Molecular dynamics simulations of thermal transport in solid state systems

Antonio Cappai[1], Luciano Colombo[1], Riccardo Dettori[2], and Claudio Melis[1]

[1]Department of Physics, University of Cagliari, Cittadella Universitaria, I-09042 Monserrato (CA), Italy.
[2]Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, USA

Summary (10% of the original content)

In a solid-state system (in fact, the only kind of media here addressed) heat transport is typically observed in the non-equilibrium regime obtained by applying a temperature gradient. Whenever this condition occurs, the observed flux of energy is the response of the system to such a thermal perturbation. In this framework, the ultimate goal to understand and predict thermal transport properties of any given material system is twofold: on the one hand, we need to establish a set of constitutive equations, robust enough to fully describe the system behavior in response to the thermal perturbation and general enough to cover a wide spectrum of situations actually found in practice; on the other hand, we must provide a workable computational protocol to calculate the thermal conductivity of the system of interest, namely that material-specific transport coefficient exploiting the relationship between the perturbation and the system response.

The first task is accomplished by nonequilibrium thermodynamics which is outlined in Sec.2, providing the Fourier flux equation and the more general energy balance equation, both valid in a steady state transport regime.

As for the computational prediction of the relevant thermal transport coefficient, we could follow different paths. At the most fundamental and superior level of erudition, we find the Boltzmann transport equation (BTE) which relies on the atomistic picture according to which phonons are the microscopic heat carriers and heat is pictured as a flux of such carriers undergoing scattering events (among themselves, with any kind of defects, and

with sample boundaries). BTE can be numerically solved by using empirical as well as fully ab initio force fields describing the system lattice dynamics. While this twofold option reflects into a rather different computational workload (the ab initio choice being of course the most demanding one), there is a common limiting feature in both approaches, namely: since BTE is based on the phonon picture, only periodically invariant systems can be rigorously treated. This certainly corresponds to a great many cases of both fundamental and applicative interest, but equally certainly it does not include a huge number of highly relevant physical situations including (but not limited to) disordered materials, glasses, porous media, and heterogeneous samples where the very concept of "phonon" is ill defined. In all these cases, it is more versatile (and, also, computationally more convenient) to use the molecular dynamics (MD) method which, however, is less fundamental since in by far the majority of applications it is based on empirical force fields describing interatomic interactions. MD is outlined in Sec.3, where the conceptual framework, some key technicalities, and a synopsis of available solutions to model the force fields are summarized.

MD simulations can be performed by mimicking equally well equilibrium or nonequilibrium situations. This manyfold choice reflects into several different computer-based protocols which are thoroughly addressed in Secs.4-5. Throughout this Chapter, we simulate thermal transport in bulk crystalline silicon, a solid-state system used as benchmark since any MD simulation strategy here discussed can be straightforwardly implemented and then compared with the others in order to define the strengths and weaknesses of each.

By choice we will develop our arguments at a tutorial level, privileging the pedagogical aspects over those of completeness. Also, the formalism will be kept at the minimum level possible, without affecting rigor or clear thinking. Finally, the deliberately non-encyclopaedic body of information here elaborated was selected to make this chapter a streamlined introduction to this huge and fascinating field. Nevertheless, we included quite a few updated references to current literature, by means of which the interested reader could gain a more in-depth knowledge of molecular dynamics simulations and their application to thermal transport.