Ph.D. School in Physics @ University of Cagliari

PROJECT

1. **Class** (Italian: ciclo): XXVII

2. **Curriculum**: Physics

3. **Tutor**: prof. L. Colombo  [http://www.dsf.unica.it/colombo](http://www.dsf.unica.it/colombo)

4. **Topic**: Nanoscale thermal transport

5. **State-of-the-art**

   Environment-friendly energy production and energy-efficient technologies are both critical issues for a modern industrialized society concerned with sustainable growth. In reply to such a demand, it is possible to conceive a materials-by-design approach where natural materials are manipulated at the nanoscale, resulting into new systems with physical properties tailored to meet energy-relevant issues and needs. Within the above framework, we focus -among many others- on two different perspectives which, to our way of thinking, will have considerable technological impact and be of paramount relevance for basic nano-science:

   - **Nano-structured thermoelectrics**: Thermoelectrics represent a potentially important energy conversion technology due to their ability to convert heat into electricity. Despite this potential, thermoelectric devices are at present only used in niche markets because of their low efficiency. The key issue is how to maximize their thermoelectric figure of merit or, equivalently, to use a material with: (i) high electrical conductivity, (ii) high Seebeck coefficient, (iii) and low thermal conductivity. A system so performing is unfortunately not provided by Nature. A way to bypass this limitation involves designing new materials where lattice thermal conductivity is more largely affected by some addition structural feature than in pristine systems (still preserving good electrical performances). It has been proposed [Snyder et al., Nat. Mater. 7, 105 (2008); Dresselhaus et al. Adv. Mater. 19, 1043 (2007); Minnich et al., Energy Environ. Sci. 2, 466 (2009)] that a primary approach to obtain this reduction is to generate suitable nano-composite semiconductor materials, where the typical grain size is smaller than the phonon mean-free-path, but it is still larger than the electron (or hole) one. Through computer experiments based on non-equilibrium molecular dynamics simulations we aim; (i) at understanding lattice thermal conductivity features in such materials; and (ii) at elaborating criteria for the design of Si-Ge interfaces maximizing phonon scattering.

   - **Graphene nano-ribbons**: The relentless scaling down of the feature sizes in electronic and optoelectronic appliances is leading to a steady increase in the power dissipation demand per unit area (despite the reduction of the supply voltage). This has in fact become a major issue for the design of the next-generation devices: it is mandatory to add large thermal conductivity functionalities in the device structure in order to efficiently remove heat. This motivates the search for new materials with high thermal conductivity to be used as heat sinks/dissipators in future ultra-large-scale-integrated electronics. Recently, it has been measured that free-standing graphene has an extraordinarily high thermal conductivity, ranging from 3000 to
6. Outline of the research plan:

A. Novel non-equilibrium molecular dynamics techniques for thermal transport

We aim at developing novel, conceptually clean, and artifact-free NonEquilibrium-MD simulation protocols for computing thermal transport features in nano-scale systems. The key idea is twofold:

First of all, we will develop a new thermostatting procedure aimed at naturally establishing a regime of steady state, characterized by a stable (in time) linear thermal gradient. This will be obtained by partitioning the simulation cell in three regions: a "hot region", a central bulk-like region, and a "cold region". While the time evolution of particles in the bulk-like region will be dictated by conservative newtonian forces derived from the interaction potentials, "hot" and "cold" particles will be aged by Langevin dynamics with thermostats gauged at different temperatures. This will impose a heat (or, equivalently, energy) flux in the most natural and physically meaningful way.

Secondly, we need to optimize the choice of the thickness of the hot/cold regions, as well as the actual values of the parameters governing the frictional and stochastic Langevin forces, in order to get reservoirs efficiently adsorbing phonons with mean-free-path longer than the simulation cell, thus avoiding unphysical scattering/reflection phenomena at boundaries. The extrapolation procedure outlined above will be replaced by a suitable adsorbing action operated through Langevin dynamics. The new technique will be applied to a variety of systems differing by geometry, chemical composition, structure, and state of aggregation in order to understand its functioning in real applications and to best tune the overall protocol. The role of different thermostatting techniques will be investigated as well.

B. Thermal transport in nano-scale systems

B1. Si-Ge nano-composites

By insertion of a pre-assigned ensemble of, say, Ge nano-grains into a carved Si crystalline host and following simulated annealing, we will generate trustworthy models of Si-Ge nano-composites with tailored structural characteristics. Alternatively, Ge nano-grains will be at first randomly inserted into a Si melt and then, upon quenching down to room temperature, the final solid-state sample will be obtained. Merits and drawbacks of these two protocols will be comparatively established. In any case, the selected protocol for the sample generation will be elaborated in such a way to keep under control the following features: (i) the grain size distribution and the average grain size; (ii) the crystallographic orientation of grains with respect to the host; (iii) the grains density and spatial distribution, (iv) the ratio between the amount of crystalline and amorphous matter (as discussed below), (v) the overall stoichiometry of the nano-composite. Another issue of great importance is the full characterization of Si-Ge boundaries, in terms of their effective area, orientation, and thickness. In particular, it is well known that high-angle grain boundaries in semiconductor materials are likely disordered (because of the release of a large amount of strain energy locally accumulated), so that the inner crystalline core of the grain is sheathed in an amorphous layer.

Then, by applying the novel NE-MD techniques described in Sec.A, we will

5000 WK\textsuperscript{-1}m\textsuperscript{-1}, according to the actual experimental setup. [Balandin et al., Nano Lett. 8, 902 (2008); Gosh et al., Appl. Phys. Lett. 92, 151911 (2009)] This large values are reduced down to about 600 WK\textsuperscript{-1}m\textsuperscript{-1}(still larger than copper!) when deposited onto a substrate. [Seol et al., Science 328, 213 (2010)] These experimental results, although currently under debate and not yet fully understood, have burst a strong interest in graphene nano-ribbons that arguably could be shaped as a "wire" to conduct thermal current and integrated onto a chip, thus allowing for efficiently sucking heat off. [Cai et al., Nano Lett. 10, 1645 (2010)] Besides its practical importance, [Prasher, Science 328, 185 (2010)] the investigation of heat transport in graphene and graphene-based systems offers other rewards, more closely related to fundamental physical issues like, e.g., the role of the reduced dimensionality and/or different shaping on transport features. We aim: (i) at investigating several aspects of this problem; and (ii) at developing proof-of-concept studies on possible thermal rectification effects in graphene nano-ribbons.
investigate how and to what extent the thermal conductivity in Si-Ge nano-composites is affected by the overall structural features, as well as by amorphous grain boundaries. In this respect it is likely that special care will need to be taken in understanding what happens at a single Si-Ge interface, as far as the flux of heat carriers is concerned. It is important to establish how such a flux is adsorbed, or transmitted, or reflected depending on the boundary crystallographic orientation, roughness, thickness, and state of aggregation. This is per se a very interesting sub-project, addressed to a fundamental issue in the physics of heat transport.

Another topic we plan to investigate is the difference, if any, between a homogeneous vs. graded distribution of grains. While the first configuration refers to an ordinary bulk nano-composite, the second one is also referred to as nano-graded interface. In this graded case, grains are distributed with decreasing average density along a given direction, for instance from left to right. In this way, it is possible to generate a structure where a pure Ge composition on the left is gradually changed into a pure Si composition on the right. Such a graded interface is inherently anisotropic and, therefore, new features are expected in thermal transport (as well as in any other physic property).

B2. Graphene nano-ribbons

As a first step we aim at fully characterizing the heat flux features in an ideal (i.e. defect- and deformation-free) nano-ribbon as function of its orientation, length, width, and lateral termination. Once again, NE-MD simulations will be employed as outlined in Sec.A. As a matter of fact, graphene can be naturally cut along two main high-symmetry direction, namely: the armchair (ac) and the zigzag (zz) directions. Therefore, it is likely that heat flows differently in differently-oriented ribbons. The same non-equivalent ac vs. zz choice can be adopted for terminating the nano-ribbon along its lateral borders. The implications in thermal transport will be thoroughly investigated. In addition we will investigate the role of surface termination and hydrogen saturation.

As a second step we will include in our analysis the role of defects. Structural defects in graphene do exist (despite its typical high crystalline quality): they are both native (as dictated by thermodynamics), or deliberately introduced by suitable processing. We argue that they likely affect thermal transport since they represent very efficient phonon scattering sources. This detrimentally affect the performances of graphene nano-ribbons as efficient heat sinks/dissipators in nano-devices. The above NE-MD simulation techniques will be applied to investigate the role of point-like (vacancies and Stone-Wales), isotopic, and extended (dislocations and grain boundaries) defects on thermal transport in graphene and graphene nano-ribbons.

Next, we remark that in most applications of current interest in nano-technology graphene ribbons are either stretched/compressed or bent. Therefore, the physical properties of interest are not those one of the pristine system, but rather those ones of the appropriately deformed system. Deformations affect, through the associated stress field distributed on the honeycomb lattice, phonons, i.e. the heat carriers. We plan to investigate this issue in order to establish how thermal transport is affected by stretching and bending.

Finally, nano-ribbons can be shaped into arbitrary forms (like, e.g., into a T-shape), possibly generating anisotropic heat currents. It has been proposed that this could generate, in turn, thermal rectification effects. [Yang et al., Appl. Phys. Lett. 95, 033107 (2009)] We believe that, at this stage of the project, we will be optimally suited to investigate thermal rectification phenomena, as function of the nano-ribbon shape, sheet orientation, lateral termination, and applied thermal gradient. Possible non-linear thermal transport phenomena in such complex nano-devices will be also investigated.

7. Collaborations
- School of Physics, University College Dublin (Eire)
- CASPUR supercomputing center, Rome (Italy)