Thermophysical properties of the novel 2D materials graphene and silicene: insights from ab-initio calculations

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Abstract

Graphene, a 2D layer of sp\textsuperscript{2} bonded carbon atoms in honeycomb arrangement, is a recently synthesized material, with exceptional mechanical, electronic, optical and thermal properties. Although theoretically studied since a long time, as it is the building block of graphite (a stacking of graphene layers), it was isolated as single or few layers only in 2004. Today graphene can be produced by several methods that depend on the quality and dimension of the material to be obtained. Applications of graphene are extensive in electronics, photonics, sensing and also in the field of energy generation and storage.

Belonging to the same chemical group of carbon, also silicon could be in principle the ingredient of a 2D material similar to graphene, named silicene. It shares with graphene the peculiar optical and electronic properties and could provide a more easy compatibility with the existing silicon-based microelectronics technology.

An extremely high thermal conductivity in the range 3000-5000 Wm\textsuperscript{-1}K\textsuperscript{-1} has been measured for graphene. Only few results exist instead on the thermal properties of silicene.

In this work we report ab-initio calculations, based on density functional theory and density functional perturbation theory, that provide the ingredients for the determination of the thermal conductivity and specific heat of graphene, silicene and 2D silicon carbide. Ab-initio calculations solve Schrödinger equation without the need of empirical parameters, only knowing the chemical nature of the system constituents. The use of consolidated approximations employed in density functional theory allows the accurate prediction of several properties of materials.

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1. Introduction

Graphene is a planar layer of sp$^2$ bonded carbon atoms in honeycomb arrangement. It is the building block of graphite (a stacking of graphene layers) but only quite recently it has been synthesized as single or few layers [1], an achievement that granted the Noble prize in physics to Geim and Novoselov in 2010. Graphene is endowed with exceptional mechanical, electronic, optical and thermal properties [2,3]. It can be produced by several methods that depend on the quality and dimension of the material to be obtained [4]. Its applications range from electronics to photonics and sensing. In the field of energy generation and storage graphene is promising for use as transparent electrode in dye-sensitized solar cells, for lithium ion batteries, and as ultracapacitor for energy storage [2].

Following the intensive research devoted to graphene, other group-IV 2D materials have been investigated to understand if they could hold promises analogous to graphene. One of these materials has been silicon in its 2D allotrope, named silicene. Silicene has been very recently synthesized on top of a metallic substrate [5]. It shares with graphene the peculiar optical and electronic properties arising from the presence of a Dirac cone in its electronic band structure and is even more promising than graphene in view of its easier integration with the existing silicon-based microelectronics technology. Several other structures could be devised: a 2D allotrope of silicon carbide, made of silicon and carbon in equal amounts, shows also interesting theoretical properties [6].

Concerning thermal properties, a largest thermal conductivity among all existing materials (in the range 3000-5000 Wm$^{-1}$K$^{-1}$) has been measured for graphene [7]. This can prove extremely useful, for example, for heat removal in microelectronics. Only few results exist instead on the thermal properties of silicene [8,9]. Lower values of the thermal conductivity have been estimated, and this could be exploited for thermoelectric applications [10].

We present in this paper a framework for calculating the thermophysical properties of materials. The context is that of ab-initio calculations, that are a powerful tool for the accurate determination of several properties of matter, from structural ones to electronics, optical and thermal properties. Ab-initio calculations are based on a solution of the many-body Schrödinger equation that is only based on the knowledge of the atom types composing the system of interest. This means that no empirical parameter is employed to solve the many-body equations. The tools to perform this task are density functional theory (DFT) and density functional perturbation theory (DFPT), and they will be briefly recalled in the next paragraph.

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**Nomenclature**

| Symbol | Description |
|--------|-------------|
| $G$    | electrical conductivity |
| $\hbar$ | reduced Planck constant |
| $n$    | electronic density |
| $n_{BE}$ | Bose-Einstein distribution function |
| $N$    | number of electrons in a many-body problem |
| $r$    | space position |
| $S$    | Seebeck coefficient |
| $T$    | absolute temperature |
| $T_{ph}$ | phonon transmission function |
| $v_{ext}$ | external potential for electrons |

**Greek symbols**

| Symbol | Description |
|--------|-------------|
| $\kappa$ | thermal conductivity |
| $\sigma$ | phonon thermal conductance |
| $\omega$ | wave number |
2. Methods

Solving the many-body Schrödinger equation requires dealing with a partial differential equation that contains kinetic and potential energy of electrons and nuclei as well as terms describing their interaction. The first step to simplify the problem is to exploit the large difference of ionic and electronic masses that makes it possible to solve the electronic problem in the potential created by fixed ions (adiabatic approximation) and then to move the atoms according to the forces that are determined deriving the total energy of the system with respect to the nuclear coordinates. Still, the solution of the electronic problem remains a formidable task to achieve. An efficient approach to tackle it is to use DFT [11]. Within this approach, the focus is shifted from the determination of the many-body wave function, that depends on $3N$ variables to that of the total electronic density of the system $n(r)$, a more easily accessible quantity, depending just on the three space variables. This is made possible by the Kohenberg-Kohn theorem that proves that there is a one-to-one correspondence between $n(r)$ and $v_{ext}(r)$, the external potential in which electrons move and that completely specifies the problem. There are two other steps that make DFT applicable. The first is to consider an auxiliary system of non-interacting particles that has the same density $n(r)$ of the system under investigation. This allows to group the energy terms appearing in Schrödinger equation in a different way and to provide effective approximations (this being the second step) of unknown quantities that turn out to be small compared to the other terms. Local Density Approximation (LDA) is the mainly used one and it is based on locally describing the so-called exchange-correlation energy (a quantity that synthetizes all what is unknown in the auxiliary non-interacting system) by that of the homogeneous electron gas, an ideal model for which the exchange and correlation energies are known.

Using DFT to minimize the total energy of a system (by moving ions in the direction of the forces), it is possible to determine its lattice structure, Young’s modulus, Poisson’s ratio… It is also possible to determine if an hypothetical system has a chance to be realizable by investigating if its geometric structure is stable, which means that its energy is (at least) a local minima in the configuration space.

Further information can be obtained by calculating, on top of DFT, the vibrational spectrum of the system under exam. The collective excitations of atoms in a lattice (phonons) describe such vibrational spectrum and are at the basis of heat transport in a solid (together with the transport provided by electrons, when they are free to move, like in a metal). Phonons can be ab-initio calculated resorting to DFPT [12]. In this approach, phonon frequencies can be calculated using DFT in which a perturbing external potential (a distortion of the nuclear geometry) has been added. Interatomic force constants, obtained by differentiating the forces with respect to the nuclear coordinates, build a dynamical matrix whose diagonalization provides phonon frequency spectra.

In semiconductors heat current is mainly due to phonons, while the electronic contributions are usually smaller. Graphene and silicene are semimetals, which means they are at the border between metals and semiconductors. It is therefore possible to restrict the calculation of the thermal conductance to its phonon contribution. This contribution can be calculated by means of the Landauer formula [13]:

$$
\sigma = \frac{1}{2\pi} \int \hbar \omega T_{ph}(\omega) \frac{\partial n_{BE}(\omega, T)}{\partial T} d\omega
$$

(1)

The knowledge of the phonon dispersion spectrum allows also evaluating the constant-volume specific heat of a solid. Finally, the thermoelectric figure of merit can be ab-initio calculated [14]:

$$
ZT = \frac{S^2GT}{\kappa}
$$

(2)
3. Results

Infinite 2D sheets of graphene, silicene and silicon carbide have been simulated by DFT, in a periodic boundary conditions scheme, with a plane-wave pseudopotential code [15]. The resulting phonon spectra along high-symmetry directions, together with the relative density of states, are reported in Fig. 1a-f.

Fig. 1. Phonon dispersion and corresponding density of states in graphene (a)-(b), silicene (c)-(d) and 2D SiC (e)-(f).
Phonon bands are labeled for graphene (in Fig. 1a), and similarly could be done for silicene and 2D silicon carbide, highlighting the three acoustic modes (longitudinal, LA, transverse TA and out of plane, ZA), where two adjacent atoms move in phase, and the optical modes (LO, TO, ZO) for which adjacent atoms move against each other (see Fig. 2 for a pictorial description of such vibrations in graphene).

![Vibration modes in graphene. Labels correspond to those in Fig. 1a.](image)

Although the geometric structure is essentially the same for the three materials, it is possible to appreciate how the modifications due to their chemical composition strongly modify the resulting phonon spectra. For example, in 2D silicon carbide, the different electronegativity of Si and C gives rise to an electric field in the crystal than can be detected by the different frequencies of LO and TO modes at $\Gamma$.

This different behavior reflects also in the density of states of the three materials. Since the phonon density of states gives a rough estimation of the phonon transmission function that, once integrated according to Eq. (1), provides the lattice contribution to the thermal conductivity, it is easy to expect large variations of thermal conductivities in the three situations. The accurate calculation of these quantities will be the subject of the continuation of this work.

4. Conclusions and perspectives

We presented a few of the ingredients that are necessary to calculate ab-initio the thermophysical parameters of a material. The power of this approach is in its ability to be predictive and in the possibility of simulating not yet realized materials. This allows going in the direction of designing a material by phonon engineering of their thermal properties. It is possible, for example, to hinder the phonon transmission by controlling the type of nanostructuring or through defects: this allows lowering the phonon contribution to thermal conductance and therefore to enhance its thermoelectric figure of merit $ZT$ (see Eq. (2)). In this particular application, where the optimization of correlated quantities is necessary, the use of nanostructures can be an effective way to overcome the limitations of existing bulk materials.

The limitations of ab-initio calculations of the type presented in this work are essentially related to the dimensions of the system to simulate: while DFT calculations can be performed on simulation cells of a few hundreds of atoms, DFPT ones are more expensive and can be performed at most for a few tens of atoms.

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