Heat transport in solids, beyond the classical approximation

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PhD may follow: Yes

Summary :

The goal of this project is to establish a methodology, based on the formalism of path integrals, allowing one to accurately take into account the influence of nuclear quantum effects on transport properties, in particular heat transport, in condensed systems. This is a very ambitious task which would have profound implications in many research fields, ranging from fundamental physics issues to the development of advanced materials for modern technological applications.

We plan to start applying the methodology a simple archetypical case study, the Lennard-Jones crystal, by focusing on simple quantities (velocity auto-correlation function, for instance) and comparing the path integral calculations with semi-classical approximations.

In case of a successful outcome, the M2 stage could be extended to a Ph.D. project on calculation of heat conductivities in solids, funded by an ANR project. This will involve systems of both fundamental and practical interest in condensed matter science. In particular, we will focus, on one side, on amorphous systems (glasses) and try to clarify in a plainly first-principles calculations framework the origin of the striking low-temperature anomalies in the thermal properties. On the other side, more in perspective and moving to systems of increased complexity, we will in contrast focus on highly ordered structures at the nano-scale, where a careful design with very high spatial resolution can trigger remarkable thermal responses.

Full description :

Heat transport in materials is a key property for a number of applications, and significant efforts are devoted to the design of materials with high (for heat transport applications) or low (e.g., for thermoelectric conversion) heat conductivity. With the exception of good metallic conductors, thermal conductivity is in general dominated by atomic vibrations. The goal of the present project is to establish a methodology for determining the vibrational contribution to thermal conductivities of materials, using the formalism of path integrals (PI). This allows one to take into account accurately the nuclear quantum effects (NQE) in condensed matter systems.

Indeed, it may come as a surprise, that, in spite of the many developments in microscopic modeling of materials in the last 40 years, we still lack a well-established, general method for computing thermal conductivities in insulating (or poor electrical conductors) solid materials. This statement may seem provocative, as many computations of heat conductivities in solids have been performed, on all types of solid materials. The key point, however, is that all these calculations make the assumption that the system under consideration can be described by classical mechanics. This is simply not correct for many condensed matter systems, even at relatively "high" temperatures. Two simple figures illustrate this problem. First, the thermal wavelength of proton at 300 K is about 0.1 nm, comparable to many typical intermolecular distances. As a consequence, proton delocalization certainly affects vibrational properties in many molecular systems. Second, in aluminum the Debye temperature is T_D=430 K. High frequency vibrations will therefore be largely depleted compared to the classical approximation, even at 300 K. In fact, a number of recent works has demonstrated the importance of nuclear quantum effects for many different condensed matter systems, ranging from the electronic structure of water to the thermoelastic properties of silicate glasses.

Our aim is therefore to develop an exact framework for the calculation of thermal conductivity in insulating materials, based on path integrals, and going beyond the approximations normally used in these kind of calculations (centroid or ring-polymer MD). In addition, as a crucial constraint, we want to develop a scheme applicable in full generality to both ordered and disordered states of matter, avoiding any reference to the existence of a

well-defined underlying lattice structure. Our approach will rely, first, on the calculation of imaginary time correlation functions of the heat flux, that can be analytically continued to real times. This will, next, allow a precise calculation of the needed transport coefficients, applying the Green-Kubo formalism. Such an approach, already formulated in the 1980s, is formally exact, but the corresponding calculation is challenging, and needs a careful choice of the estimators of the operators involved. It also is computationally extremely intensive. The requested computing resources, at the present level of performances, should allow, however, to circumvent these limitations providing the ultra-accurate determination of the necessary correlation functions. Alternative methods, such as the use of quantum thermal baths, will be also used to complement the PI approach or to compare our results to previous works.

The development of the methods introduced above constitutes the most challenging task of the project. It will also be the springboard to attack long-standing issues which can significantly benefit from an approach that samples exactly the fluctuations associated with nuclear quantum effects. These include, among others, several properties and microscopic mechanisms related to the thermal behavior of materials, e.g., the existence (or absence) of two-level systems in the vibrational spectra of disordered solids, or the possibility to control conductivity by tailoring structure at the nano-scale.

Requested skills :

Training as a physicist. Outstanding knowledge in general physics and quantum mechanics. Programming skills (Python, C/C++,...) in Linux environment. Fluent spoken and written English.