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Electronic Supplementary Information for Tuning thermal transport in Si nanowires by isotope engineering

Miquel Royo and Riccardo Rurali*

Institut de Ciència de Materials de Barcelona (ICMAB–CSIC), Campus de Bellaterra, 08193 Bellaterra, Barcelona, Spain

E-mail: rrurali@icmab.es

Computational Methods

Approach-to-equilibrium molecular dynamics calculations

The approach-to-equilibrium molecular dynamics (AEMD) method[1] is a practical alternative to the most common equilibrium and nonequilibrium molecular dynamics techniques.[2] Rather than maintaining the system at equilibrium or in a steady-state non equilibrium condition, it is first driven to a suitable nonequilibrium state and then is left free to reach equilibrium. The transient of the temperature carries information on its thermal conductivity. An exhaustive description of the method, including a thorough assessment of the convergence of the thermal conductivity with a number of parameters of the simulation, can be found in the paper of Melis and coworkers.[3]

The nanowire geometry requires some additional care in the equilibration phase, thus we adopted the following simulation protocol. At first we perform a preliminary structural relaxation with a standard conjugate gradient algorithm, isotopes do not distort the lattice, but the nanowire is cut out of a bulk system and its geometry must be optimized. Next we heat the system from 300 to 900 K in 600 ps and anneal it at 900 K for 400 ps; then we cool it back to 300 K in 800 ps and than keep it for 200 ps at 300 K. All these steps are carried out in a NVT ensemble, where a Nosé-Hoover thermostat is used to control the temperature of the system. Next we perform a 400 ps NVE microcanonical run.

After this initial equilibration phase, which proved to be necessary in nanowires,[4] we start the real AEMD protocol. First we perform two separate runs in which half of the system is equilibrated at a certain temperature by velocity rescaling, while the atoms of other half are kept frozen. Each of these runs last 200 ps: in the first, half of the system is driven to a temperature $T_H = T_0 + \Delta T/2$; in the second, the other half is driven to a temperature $T_C = T_0 - \Delta T/2$. After these equilibration cycle the system has a step-like temperature profile across the nanowire axis. Then we remove any constraint on the velocities, i.e. on the temperature, and leave the system evolve in a NVE ensemble: in the long run the whole system will reach equilibrium at T_0. We calculate the average temperature of each half of the nanowire every 200 fs and keep track of the time dependence of the temperature difference between the two halves:

$$\Delta T(t) = \langle T_H(t)\rangle - \langle T_C(t)\rangle. \tag{1}$$

This last part of our simulation protocol last from 1 to 10 ns, because the accuracy of the fit described below depends on how close $\Delta T(t)$ is to zero at the end of the NVE run and the equilibration time depends on the size of the system.

We fit $\Delta T(t)$ to the analytical solution of the heat equation

$$\Delta T(t) = \sum_{n=1}^{\infty} C_n e^{-(2\pi n/L_z)^2 \bar{\kappa} t}, \tag{2}$$

where

$$C_n = 8(T_H - T_C)\frac{[\cos(\pi n) - 1]^2}{4\pi^2 n^2}, \tag{3}$$

and extract the thermal diffusivity, $\bar{\kappa}$. We truncate the sum of 2 to the first 20 terms, a choice that has been shown to provide well converged values.[3] The thermal conductivity, κ, can be calculated from the fitted thermal diffusivity as

$$\kappa = \rho C_v \bar{\kappa} \tag{4}$$

where ρ is the density and C_v is the specific heat capacity. Notice that it has been shown that the estimate of κ is rather insensitive to the magnitude of the initial temperature step-like profile, 200 K in our case.[3]

In the molecular dynamics simulations the atoms move classically, following Newton's laws. As a consequence, phonons population is described by a Maxwell-Boltzmann, rather than a Bose-Einstein distribution. This approximation is in principle not very accurate at low temperatures, where quantum effects cannot be neglected. Quantum corrections that take into account the deviations from the Maxwell-Boltzmann distribution below the Debye temperature[5] can be included by renormalizing the classical heat capacity, $C_v = 3Nk_B$, by a factor $\bar{q}$ which is the ratio between the actual temperature and the Debye temperature.

The total energies and the force are calculated within the environment-dependent interatomic potential (EDIP) developed and parameterized by Bazant and coworkers.[6] The superior, simultaneous description of liquid and solid diamond-like Si[7] is not particular important for our work, but remarkably, EDIP exhibits an excellent conservation of the energy with a rather large timestep of 2 fs (to be compared with the 0.5-0.7 fs required by the Tersoff potential[8]), thus allowing spanning much longer simulation times for a given number of MD steps. Notice also that, in general, EDIP potential gives estimate for the thermal conductivity of bulk Si in line with the predictions of Tersoff and Stillinger-Weber potentials.[3]

Nonequilibrum Green's Functions

Thermal transport is analyzed in the ballistic regime using the Landauer formalism within the nonequilibrium Green's function (NEGF) approach.[9,10] These calculations are performed in the harmonic approximation neglecting any kind of phonon-phonon or electron-phonon interactions.

Following the typical procedure in NEGF calculations, we connect a nanowire section (channel) to two reservoirs (contacts) that are held at a constant temperature. The channel has a given isotopic blend while the contacts, being semi-infinite extensions of the channel in shape, have pure ^{28}Si composition (see 1).

In the limit of small temperature difference between the contacts, the thermal conductance of the system is given by the Landauer formula,

$$G(T) = \frac{\hbar^2}{2\pi k_B T^2} \int_0^\infty d\omega\, \omega^2\, \Xi(\omega)\, \frac{e^{\frac{\hbar\omega}{k_B T}}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2}, \tag{5}$$

where $\Xi(\omega)$ is the phonon transmission function and the last factor arises from the temperature derivative of the Bose-Einstein phonon distribution function. The phonon transmission function is calculated from the Caroli formula,[11]

$$\Xi(\omega) = Tr\left[\mathbf{\Gamma}_L(\omega)\, \mathbf{G}^r(\omega)\, \mathbf{\Gamma}_R(\omega)\, \mathbf{G}^a(\omega)\right], \tag{6}$$

in which $\mathbf{G}^{r(a)}(\omega)$ is the retarded (advanced) channel Green's function and $\mathbf{\Gamma}_{L/R}(\omega)$ are broadening functions describing the coupling between the contacts and the channel.

The retarded channel Green's function ($\mathbf{G}^a(\omega) = \mathbf{G}^r(\omega)^\dagger$)) including the effect of the contacts is given by

$$\mathbf{G}^r(\omega) = \left[\omega^2\, \mathbf{I} - \mathbf{H}_C - \mathbf{\Sigma}^r_L(\omega) - \mathbf{\Sigma}^r_R(\omega)\right]^{-1}, \tag{7}$$

here, $\mathbf{I}$ is the identity matrix, $\mathbf{H}_C$ is the force-constant matrix of the atoms in the channel, and $\mathbf{\Sigma}^r_{L/R}(\omega)$ are the contacts retarded self-energies. The latter are also used to calculate the broadening functions of 6 as follows,

$$\mathbf{\Gamma}_{L/R}(\omega) = i\,\left(\mathbf{\Sigma}^r_{L/R}(\omega) - \mathbf{\Sigma}^a_{L/R}(\omega)\right). \tag{8}$$

Obtaining the contacts self-energies is the most involved part of the NEGF approach as, in principle, it involves the computation of the Green's function for the semi-infinite contacts. The task is however simplified if one takes into account that only a certain number of atoms in the contact will effectively interact with any atom in the channel. We will refer to this group of contact atoms as the surface principal layer. Following this reasoning, it suffices to calculate the self-energies as,

$$\mathbf{\Sigma}^r_L(\omega) = \boldsymbol{\tau}_{C,LS}\,\mathbf{g}_{LS}(\omega)\,\boldsymbol{\tau}_{LS,C} \tag{9a}$$

$$\mathbf{\Sigma}^r_R(\omega) = \boldsymbol{\tau}_{C,RS}\,\mathbf{g}_{RS}(\omega)\,\boldsymbol{\tau}_{RS,C}, \tag{9b}$$

where $\mathbf{g}_{LS/RS}(\omega)$ are the surface Green's functions of the contacts principal layers and $\boldsymbol{\tau}_{C,LS} = (\boldsymbol{\tau}_{LS,C})^\dagger$ ($\boldsymbol{\tau}_{C,RS} = (\boldsymbol{\tau}_{RS,C})^\dagger$) are force-constant matrices describing the interaction between the atoms in the contact principal layer and the atoms in the channel.

To obtain the surface Green's functions we use the Sancho-Rubio iterative method.[12] Within this method, the contact is partitioned in principal layers that are assumed to be equivalent and to interact only through first neighbor layers. In this regard, we note that in the way we have partitioned the system (see 1) the surface principal layer of each contact is not equivalent to the subsequent principal layers placed deeper in the contact, precisely because it is the only one that interacts with the channel. By this reason, we proceed with the Sancho-Rubio calculation to obtain the Green's function of the second principal layer in the contact, $\mathbf{g}_{L/R}(\omega)$, and then we can properly compute the surface Green's function as

$$\mathbf{g}_{LS}(\omega) = \left[(\omega^2 + i\eta)\mathbf{I} - \mathbf{H}_{LS} - \boldsymbol{\tau}_{LS,L}\, \mathbf{g}_L(\omega)\, \boldsymbol{\tau}_{L,LS}\right]^{-1} \tag{10a}$$

$$\mathbf{g}_{RS}(\omega) = \left[(\omega^2 + i\eta)\mathbf{I} - \mathbf{H}_{RS} - \boldsymbol{\tau}_{RS,R}\, \mathbf{g}_R(\omega)\, \boldsymbol{\tau}_{R,RS}\right]^{-1}. \tag{10b}$$

Here, $\mathbf{H}_{LS/RS}$ is the force-constant matrix of the surface principal layer and $\boldsymbol{\tau}_{LS,L} = (\boldsymbol{\tau}_{L,LS})^\dagger$ ($\boldsymbol{\tau}_{RS,R} = (\boldsymbol{\tau}_{R,RS})^\dagger$) are force-constant matrices describing the interaction between the first (surface) and second principal layers. 10 also includes an infinitesimal imaginary damping, η.

In order to obtain the phonon transmission function we model a nanowire supercell as the one shown in 1. The supercell is formed from the channel and three principal layers per contact. The third or deepest principal layer is necessary to perform the Sancho-Rubio iterative calculation as it requires force-constant matrix elements describing the interaction between two equivalent layers. All together the supercell includes 2934 atoms distributed in a nanowire of 3nm diameter, the channel has a length $\sim$ 2.82 nm, and the principal layers in the contacts include 326 atoms and have a length $\sim$ 0.94 nm.

We use the generalized utility lattice program[13] (GULP) with therein implemented interatomic EDIP potential[6] to relax the whole structure, assuming periodic boundary conditions in the axial direction, and to calculate the force-constant matrix elements.

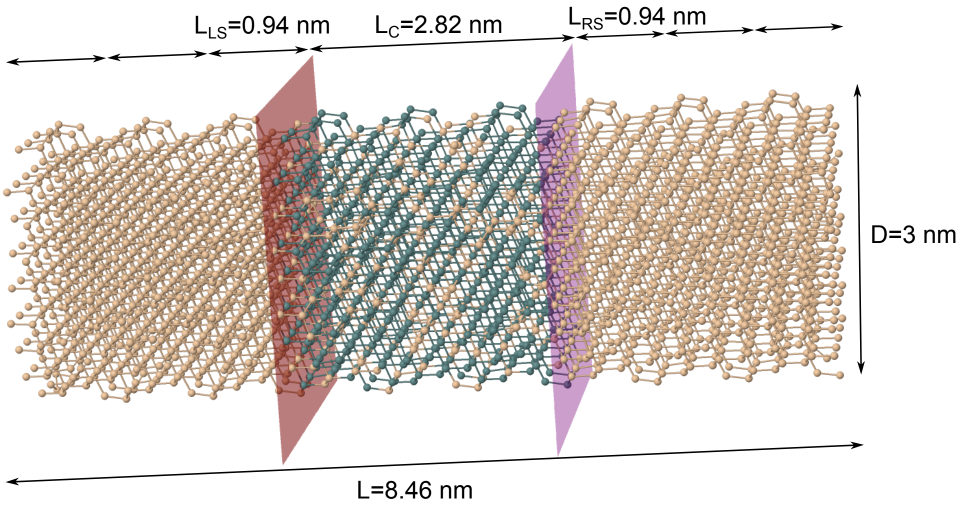

Figure 1: Schematic atomistic structure of the modeled supercell. Beige (green) balls are used for ^{28}Si (^{30}Si). The two transverse planes show the position of the channel-contact interfaces.

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