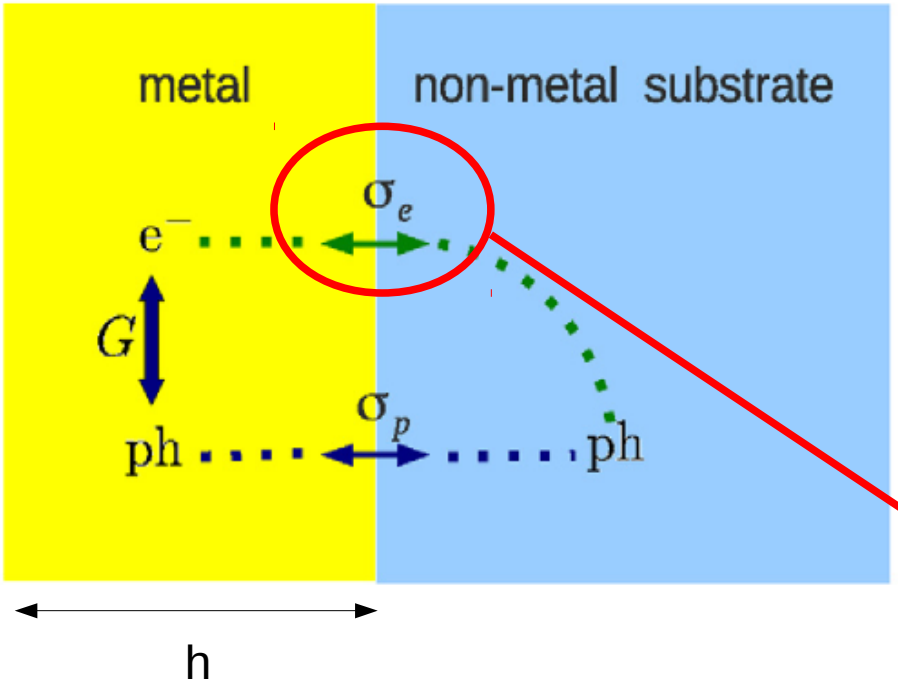
$$c_p\,\partial_t T_p = k_p\,\partial^2_{xx} T_p + G(T_e - T_p),$$

$$c_s\,\partial_t T_s = k_s\,\partial^2_{xx} T_s.$$

+ boundary conditions

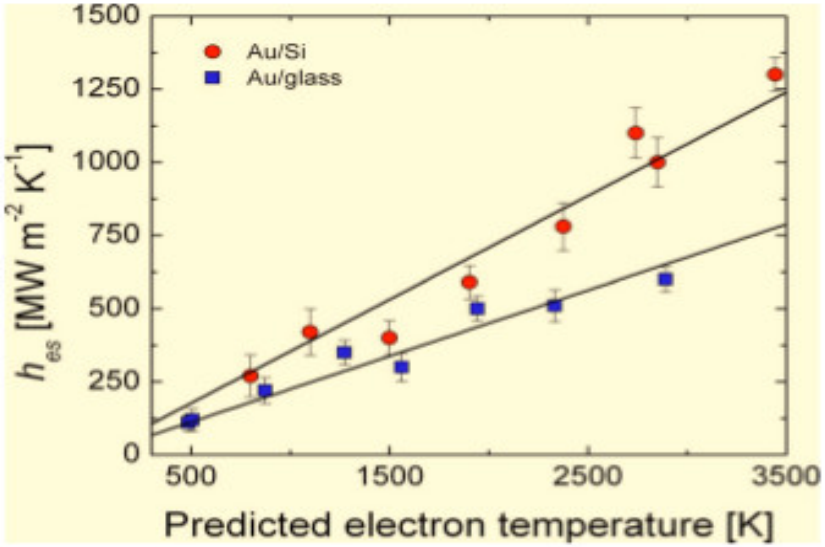
$$-k_s\,\partial_x T_s = \sigma_e(T_e - T_s) + \sigma_p(T_p - T_s),$$

$$= -k_e\,\partial_x T_e - k_p\,\partial_x T_p.$$



Effective conductance :

$$1/\sigma_{eff} = 1/Gh + 1/(\sigma_e + \sigma_p)$$



J. Lombard, F. Detcheverry and SM, *J. Phys. Cond. Mat.*, 2015

Challenge in LAMMPS :

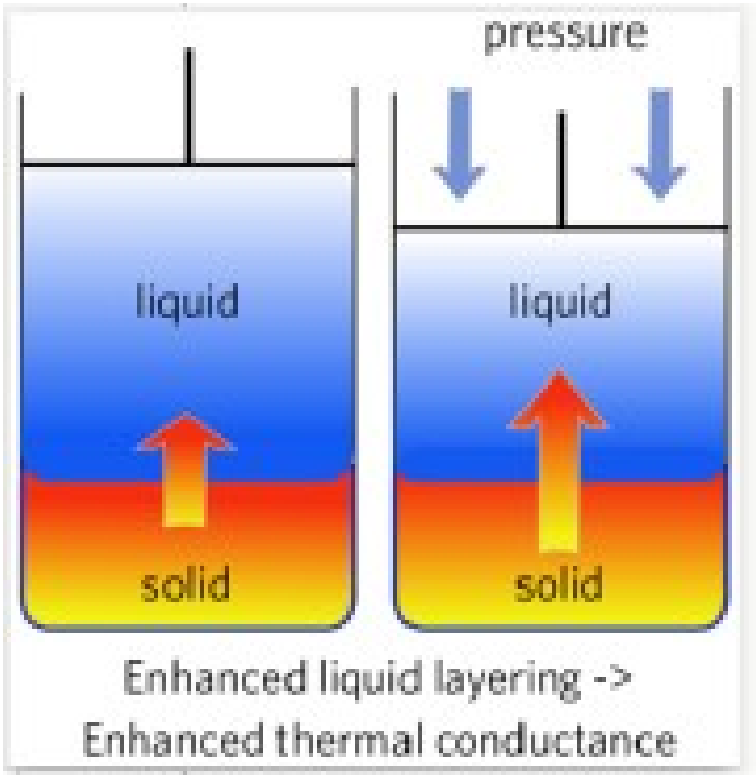
-couple MD with two-temperature model

-including the cross interaction at the interface

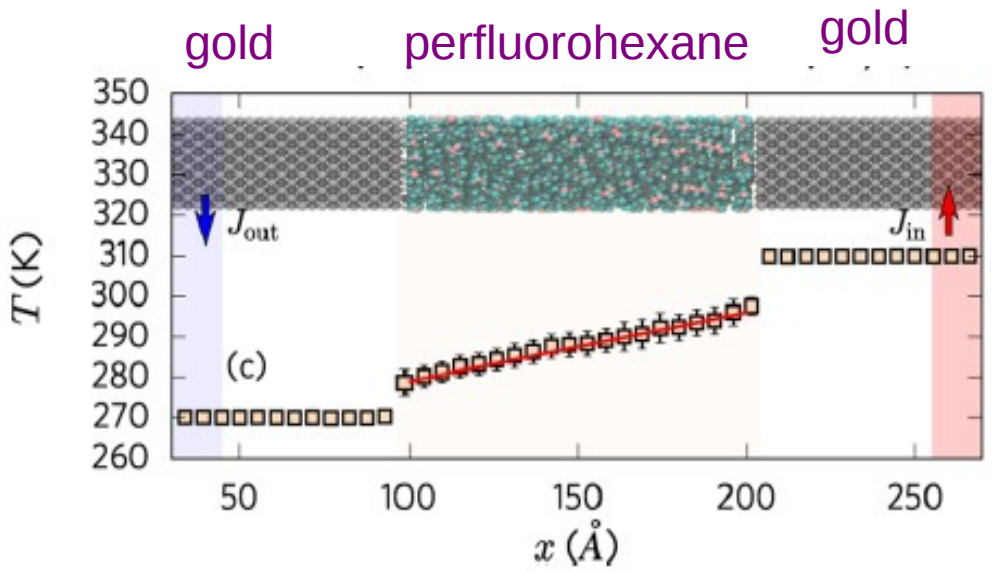
Applications :
How to tune interfacial heat transfer ?

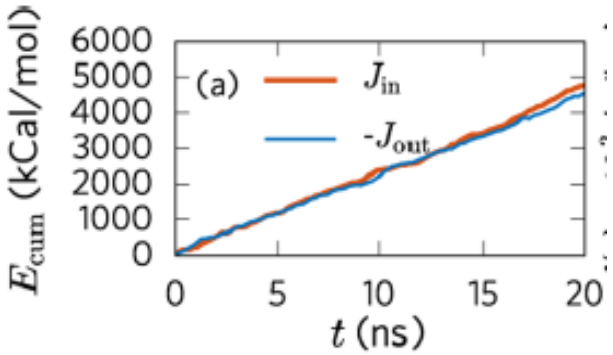
Role of the pressure

Molecular dynamics simulations (OPLS force field)



Temperature profile





conductance

$$G = J / \Delta T$$

Enhanced conductance

Gold sound velocities

110 :

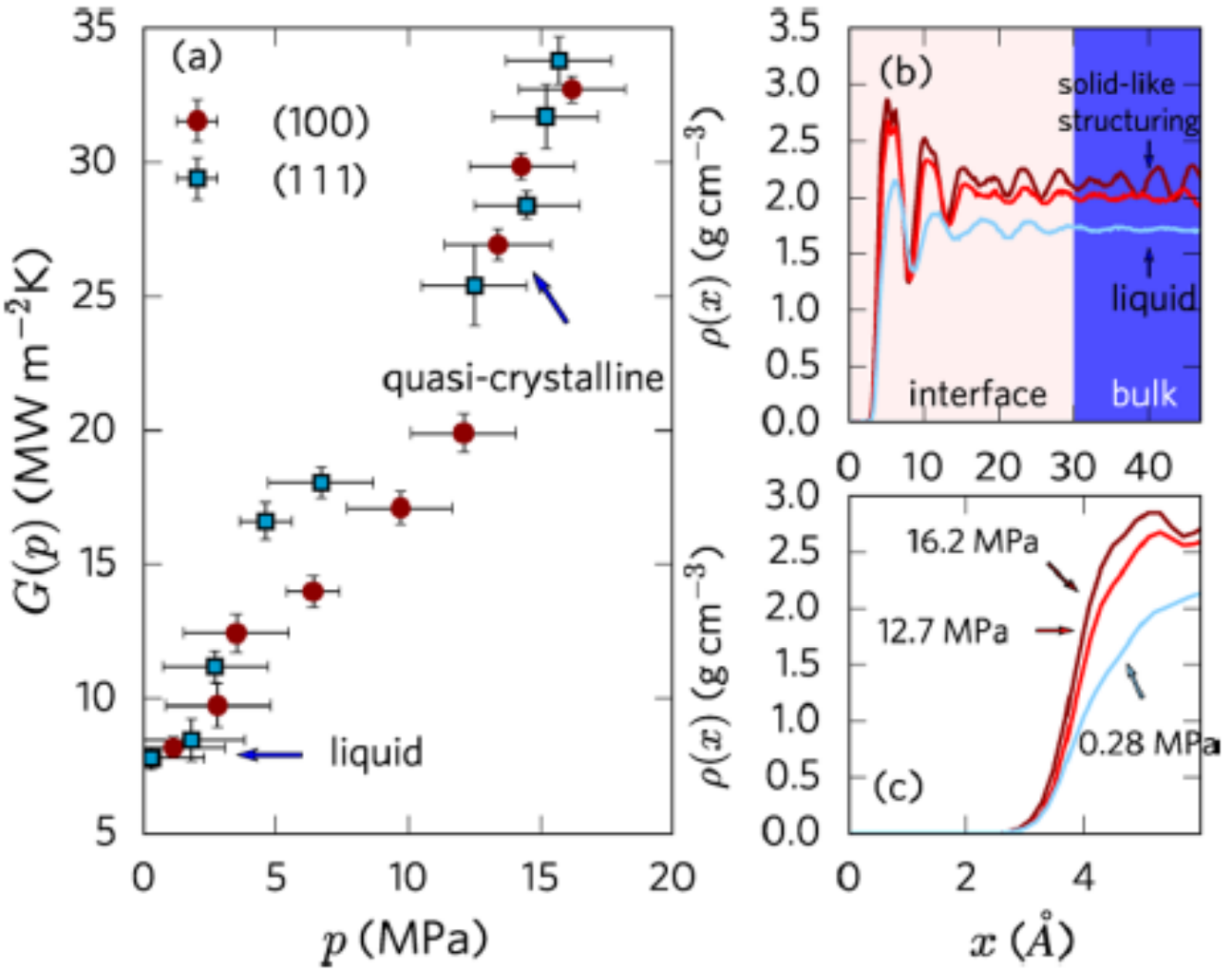
$v_L(110) = 3400\, m/s$

$v_T(110) = 1500\, m/s$

111 :

$v_L(111) = 3900\, m/s$

$v_T(111) = 1400\, m/s$



Three-four fold increase of the conductance with pressure

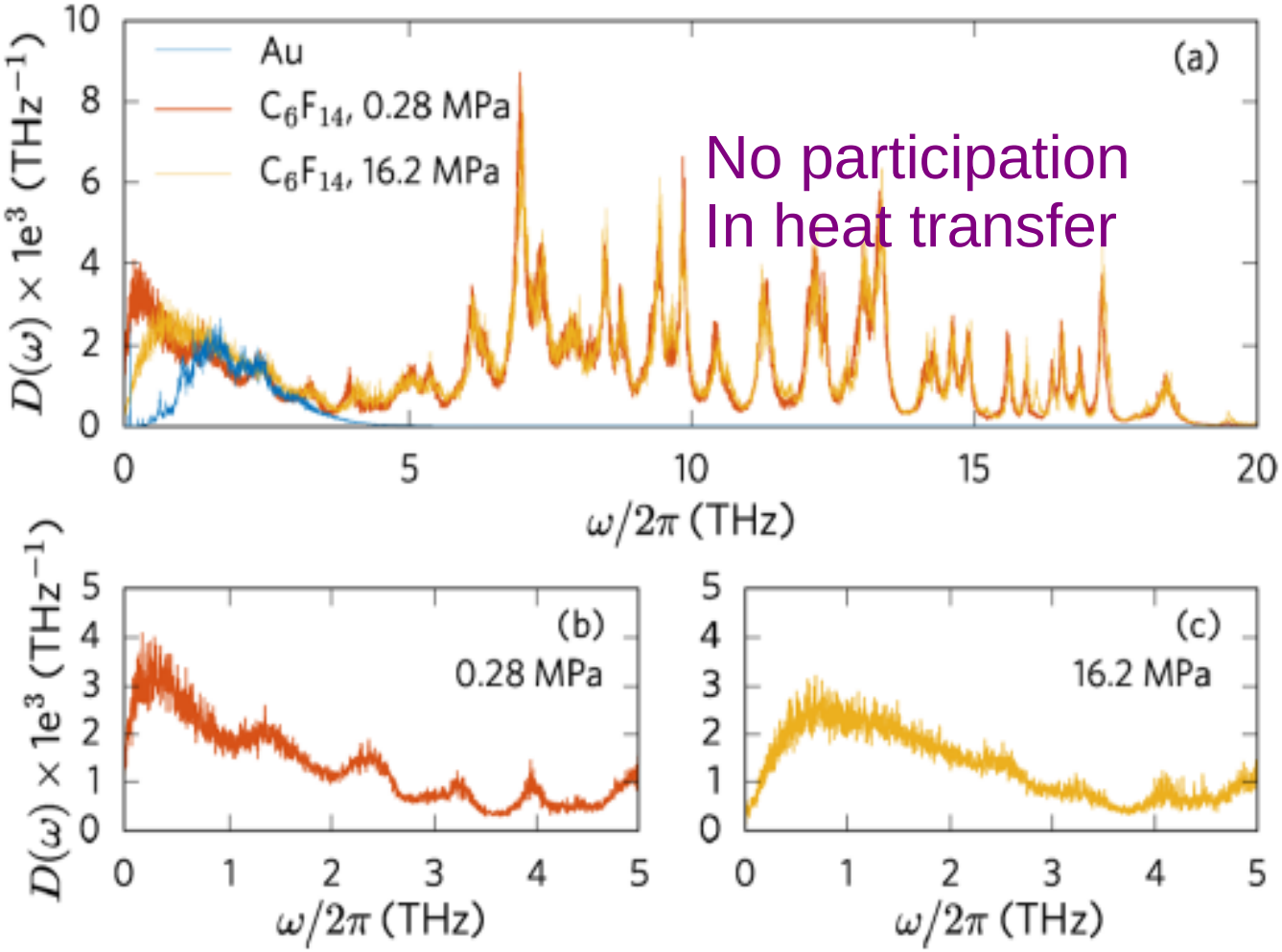
H. Han, S. Merabia, F. Müller-Plathe, *J. Phys. Chem. Lett.*, 2017

Vibrational analysis

Vibrational DOS

$$D(\omega) \propto \int_0^{+\infty} C_{vv}(t) \exp(i\,\omega t)\, d\,\omega$$

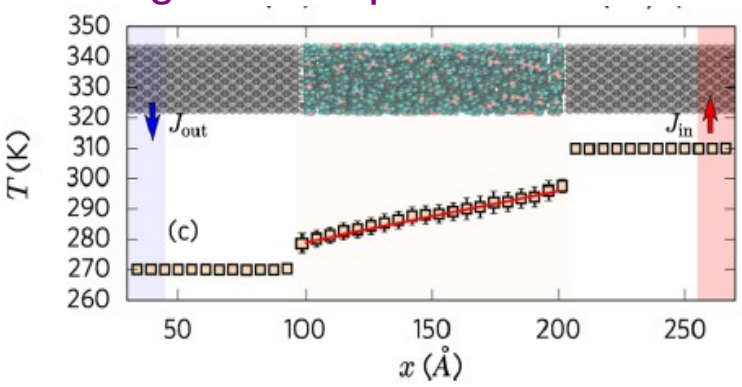
$$C_{vv}(t) = \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle$$



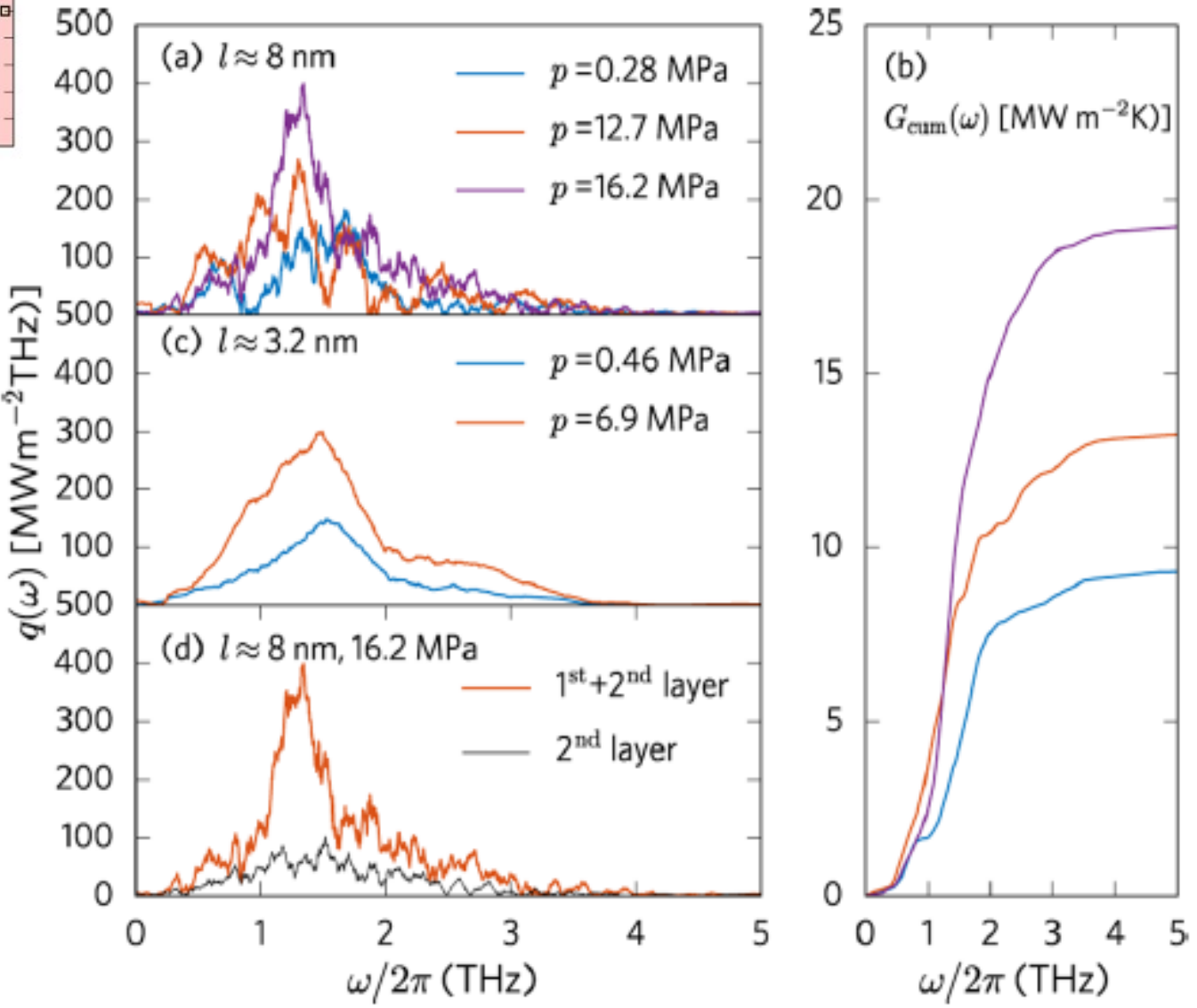
Pressure induced DOS broadening

Enhanced conductance

gold perfluorohexane



Thermal heat flux : $q(\omega) = \frac{2}{A}\mathcal{R} \sum_{j\in l, i\in s} \int_{-\infty}^{\infty} d\tau \langle \mathbf{F}_{ij}(\tau)\cdot\mathbf{v}_i(0)\rangle e^{i\omega\tau}$



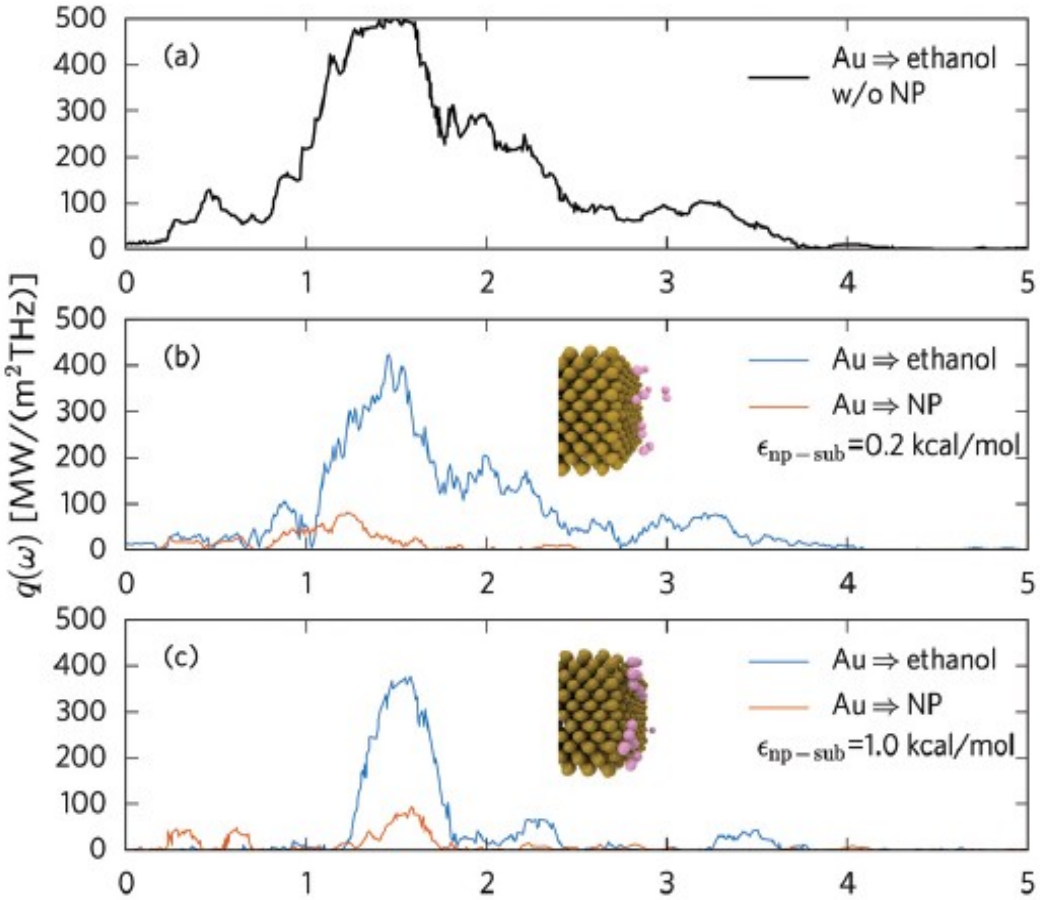
Spectral heat flux

Frequency dependent heat flux :

$$q(\omega) = \frac{2}{A}\Re \sum_{j\in \mathrm{liq}, i\in \mathrm{sub}} \int_{-\infty}^{\infty} \mathrm{d}\tau \langle \boldsymbol{F}_{ij}(\tau)\cdot \boldsymbol{v}_i(0)\rangle \mathrm{e}^{\mathrm{i}\omega\tau}$$

Table 1 Decomposition of the interfacial heat flux q (unit: MW m^{-2})

		Nanofluid ε_{np-sub}	
	Ethanol	0.2 kcal mol^{-1}	1.0 kcal mol^{-1}
Surface ⇒ liquid	634 ± 6	368 ± 8	187 ± 3
Surface ⇒ particles	—	36 ± 5	37 ± 6
Total flux	634 ± 6	404 ± 11	224 ± 9



Pure ethanol

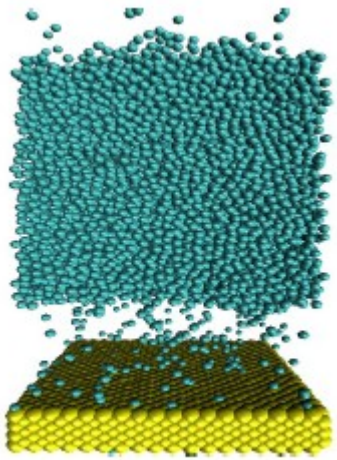
Partially wetting surface

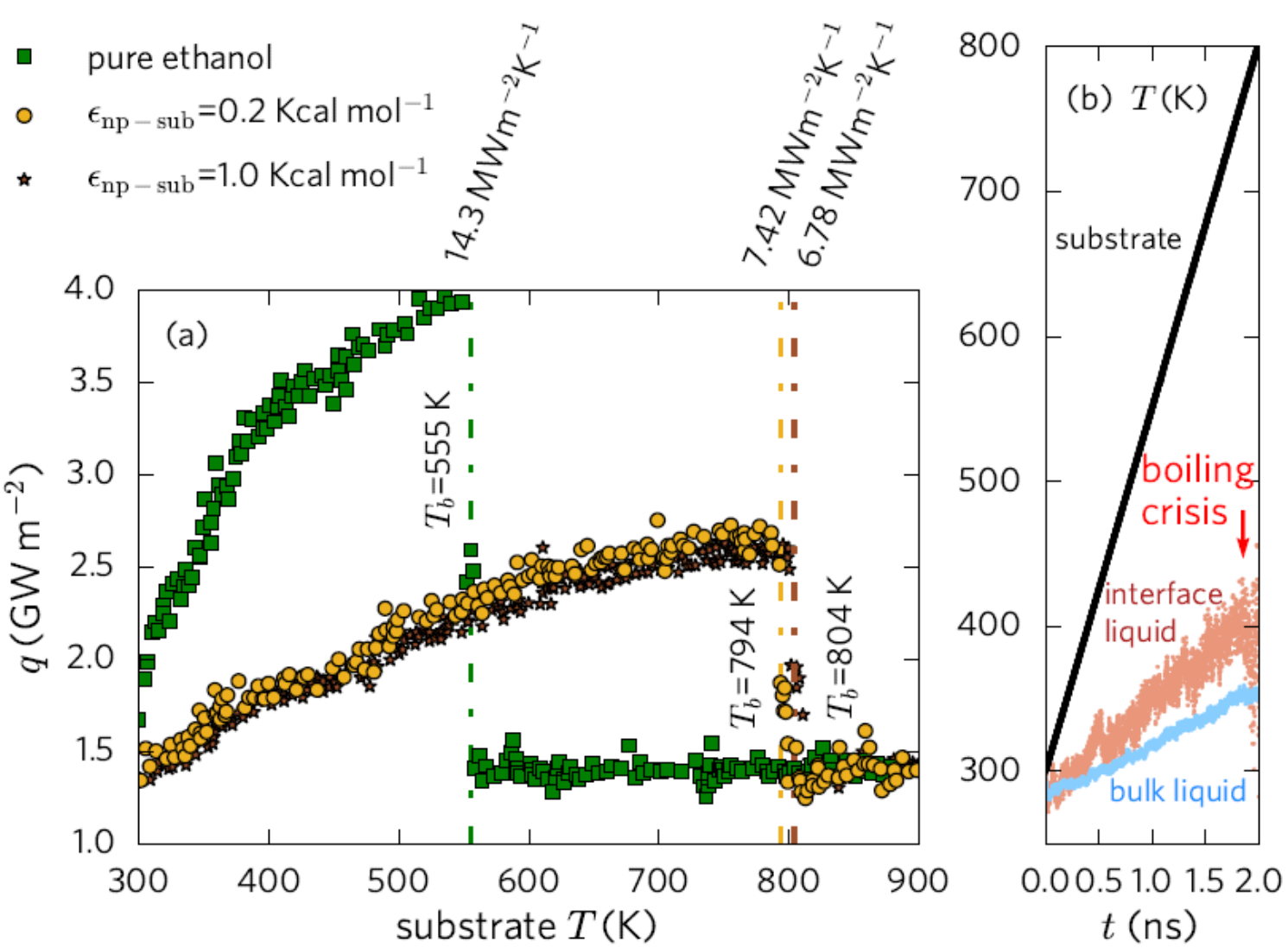
$$\epsilon_{np-subs} = 0.2\, kcal\, mol^{-1}$$

Wetting surface

$$\epsilon_{np-subs} = 1.0\, kcal\, mol^{-1}$$

Boiling simulations





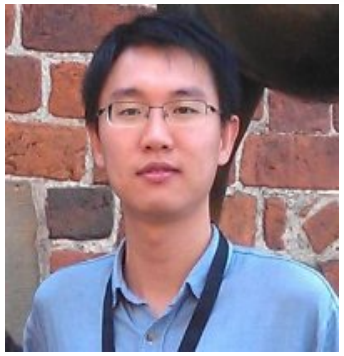
Significant shift of the boiling temperature due to the presence of the nanoparticles

Conclusion

-Implement interfacial heat flux calculations

-Use potentials derived from ab-initio calculations

-Extend two temperature models
Interfacial electron-phonon couplings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Thank your for your attention !