

FUNDAMENTAL ISSUES IN NANOSCALE HEAT TRANSFER: FROM COHERENCE TO INTERFACIAL RESISTANCE IN HEAT CONDUCTION

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ABSTRACT

When system sizes shrink to nanoscales as in the case of electronic and optical devices, heat transfer laws are altered due to the modification of the basic physical mechanisms at play, especially in the fields of conduction. We expose recent advances in the understanding of heat conduction in semi-conductor superlattices. The effect of (i) coherence and (ii) interfaces becoming predominant, we use a direct simulation technique -i.e. Molecular Dynamics- to estimate the thermal resistance generated by those effects.

INTRODUCTION

Understanding the heat transport at interfaces is a challenging theoretical issue in solid-state physics [1, 2]. Thermal boundary resistances are of considerable interest in fields such as energy conversion—thermoelectricity, photovoltaics-, microchip cooling with thermal interface materials, thermal protection with insulating boundary layers in engines or even in phononics, which defines information technology based on phonon heat conduction. Not only designing but also defining thermal boundary resistance remains a difficult task. When two bodies with different equilibrium temperatures are interacting, the boundary resistance is usually derived as the difference between those latter temperatures divided by the net heat flux transferred from one body to the other. However, temperature is defined at thermodynamic equilibrium and heat flux in a non-equilibrium regime. Therefore, a thermal resistance is always a quantity with a limited robustness in terms of physical definition. In this paper, we highlight that the physical mechanisms involved are not only the well-known transmission and reflection of heat carriers –e.g. phonons in dielectric and solids and semi-conductors-, but also the loss of coherence of phonon wave-packets when crossing the interface. In this aim, we analyse the different regimes characterizing heat conduction in superlattices as a function of the structure period. Therefore we will propose a general definition of the thermal resistance

that will reveal the interplay between phonon-phonon and phonon-interface scattering when the period is larger than a few nanometers. We then show that if the period becomes smaller, phonon wave-packet coherence has to be taken into account.

NOMENCLATURE

G	[W/K]	Interfacial thermal conductance
H_i	[J]	Hamiltonian of i =sys the total system, $i=L,R$ the left or right subsystem, $i=D$ the contact area
i	[-]	Complex number
k_{ij}	[N/m]	Force constant between atoms i and j
L	[m]	Film thickness in the superlattice
m	[kg]	Atomic mass
N_i	[-]	Number of degree of freedom divided by two in subsystems $i=1$ and $i=2$
P	[J]	Potential energy operator
p_i	[kg.m/s]	Momentum of atom i
Q	[W]	Power exchange at the interface between the two subsystems
R	[K/W]	Interfacial thermal resistance
s	[-]	Laplace variable
T_i	[K]	Temperatures in subsystems $i=1$ and $i=2$, at equilibrium $i=0$
u_i	[m]	Displacement of atom i
\dot{u}_i	[m/s]	Velocity of atom i
Special characters		
ω	[rad/s]	Volume fraction ratio

Subscripts

NANOSCALE HEAT CONDUCTION REGIMES

Superlattices consist in the superposition of thin film layers of alternative chemical nature having thicknesses ranging from a few atomic planes to several tens of nanometers. Those objects are of special interest as they reveal the nature of phonon

scattering and wave-packets when their period (the sum of the thicknesses of two successive layers) varies.

Phonons are the quanta of energy of the lattice waves, which are defined from the plane wave decomposition of the atomic motions. Phonon wave-packets –a combination of several plane waves having wave-vectors within a short wave-vector interval- can be considered as particles forming a gas in such a way that the classical kinetic theory of gases provides the definition for the phonon thermal conductivity.

Three different heat transport regimes can be identified. The first one is the well-known diffusive regime illustrated in Figure 1 when the phonon mean free path Λ –the path between two phonon-phonon interactions- is smaller than the period D of the superlattice, i.e. the Knudsen number is smaller than unity. In this latter situation, heat flux is defined from the classical Fourier Law where the thermal conductivity λ_{eff} is the arithmetic average of the thermal conductivities of both materials.

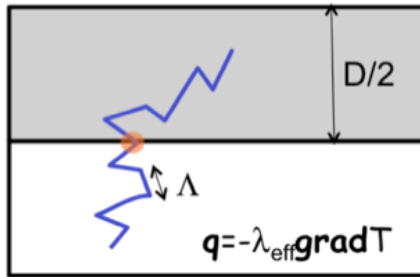


Figure 1 Diffusive regime: Phonon path (blue line) in a superlattice with a period D larger than the phonon mean free path Λ .

The second regime represented in Figure 2 appears when the period becomes smaller than the mean free path (typically a few hundreds of nanometers in semi-conductors at ambient temperature). If the interfacial scattering becomes predominant towards the phonon-phonon scattering, the total system resistance is obtained by setting the interfacial resistances in series so that thermal conductivity is found proportional to the period and reversely proportional to the interfacial thermal resistance R . This latter transport regime is called ballistic in so far as phonons have ballistic travels from one interface to the next one.

This latter regime only occurs if the size of the wave-packets, or the phonon coherence lengths, are smaller than the period as shown in Figure 3. Wave-packets are here defined by the properties of the layer that they are crossing and they are scattered by the interface.

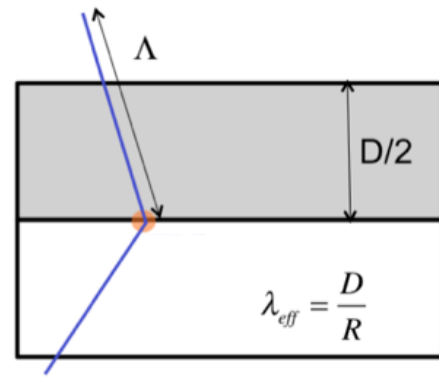


Figure 2 Ballistic regime: Phonon path (blue line) in a superlattice with a period D smaller than the phonon mean free path Λ

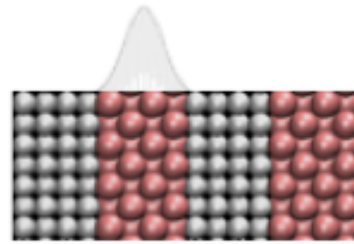


Figure 3 Schematic of a phonon wave-packet with a size smaller than the period so that its properties are defined by the single material of the layer supporting it. The wave-packet will be scattered by the interfaces.

The third regime appears when the wave-packet size becomes larger than the period as shown in Figure 4. Now, the wave-packet “sees” the superlattice as a continuum and does not scatter on the interface. This transport regime can be defined as a “coherent” one.

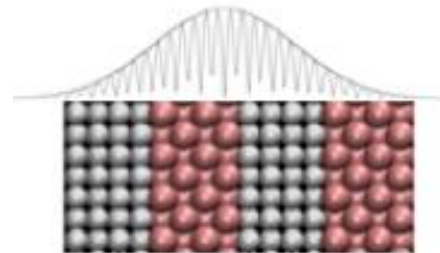


Figure 4 Schematic of a phonon wave-packet with a size larger than the period so that its properties are defined by a continuous medium where interfaces have disappeared. The wave-packet will not be scattered by the interfaces.

After the derivation of the interfacial resistance in the frame of fluctuational thermodynamics, the transition from the diffusive

to the ballistic regime and the transition from the ballistic to the coherent ones are addressed.

INTERFACIAL THERMAL RESISTANCE FROM EQUILIBRIUM TEMPERATURE FLUCTUATIONS

To show the interplay between the diffusive and the ballistic regimes, we use Molecular Dynamics technique to describe interfacial heat transfer at the atomic level. Molecular Dynamics technique consists in solving the time dependent atom trajectories when considering those as classical point masses. The governing 2nd Newton Law is thus integrated over time by updating the interaction forces at each time step. This approach only relies on the validity of the interaction potentials from which the forces are derived and that are fitted to key properties related to the quantities that are targeted. In the following, we will define the thermal interface resistance from the temperature fluctuations. Molecular Dynamics directly provides the atomic kinetic energy and therefore the local temperature.

The thermal conductance G , the reverse of the resistance, between two heat baths 1 and 2 at equilibrium temperatures T_1 and T_2 respectively and exchanging a net heat flux Q is classically defined by a linear relation including the temperature difference $\Delta T = T_1 - T_2$ as follows:

$$Q = G\Delta T \quad (1)$$

A conventional expression used for measuring and computing the thermal conductance is based on the time dependent energy conservation equation including the exchanged heat flux Q . The subtraction between the energy conservation equations of both bodies:

$$\frac{\partial T_1}{\partial t} = -\frac{1}{k_B N_1} G\Delta T \quad (2)$$

and

$$\frac{\partial T_2}{\partial t} = -\frac{1}{k_B N_2} G\Delta T \quad (3)$$

yields the equation of the temperature difference ΔT :

$$\frac{\partial \Delta T}{\partial t} = -\frac{1}{k_B} \left(\frac{1}{N_1} + \frac{1}{N_2} \right) G\Delta T \quad (4)$$

where k_B is the Boltzmann constant and N_i is half the number of degrees of freedom in the heat bath i . However, the linear response theory establishes the heat flux as a convolution product between the conductance and the temperature difference. Eq. (4) corrected with a Langevin flux $F(t)$ can be written as:

$$\frac{d\Delta T}{dt} = -\frac{1}{k_B} \left(\frac{1}{N_1} + \frac{1}{N_2} \right) \int_0^t G(t-t')\Delta T(t')dt' + F(t) \quad (5)$$

Multiplying this equation by $\Delta T(0)$ and performing phase average allows for removing the $F(t)$ dependent term in Equation (5) because the Langevin flux and ΔT have an infinitely short correlation time: $\langle \Delta T(0)F(t) \rangle = 0$. The resulting equation is:

$$\frac{d \langle \Delta T(0)\Delta T(t) \rangle}{dt} = -\frac{1}{k_B} \left(\frac{1}{N_1} + \frac{1}{N_2} \right) \int_0^t G(t-t') \langle \Delta T(0)\Delta T(t') \rangle dt' \quad (6)$$

The brackets denote the phase average or the well-known autocorrelation function. This function here applies to the equilibrium fluctuations of the temperature difference ΔT . To simplify the notations, we propose to define

$$C(t) = \langle \Delta T(0)\Delta T(t) \rangle \quad \text{and} \quad C_v = k_B / \left(\frac{1}{N_1} + \frac{1}{N_2} \right) \quad \text{to rewrite}$$

Equation (6) as:

$$C_v \frac{dC(t)}{dt} = -G(t) * C(t) \quad (7)$$

where the star $*$ is the convolution product. Taking the Laplace transform of Eq.(2.8) yields [3]:

$$sC(s) - C(t=0) = \frac{-G(s)C(s)}{C_v} \quad (8)$$

At the static limit ($s=0$), the reverse of the spectral conductance, $R(s)$, is yielded as:

$$Rk_B = \frac{C(s=0)}{C(t=0)} \left(\frac{1}{N_1} + \frac{1}{N_2} \right) = \frac{\int_0^\infty \langle \Delta T(t)\Delta T(0) \rangle dt}{\langle \Delta T^2(0) \rangle} \left(\frac{1}{N_1} + \frac{1}{N_2} \right) \quad (9)$$

This last equation clearly provides the interfacial resistance from temperature fluctuations and the number of degrees of freedom. We will now use it to investigate the contribution of the interface in the total superlattice thermal conductivity.

The zone defining temperature in Eq. (9) has however to be specified, whether all the subsystems should be involved in this definition or only a restricted area around the interface.

Eq. (9) can be further derived using the well-known expression of the static deviation of the temperature difference

$$\frac{\langle \Delta T(0)^2 \rangle}{T_0^2} = \frac{1}{N_1} + \frac{1}{N_2} \quad (10)$$

where T_0 refers to the equilibrium temperature, which yields

$$Rk_B = \frac{k_B}{G(\omega=0)} = \frac{1}{T_0^2} \int_0^\infty \langle \Delta T(0) \Delta T(t) \rangle dt \quad (11)$$

Expression (11) can also be stated in terms of the frequency dependent resistance $R(\omega)$ when introducing the Fourier transform of the temperature autocorrelation. As predicted by the linear response theory, the temporal evolution of the net exchanged power Q is a convolution product provided by the following constitutive relation:

$$Q = G * \Delta T, \quad (12)$$

Using the fact that the Fourier transform of the convolution product $*$ is the product of the Fourier transforms, Eq. (12) implies that the temperature Fourier transform is also equal to the ratio of the heat flux Fourier transform by the conductance Fourier transform.

Using Wiener-Kinchin theorem, the Fourier transform of the temperature autocorrelation function can then be expressed as proportional to the modulus square of the temperature Fourier transform. The frequency dependent resistance then arises as:

$$Rk_B = \frac{1}{T_0^2} \frac{|F_0(Q(\omega=0))|^2}{|F_0(G(\omega=0))|^2} \quad (13)$$

where F_0 denotes the Fourier transform. Finally, Eq. (13) allows for reformulating the conductance under a new form:

$$Gk_B = \frac{1}{T_0^2} \int_0^\infty \langle Q(0)Q(t) \rangle dt \quad (14)$$

the spectral conductance being real and positive. Q represents the temporal evolution of the fluctuations of exchanged power when both bodies are at thermal equilibrium. The exchanged power Q can be derived from the commutator of the Hamiltonian of one side of the system say the left side H_L and the one of the total system H_{sys} :

$$Q = \left\langle \frac{d}{dt} H_L \right\rangle = -\frac{1}{i\hbar} [H_L, H_{\text{sys}}] \quad (15)$$

If the total Hamiltonian is decomposed into H_L , H_D and H_R , which respectively correspond to the left subsystem, the right subsystem and the contact area, the commutator can be decomposed as follows:

$$[H_L, H_{\text{sys}}] = \underbrace{[H_L, H_L]}_{=0} + [H_L, H_D] + \underbrace{[H_L, H_R]}_{=0} \quad (16)$$

The commutator of the left and the right subsystems cancels because there is no direct energy exchange between both of them. The Hamiltonian of each region is then decomposed into the kinetic and the potential energies T and P , i.e. $H_\alpha = T_\alpha + P_\alpha$:

$$[H_L, H_D] = \underbrace{[T_L, T_D]}_{=0} + \underbrace{[T_L, P_D]}_{(a)} + \underbrace{[P_L, T_D]}_{(b)} + \underbrace{[P_L, P_D]}_{=0} \quad (17)$$

where T and P refer to the kinetic and the potential energies respectively. The first and last commutators cancel because the atomic displacements u_i and the momenta p_i operators commute with themselves. The expressions of T and P yield the expression of (a):

$$(a) = [T_L, P_D] = \left[\sum_{i \in L} \frac{p_i^2}{2m}, \sum_{\substack{i \in L \\ j \in D}} \frac{k_{ij}}{2} u_i u_j \right] = \sum_{\substack{i \in L \\ i \neq j}} \frac{1}{2m} \frac{k_{ij}}{2} [p_i^2, u_i u_j] \quad (18)$$

k_{ij} refer here to the force constant between atom i and j . When considering the following operator association property $[a, bc] = b[a, c] + [a, b]c$,

$$\underbrace{[p_i^2, u_i u_j]}_{i \in L, i \neq j} = 2p_i u_i \underbrace{[p_i, u_j]}_{-i\delta_{ij}=0} + 2p_i \underbrace{[p_i, u_i]}_{i\delta_{ij}} u_j \quad (19)$$

The first commutator in the RHS is discarded because atoms i and j belong to two different regions, in such a way that:

$$(a) = [T_L, P_D] = \sum_{\substack{i \in L \\ j \in D}} \frac{-i\hbar k_{ij}}{m} \frac{k_{ij}}{2} u_j = \sum_{\substack{i \in L \\ j \in D}} -i\hbar \frac{k_{ij}}{2} \dot{u}_i u_j \quad (20)$$

According to the same reasoning, the (b) term can be written as:

$$(b) = [P_L, T_D] = i\hbar \sum_{\substack{i \in L \\ j \in D}} \frac{k_{ij}}{2} \dot{u}_i u_j, \quad (21)$$

which finally provides the final expression of the exchanged power:

$$Q = \sum_{\substack{i \in L \\ j \in D}} \frac{k_{ij}}{2} \left(\langle \dot{u}_i(t) u_j(t) \rangle - \langle u_i(t) \dot{u}_j(t) \rangle \right) \quad (22)$$

Coming back to the initial question of the definition of the temperatures in Eq. (11), it clearly appears that the resistance only depends on the motions of atoms interacting across the interface. The reason is that R depends on the same variables as G and G depends on the power exchange (Eq. (14)). The power exchange in turn depends on the velocities and positions of atoms that are interacting across the interface. Eq. (22) indeed involve the force constant between atoms i and j that belong each to different subsystems. Consequently, all the information necessary to define the resistance is included in the motions of few atoms in the vicinity of the interface.

DIFFUSIVE TO BALLISTIC HEAT CONDUCTION IN SUPERLATTICES

As represented in Figure 5, we have computed the interfacial conductance in a Silicon/Germanium superlattice using Molecular Dynamics technique. We have implemented the three-body Stillinger-Weber [4] interatomic potential to reproduce the Si-Si and Ge-Ge covalent interactions. Potentials parameters have also been combined according to the mixing rules described by [5] to model the interfacial Si-Ge interactions.

We have included at least two interfaces in the system “supercell” and applied periodic boundary condition in the three directions. The structure is relaxed using a steepest descent energy minimization algorithm. Atomic trajectories are then calculated in the microcanonical ensemble with a time step of 1fs. Thermal equilibrium has been achieved within 500ps.

We assume a perfect interface between Si and Ge and a perfect lattice match. This is often achieved through the introduction of artificial strains in one or both of the phases. The lattice parameter difference of 4 percents between Si (0.543nm) and Ge (0.565nm) has been matched to 0.554nm in the direction perpendicular to the interface. The resulting lattice parameters in the direction parallel to the contact correspond respectively to 0.531nm and 0.573nm for Si and Ge phases.

Obtaining thermal conductance from equilibrium thermal fluctuations according to Eq. (9) requires large ensemble averages. In practice, dozens of simulations with different atomic random velocities distributions have to be considered to ensure an accurate prediction.

The thermal conductance is calculated through the following two-step procedure. Several MD simulations are performed to capture the time dependent fluctuations of the temperature fluctuations at a given equilibrium temperature. Averaging the autocorrelation functions then allows for the proper convergence of the thermal interface conductance.

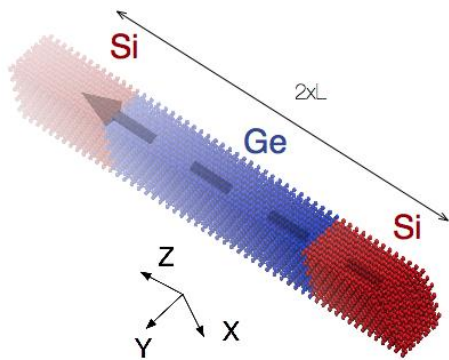


Figure 5 Schematic of the Si/Ge superlattice system simulated with the Molecular Dynamics technique. The length L refers to the film thickness.

Figure 6 reports the thermal conductivity as a function of layer thickness L according to our interfacial resistance and Green Kubo formula predictions. The Green Kubo method is based on the linear response theory yielding transport

coefficients at equilibrium from the flux fluctuations. It is including all possible scattering related to atomic motions.

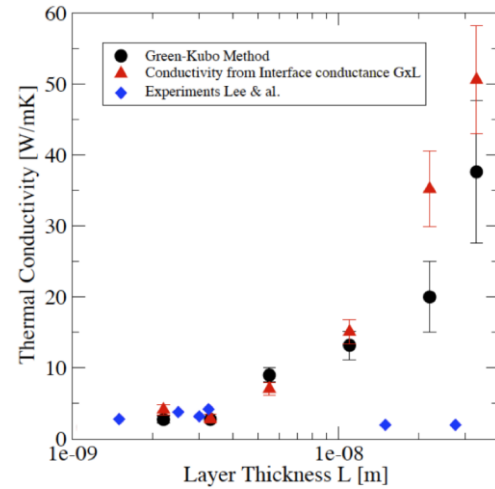


Figure 6 Si/Ge superlattice thermal conductivity as a function of layer thickness L from the interfacial resistance and from the Green Kubo formula [6].

Figure 6 reveals the transition between a transport regime governed by interfacial scattering (or ballistic) and the one due to phonon-phonon scattering (or diffusive). Indeed, both predictions agree up to layer thicknesses of 10nm, which shows that interface resistances are fully capturing the heat conduction mechanisms. Above this thickness limit, the interfacial resistance based thermal conductivity overestimates Green Kubo data. This indicates that phonon-phonon scattering becomes significant and add resistance to heat conduction.

BALLISTIC TO COHERENT TRANSPORT

In superlattices with perfect interfaces, a minimum thermal conductivity at a particular period in the nanometer range has been widely reported [7]. On the other hand, for superlattices with imperfect interfaces -e.g. structural interfacial defects [8,9] or stress [10] - the thermal conductivity increases monotonically with the period thickness.

The concept of phonon coherent transport was invoked in most of these works to explain the thermal conductivity trend. We therefore quantify the phonon coherence length, i.e. the phonon wave-packet size, as a function of the superlattice period.

In order to evaluate the phase coherence between the motions of two atoms separated by a given distance, we compute the product between the time Fourier transforms of the velocities of those atoms from the time dependent velocities provided by MD simulations. For each frequency, the modulus of this latter product is analyzed as a function of the distance. The wave packet size is then identified as the decay length in this representation. The coherence length spectrum reported in Figure 7 is then retrieved by analyzing the all set of frequencies.

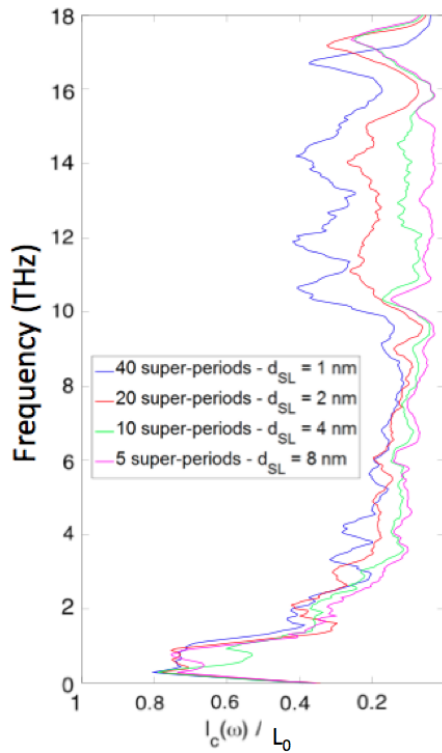


Figure 7 Phonon Coherence length l_c spectrum normalized by the system length L_0 as a function the superlattice period d_{SL} .

As shown by Figure 7, when the period length d_{SL} increases, the coherence length l_c decreases by 70% between $d_{SL}=1$ nm and 8nm. The transition from a coherent to an interfacial scattering type of transport defines a threshold length between 4 and 8 nm. This estimation was confirmed by MD computations of the thermal conductivity in this range of periods, where the thermal conductivity dip was retrieved.

The dip in thermal conductivity can then simply considered as (i) the loss of coherence when the period increases from the sub-nanometer range –an additional impact of the decrease in the group velocity due to zone folding can also be invoked- and (ii) the predominance of interfacial scattering that decreases due to the reduction in the linear density of interfaces. This latter regime is the ballistic regime that was highlighted in the previous section.

CONCLUSION

We present the different heat conduction regimes when the characteristic system size in solid decreases from macroscale down to a few atomic layers. Superlattices were considered as reference systems where classical heat diffusion is observed when the period exceeds several phonon mean free paths while interfacial scattering is found to predominate if the period is smaller than this same path. The last regime appearing for periods of a few nanometers is characterized by a coherent heat transport where phonon wave packets have a width, i.e. a coherence length, larger than the period.

To investigate those mechanisms, we have first defined the thermal resistance as a function of atomic velocities and

positions. This resistance was found to depend on the motions of atoms interacting across the interface and proportional to the integral of the autocorrelation of the temperature difference of those atom populations.

Molecular Dynamics simulations were conducted at equilibrium to compute those atomic motions and the superlattice thermal conductivities deduced from interfacial resistance were found to be in agreement with other computations of the thermal conductivity including the full set of heat conduction processes. Interfacial scattering predominates below periods of 20nm in Si/Ge superlattices and a competition between interfacial and phonon-phonon scattering arises for larger periods.

We finally show that the coherence length of phonon wave packets is affected by the superlattice period in the 1 to 8nm range due to the impact of interfacial scattering on coherence. This provides qualitative argument to explain the dip observed in superlattice thermal conductivity in terms of the interplay between coherence and interfacial scattering.

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