First-principles simulations of heat transport

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First Principles Simulations of Heat Transport

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Advances in understanding heat transport in solids were recently reported by both experiment and theory. However an efficient and predictive quantum simulation framework to investigate thermal properties of solids, with the same complexity as classical simulations, has not yet been developed. Here we present a method to compute the thermal conductivity of solids by performing *ab initio* molecular dynamics at close to equilibrium conditions, which only requires calculations of first principles trajectories and atomic forces, thus avoiding direct computation of heat currents and energy densities. In addition the method requires much shorter sequential simulation times than ordinary molecular dynamics techniques, making it applicable within density functional theory. We discuss results for a representative oxide, MgO, at different temperatures and for ordered and nanostructured morphologies, showing the performance of the method in different conditions.

The ability to predict the thermal properties of solids is critical to understanding the thermal management of opto-electronic and energy conversion devices[1, 2], and to designing efficient thermoelectric materials [3–5]. Many studies have been devoted in recent years to both gaining a deeper understanding of heat transport of solids at the atomistic and molecular level [6], and to developing experimental and computational techniques to study the thermal properties of complex materials[7–13]. Robust progress has been made in the measurement and computation of fundamental properties, such as the thermal conductivity. For example the development of 3ω [14], and of time or frequency domain thermo-reflectance (TDTR and FDTR) methods has allowed one to probe phonon mean free path distributions [15–17] and to revisit the concept of average phonon mean free path; this concept has been widely used to interpret experiments but it may be insufficient to describe the thermal transport of solids, even that of simple crystals such as Si. [18].

To date, most calculations of the thermal conductivity, especially those for large systems, have been carried out using empirical interatomic potentials (EIP), that are available only for some classes of materials and often have limited predictive power. However several ab initio methods have been proposed in the recent literature, based on approximate solutions of the Boltzmann Transport Equation (BTE) [7, 8], on Green Kubo (GK) formulations [9, 10], and using non equilibrium molecular dynamics (NEMD) [12, 13]. Approximate solutions of the BTE include several techniques to compute force constants, e.g. compressive sensing[12], and often incorporate anharmonic terms only up to the third derivatives of the energy. The BTE can then be solved employing iterative methods [19, 20], the simpler single mode relaxation time approximation [21], or the eigenstates of the phonon scattering matrix (relaxons)[11].

The methods proposed in Ref. [9, 10] are the only available ab initio GK dynamical formulations to date, and they represent remarkable progress in the field. Nevertheless these approaches are computationally rather demanding, as they involve either repeated solutions of the Sternheimer equation to calculate the heat current within Density Functional Perturbation Theory [22], or the calculation of electronic contributions to the virial tensor of each atom [10]. In addition, the method of ref. [10] is specifically designed for solids at equilibrium, as it involves the diagonalization of the dynamical matrix. Ab initio non equilibrium MD calculations have been reported, using homogeneous NEMD [12] and hence involving the explicit calculations of heat currents or using the method of Ref. [13, 23], which faces serious convergence challenges as a function of simulation time (see SI [24] for specific examples).

Addressing the need for an efficient and general quantum simulation framework for thermal properties of materials, we present a method to simulate heat transport from first principles, which can be employed for predictive calculations of complex, homogeneous and heterogeneous solids. We generalize the approach to equilibrium molecular dynamics [25, 26] (AEMD) method by implementing sinusoidal temperature gradients, thus avoiding temperature discontinuities. We call this approach sinusoidal AEMD (SAEMD). We then show that SAEMD can be applied in a straightforward manner to the calculation of thermal conductivity using density functional theory

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(DFT). This approach only requires the computation of MD trajectories and atomic forces, with no additional calculation of energy derivatives, e.g. force constants, energy densities or direct calculations of currents. The precision of the method can be systematically increased by parallel computations on multiple replicas, thus requiring much shorter sequential simulation times than ordinary non equilibrium techniques. Below we briefly describe our formulation and we discuss results obtained with classical potentials and first principles molecular dynamics. We then compare our findings to experimental data, previous simulations and our own calculations using the GK method.

Within the AEMD approach the average temperature of a solid is arbitrarily changed by a discontinuous temperature profile; subsequently the way equilibrium is approached after applying the perturbation is monitored, by carrying out an NVE (constant number of particles N, volume V and energy E) simulation. In particular the temporal decay of T towards an equilibrium value is used to calculate the thermal conductivity. AEMD has been successfully applied to crystalline and amorphous solids and alloys [26], as well as to 2D and nanostructured materials such as nanocrystalline silicon [26], Si-Ge alloy nanocomposites [27], graphene [28, 29], graphane, [30], and porous Si nanowires[31]. In our calculations we used local Nose-Hoover thermostats to impose the initial sinusoidal, and hence continuous, temperature profile T(z,0), which is position dependent:

$$T(z,0) = T_0 + \frac{\Delta T_0}{2}\sin(\frac{2\pi z}{L_z}) \tag{1}$$

where z is the direction of heat propagation, T_0 is the average temperature and ΔT_0 is the peak to peak difference in the temperature applied to a slab chosen to represent the system of interest, and periodically repeated in x,y,z. These initial conditions lead to a simple, analytical solution of the heat equation, given by:

$$T(z,t) = T_0 + \frac{\Delta T_0}{2}\sin(\frac{2\pi z}{L_z})e^{-\gamma_1^2\alpha t} \tag{2}$$

where $\gamma_1 = 2\pi/L_z$ and the thermal diffusivity $\alpha = \kappa/\rho c_v$, where ρ is the density and c_v is the volumetric heat capacity. The difference between the average temperature of the two sides of the system subject to the sinusoidal T profile is

$$\Delta T(t) = \frac{2}{L_z}\int_0^{\frac{L_z}{2}} T(z,t)\,\mathrm{d}z - \frac{2}{L_z}\int_{\frac{L_z}{2}}^{L_z} T(z,t)\,\mathrm{d}z \tag{3}$$

$$= \frac{2\Delta T_0}{\pi}e^{-\gamma_1^2\alpha t} \tag{4}$$

At variance with the original AEMD approach, only the fundamental mode is present when using sinusoidal gradients, and thus no higher harmonics in the Fourier expansion of the temperature profile need be considered.

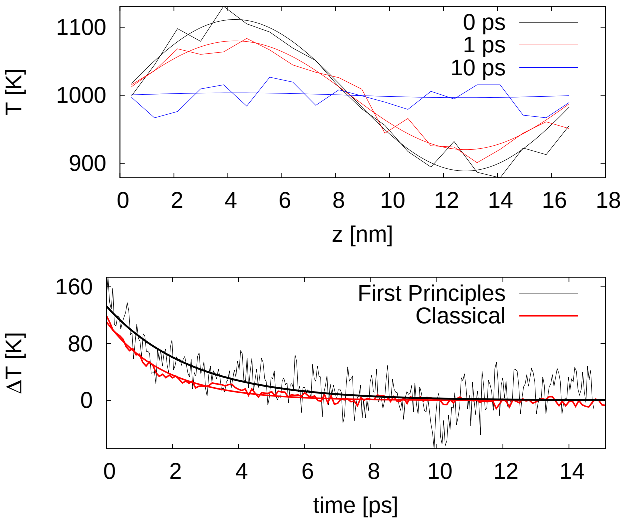

FIG. 1. Top: Temperature profile along the heat transport direction z, averaged over 30 samples, for a classical molecular dynamics run performed at 1000K for MgO. Smooth, continuous solid lines represent analytical solutions of the heat equation. Note the rapid decay of the sinusoidal profile to zero over 10 ps (blue line). Bottom: Difference in the average temperature ($\Delta T(t)$) between the hot and cold side of a periodic slab representing MgO, as a function of time, during a molecular dynamics run at constant volume and energy, carried out after the application of a sinusoidal temperature profile (Eq.1). We show first principles results (black line) obtained for a slab with 960 atoms at 500K, and classical result (red line) for the same size slab, but averaged over 30 samples. Solid lines are the results of a fit to Eq. 4. The rate of decay of ΔT is proportional to the thermal conductivity.

The thermal diffusivity α is obtained by fitting the expression of ΔT in Eq. 4, as obtained during an NVE run. As an example, in Fig. 1 (top panel) we show the instantaneous temperature averaged over 30 samples of crystalline MgO (1280 atom samples) at the beginning and during the NVE simulation, along with the analytical solution of the heat equation (continuous lines). In the lower panel of Fig 1 we show the difference in temperature as a function of time and the fitted function (Eq. 4) used to calculate the thermal diffusivity. In addition, separate calculations to compute the heat capacity as a function of T were carried out and the thermal conductivity is readily obtained from $\kappa = \alpha\rho c_v$, where ρ is the known density of the system (set by choosing the volume V).

We note that within the SAEMD approach, typical simulation times to reach equilibrium are shorter by about 2 order of magnitude, compared to those required by the NEMD method, thus making the technique presented here amenable to use with first principles approaches, i.e. density functional theory (see SI for a detailed comparison between techniques). Simulations times are also one order of magnitude shorter than in the GK approach. When using a GK formulation, the

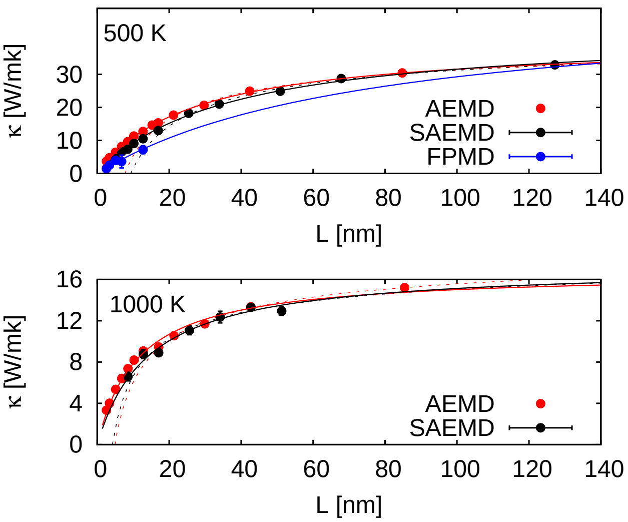

FIG. 2. Thermal conductivity (κ) of crystalline MgO computed at 500 (top panel) and 1000K (lower panel), as a function of the length of the periodic slab (L), using approach to equilibrium molecular dynamics (AEMD, red curves), sinusoidal approach to equilibrium (SAEMD, black curves) and classical potentials. We compare results obtained with the two methods using classical potentials and we show (blue curve) first principles results obtained with the SAEMD method. Solid and dotted lines represent a fit to Eq. 5, and 6, respectively.

simulation time scale is determined by the time required to reduce the noise in the tail of the heat current autocorrelation function; in NEMD it is the time needed to reach a stationary state between the cold and hot ends of the system, plus the additional time required to obtain an accurate temperature gradient that determine the length of thermal conductivity simulations. These simulation times are of course system dependent, but they can be estimated to be, in general, [32, 33] two order of magnitude longer than the time required to reach equilibrium within SAEMD (see SI for a detailed comparison between techniques for the case of MgO).

The efficiency of the SAEMD method relies on the ability to reduce statistical errors in the determination of the thermal conductivity, which arise due to the intrinsic noise in the temperature profile of a finite system. Given the transient nature of our MD simulations, statistical errors may not be improved by increasing the simulation time once the temperature difference (Eq. 4) vanishes. Instead, one may carry out multiple, parallel runs and then average the results obtained for the various replicas. However care must be exercised in the way averages are performed and direct averaging over values of α from different replicas may lead to inaccurate or even wrong results. In the absence of noise, the difference in temperature $\Delta T(t)$ decays to zero at a rate proportional to the thermal diffusivity α. In the presence of noise this rate is modified: the probability distribution of α is an asymmetrical function (we report an example in the SI) and its average value increases as a function of increasing noise. The value of α obtained by averaging over different replicas may thus result to be greatly overestimated. In our calculations we averaged over instantaneous temperature differences $\Delta T(t)$ obtained for several replicas, and then we performed a single fit to the average value to compute the diffusivity.

A well known challenge in realistic predictions of thermal conductivity of solids is posed by finite size effects. Within the AEMD approach, check of convergence is required with respect to the lateral section of the sample used, as well as the length of the system in the direction of heat transport, so as to ensure that all relevant phonon mean free paths are correctly taken into account. In our calculations, finite size scaling was performed by computing κ for several samples of length L, as illustrated in Fig. 2 and Fig. 3. The extrapolation implicitly assumes that there exist a certain sample length after which only one dominant phonon mean free path is present. Under the additional assumption of validity of the Matthiessen's rule one obtains [34]

$$\kappa(L) = \kappa_\infty/(1+\frac{\lambda}{L}) \tag{5}$$

This equation appears to properly fit results obtained at finite sizes within both NEMD, for which it was developed, and AEMD, although it is not fully justified for the latter (in particular the assumption of an additional scattering term due to the thermostat, valid within NEMD, is not justified). Very recently a new fitting equation for the AEMD method has been proposed [35], not based on the Matthiessen's rule, where it is assumed that acoustic phonons, whose lifetime is proportional to $1/\omega^2$, are the major contributors to heat transport.

$$\kappa(L) = \kappa_\infty(1-\sqrt{\Lambda/L}) \tag{6}$$

We show in Fig. 2 that eq. 5 and 6 yield nearly the same results for the case of MgO, for large sizes, in spite of having been derived under different assumptions.

We now turn to the presentation of our results for a representative solid, MgO, chosen because of the availability of experimental data and of several results from other studies to compare with. We first describe classical and first principles simulations of bulk MgO and compare data obtained with discontinuous and sinusoidal temperature gradients, as well as using the GK method. We then show that the SAEMD approach is general and it can be used also for systems containing nano-grains, and not only for ordered bulk systems.

All classical simulations were carried out using LAMMPS [36], with a Buckingham Coulomb potential shown [37] to describe reasonably well density, thermal expansion and thermal conductivity of crystalline MgO. First principles MD simulations were carried out by coupling the LAMMPS and Qbox [38] codes within a client-server strategy. The former was used to integrate the equation of motion and to apply the local thermostats,

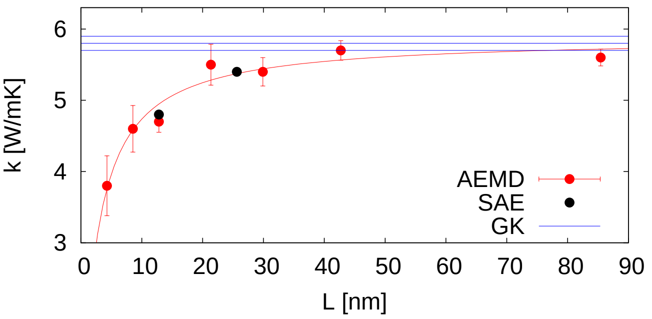

FIG. 3. Thermal conductivity (κ) of a periodic slab representing nanocrystalline MgO, as a function of the slab length L, computed at 1000K using a classical potential. The average radius of nanocrystalline grains is 2 nm. We compare simulation results obtained with approach to equilibrium molecular dynamics (AEMD method, red dots), sinusoidal approach to equilibrium molecular dynamics (SAEMD, black dots) and equilibrium molecular dynamics using a Green Kubo (GK) formulation (blue lines). The blue lines represent the results of converged GK simulations as a function of size (see SI). Convergence was obtained for L $\approx$ 8nm with a cubic supercell; the top and bottom blue lines represent the population standard deviation of the samples used for GK calculations (see SI).

and the latter to compute DFT forces on atoms at each time step and to carry out the NVE part of the simulation. Alternatively a position dependent thermostat can be implemented directly in the first principles MD engine. The time needed to generate the temperature profile, the approximate time necessary to reach equilibrium and the number of replicas necessary to obtain a $\approx 10\%$ statistical error were the same for classical and first principles simulations. A timestep of 1 fs was adopted in our MD simulations and a constant lateral section of 2X2 elementary cells was chosen, as a reasonable compromise between computational cost and accuracy. However finite size scaling tests for the lateral sections conducted with classical potentials (see SI) showed this cross section not to be fully converged. Unfortunately carrying out first principles simulations with a (4X4) lateral section is prohibitively expensive at present, hence we used a correction factor α_c for the first principles result, namely we multiplied them by $\alpha_c = 32/43 \approx 0.744$; α_c equals the ratio $[\kappa\_\mathrm{SAEMD}(4X4)]/[\kappa\_\mathrm{SAEMD}(2X2)]$ of values of κ computed in SAEMD simulations with classical potentials. We realize this is an approximation, which could be eliminated using larger simulation cells in the future. Green Kubo simulations with classical potentials were performed with the same 1 fs timestep in the NVE ensemble and using a cubic supercell. We averaged the thermal conductivity over multiple replicas and tested convergence with respect to both time and number of atoms.

Results obtained with classical potentials are shown in Fig. 2 for bulk MgO at 500 and 1000K. We found very good agreement between AEMD and SAEMD calculations at both temperatures, as well as between different extrapolation methods. For the thermal conductivity of MgO at 500 K computed with SAEMD we obtained 32 ± 1.6 W/mK using Eq. 5 and a 4x4 lateral section, against a value of 32 ± 1 using GK and an experimental value of 34.1 [39]. Note that, as pointed out in Ref. [35], Eq. 6 is appropriate to describe thermal conductivity extrapolations at large sizes, but not at short sample lengths. We thus used a minimal length of ≈ 20 nm when fitting Eq. 6. First principles MD results are presented in the top panel of Fig. 2. We carried out calculations for crystalline samples with 192, 256, 384, 512 and 960 atoms using gradient corrected exchange correlation functionals (the Perdew-Burke-Ernzerhof (PBE) [40] functional; see SI). We averaged the temperature difference over 12, 8, 4, 4 and 1 replicas for 3, 4, 5, 7 and 15 ps, respectively, for the five chosen sizes, with a 10 % target error. The results and their extrapolation using Eq. 5 (50 W/mK) turned out to be consistent with those of classical calculations using the same lateral section (43 W/mK for SAEMD simulations), giving a bulk thermal conductivity of 37 W/mK for MgO at 500K, when corrected to account for the difference between 4x4 and 2x2 results ($\alpha_c = 0.744$). We emphasize that the main finding of our first principles MD simulations is the demonstration of their feasibility, opening the way to studying heat transport in complex and realistic systems, without the need to compute any heat current or energy densities. It is also reassuring to find good agreement with experiment and classical potentials and with previous simulations. [13, 37, 39, 41].

Finally we tested the validity of the SAEMD approach for nanostructured MgO. In Fig. 3 we show the thermal conductivity of nanocrystalline MgO obtained using Green Kubo, AEMD and SAEMD methods. The grains were created by insertion of small crystalline seeds in random points of the molten phase, followed by grains growth. We averaged over multiple simulations in order to account for the random nature of grains in the samples, using classical potentials. We found again remarkable agreement between AEMD, SAEMD and GK calculations, indicating that the analytical solution of the heat equation is valid also at the nanoscale, at least for the 3D material investigated here. As expected we also found a reduction of the thermal conductivity with respect to bulk MgO, by approximately a factor of 3, for 2 nm grains at 1000K. More detailed results are reported in the SI.

In summary, we presented a first principles non equilibrium molecular dynamics approach for the calculations of the thermal conductivity of materials. The method is a variant of AEMD, utilizing simpler initial conditions and a fit to the analytic solution of the heat equation with just one Fourier coefficient. The method avoids the use of discontinuous temperature gradients, and it permits to employ noise reduction techniques, which in turn allow one to reduce the number of parallel replicas used in the calculation. Within SAEMD only atomic trajectories and forces are needed and no other calculation of energy densities, force constants or heat current are required, making the framework presented here amenable to calculations within density functional theory. Furthermore slabs of different sizes may be equilibrated at the target temperature at the same time, thus allowing one to exploit the parallel architecture of modern high performance computers. All of these characteristics make the SAEMD method ideal to be used with first principles Hamiltonians, as demonstrated here for a representative oxide, MgO. Work is in progress to apply this method to complex materials, for which no empirical potential exist and to extend it to the study of heat transport in fluid systems.

CONTRIBUTIONS

M.P. and G.G. designed the research, M.P. carried out all simulations and analysis of data, F.G. and M.P. carried out all computational optimizations. All authors contributed to writing the paper.

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