Thermoelectric properties of nanocarbons: Atomistic modeling

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We present a general atomistic ab initio-based modeling approach and numerical implementation for the calculation of thermoelectric properties of carbon nanomaterials. The approach is based on density functional theory calculations of electronic and vibrational properties in combination with quantum transport theory in the Green function formalism. It allows to calculate charge and heat transport, and therefore electrical conductance, thermopower (Seebeck coefficient), electron thermal conductance, phonon thermal conductance, and thermoelectric efficiency, i.e., figure of merit. We systematically investigated temperature, doping, and disorder dependence of the thermoelectric properties of the fundamental types of nanocarbons, such as graphene, metallic and semiconducting nanoribbons, as well as metallic and semiconducting nanotubes.

1 Introduction Electron transport in carbon nanostructures, such as graphene, carbon nanotubes, and graphene nanoribbons, is in focus of experimental and theoretical research since a few years now. However, it is important to notice that for applications also phonon transport is of central importance in low-dimensional systems. The ability of properly controlling the thermal properties could effectively enhance the device performance, tailored specifically to its application. In most electronic devices, high values of both electronic and phononic conductances are desired for better thermal management. On the other hand, suppressing the conduction of heat is required in order to have efficient energy conversion in thermoelectric materials.

Today, nanostructures open exciting new possibilities to tune electric and thermal properties of materials for specific applications. The controlled modification of phonon transport is often referred to as phononics, following the notation of electronics for its electronic counterpart. In particular, low-dimensional systems provide an easy access to thermal control by studying the effect of system geometry, edge structure, grain boundaries, hetero-structures, isotope or defect concentration, etc. The average phonon mean free path in the system is playing a central role in phonon engineering, as nanostructuring affects phonon transport only at length scales well below the mean free path. Phonon engineering is one of the promising pathways facing the numerous challenges related to limited energy supply. There is a driving demand in increasing the power efficiency, and supplementary to that the power regeneration from waste heat energy. The current thermoelectric materials exhibit relatively low efficiency, limiting the applicability of those materials. But theoretical predictions raise hope in the development of nanostructured low-dimensional materials with significantly higher thermoelectric figure of merits $ZT$ than usual bulk materials. In this case, usual material properties, like $ZT$, become size dependent and should be considered as system specific properties. In semiconductor materials, phonons dominantly contribute to heat transport and it has been shown that device dimensions strongly influence the thermal conduction [1]. For example, recently it has been observed that in silicon nanowires the phonon transmission can be reduced without significantly affecting electronic transport, which leads to an enhancement in the thermoelectric figure of merit $ZT$ by two orders of magnitude compared to its bulk value [2–4]. The scattering of phonons mainly happens at the disordered surface, leading to a decrease in thermal conduction, whereas electron transfer...
is maintained in bulk-like states. Evidently, the dimensionality of the system is influencing its thermoelectric properties, with system size and surface-to-volume ratio as parameters to control the transport. With this in mind, carbon allotropes with its low dimensionality and exceptional structure sizes like one atom thickness in graphene and nanoribbons depict a particular interesting candidate. Accordingly, there is a growing interest in the research area of phononic energy transport in carbon-based materials and engaging results have already been achieved. For example, it was shown that thermal conductance of multi-walled nanotubes can be tuned by sliding the inner shell inside the outer shell [5]. Disorder-induced localization is believed to be a possible explanation of the exponential dependence of thermal resistance on the telescoping distance, while it is independent of the device length if the device is pristine. Real systems, on the other hand, always involve some degree of disorder, which can be modeled by a distribution in force constants. The effect of isotopic disorder on the thermal conduction of carbon nanotubes has been studied theoretically recently [6–8] and is in good agreement with experiment [9]. Other studies show a significant increase in $ZT$ due to the edge-effect in low-dimensional materials, such as random edge-disorder in zig-zag nanoribbons [10] or a well-defined bottom-up route for nanostuctured graphene nanoribbons [11]. Furthermore, studies on topological insulators reveal remarkable results, due to its low-dimensional edge states which effectively decouple electrons and phonons, coinciding with excellent electronic transport properties, unveiling a large thermopower while maintaining high mobility, tuneable by system size [12, 13].

In this article, we will summarize previous findings related to thermo-electric properties in nanocarbons and present briefly the conceptual framework for the computation of electron, phonon, and thermoelectric characteristics. The next section, Section 2, gives an introduction to the theory necessary for charge and heat transport calculation as well as definitions of certain characteristic properties. This summary is rather a guideline to the interested reader than an exhaustive handbook. For further details, we refer to the appropriate literature. Subsequently, findings for thermoelectric properties are presented. Section 3 focusses on pristine carbon nanostuctures, while in Section 4 the effect of vacancy defects is discussed. The last section, Section 5, considers the case of polycrystallinity in graphene, carbon nanotubes, and ribbons, before we summarize and conclude.

2 Theoretical models and methods Let us briefly introduce the computational approach used throughout this work. The transport calculations are based on Landauer theory [14] and the atomistic Green function formalism, which can be formulated equivalently for electrons and phonons. Obtaining both transmission characteristics is crucial in understanding electric and thermal properties.

As it is common in transport calculations, we apply the partitioning scheme and divide the system into left electrode (L), center (C), also denoted as scattering region, and right electrode (R), see Fig. 1. Left and right electrodes are considered to be in equilibrium, but with different electrical potentials $\varphi_L$ and $\varphi_R$, as well as different temperatures $T_L$ and $T_R$. Any effect of disorder or defects is included in the central scattering region, where as the electrodes are considered as ideal and infinite. Several quantities, like the Hamiltonian, of this three-partitioned system can then be written as

$$\hat{H} = \begin{pmatrix} ... & \hat{H}_L & \hat{H}_{LL} & \hat{H}_{L} & \hat{H}_{L} & \hat{H}_C & \hat{H}_{CR} & \hat{H}_R & \hat{H}_{RR} & \hat{H}_R \end{pmatrix}$$

(1)

2.1 Green function formalism We calculate the transport properties with an atomistic approach and employ nonequilibrium Green functions within the Landauer formalism. Combined with a decimation technique to account for the contacts, we obtain the transmission functions $T_{el}(\omega)$ and $T_{el}(E)$ for phonons and electrons, respectively. We refer the reader to appropriate literature, like in Refs. [15–19], for details of the Green function technique. In this work, we neglect electron–phonon coupling since the electron–phonon mean free path in nanoscale carbon tubes and ribbons succeeds tens of $\mu$m, even at room temperature [20].

2.1.1 Electron transport The electron transmission function $T_{el}$ is defined as

$$T_{el}(E) = \text{Tr} \left( \hat{T}_L(E) \hat{G}_C^R(E) \hat{T}_R(E) \hat{G}_C^L(E) \right),$$

(2)

where the matrix Green functions in the central region $\hat{G}_C$ and level-width functions $\hat{T}$ are determined by the Hamiltonian and overlap matrix of the central region $\hat{H}_C$, $\hat{S}_C$, and the contact self-energies $\hat{\Sigma}_i$

$$\hat{G}_C^R(E) = \left( (E + i\delta)^{-1} \hat{S}_C - \hat{H}_C - \hat{\Sigma}_C - \hat{\Sigma}_R \right)^{-1}$$

(3)

$$\hat{T}_{i=LR} = i \left( \hat{\Sigma}_i^R - \hat{\Sigma}_i^A \right) = -2\text{Im} \hat{\Sigma}_i^R.$$
As we use a tight-binding model, all Green functions are matrices in an atomic basis obtained from density functional tight-binding (DFTB) Hamiltonians. Due to the highly covalent nature of nanocarbons, DFTB as a tight-binding method is well suited and provides an efficient and consistent approach to electronic and phononic properties. In the framework of DFTB, the Kohn–Sham equations are rewritten in a basis of compressed atomic orbitals, which allows a Slater-Koster parameterization of overlap and Hamiltonian matrix elements. This computationally efficient method allows the self-consistent charge (SCC) calculation of the Hamiltonian for large systems. The Hamiltonian is then partitioned to extract \( \hat{H}_C \) and the electrode matrices for the self-energies.

The self-energy \( \Sigma \) describes the effect of the leads on the scattering region and provides a way to truncate the otherwise infinite-dimensional Hamiltonian matrix by folding the leads into the center, such that only the interfaces of the device are affected. They are calculated from the surface Green functions \( \hat{G}_S \) of the leads by using the following equation:

\[
\Sigma_{\nu L/R} = \left[ (E + i0^+) \hat{S}_C - \hat{H}_C \right] \hat{G}_S \left[ (E + i0^+) \hat{S}_C - \hat{H}_C \right].
\]

The most common approach to calculate the surface Green function \( \hat{G}_S \), which is the Green function of the isolated lead projected on the surface layer, is the iterative renormalization-decimation technique developed by López-Sancho et al. [21, 22].

### 2.1.2 Phonon transport

The treatment of phonon transport can be formulated methodologically in the same way as the electronic part. The phonon transmission function is then obtained by the atomistic single-particle Green function method [23–32], which is equivalent to the Meir–Wingreen method for electron transport [33]. \( T_{\text{ph}}(\omega) \) is determined by the matrix-retarded phonon Green function in the central region \( \hat{D}_C(\omega) \) and the phonon level-width functions \( \hat{\Gamma}_{\text{ph}} \) of left and right electrodes:

\[
T_{\text{ph}}(\omega) = \text{Tr} \left[ \hat{D}_C(\omega) \hat{\Gamma}_{\text{ph}}(\omega) \hat{D}_C(\omega) \right].
\]

The retarded Green functions of the isolated subsystems \( \alpha \), i.e., in absence of coupling between the central system and the electrodes, are defined as

\[
D^{(0)}(\omega) = \left[ (\omega + i0^+) \hat{\Sigma} - \hat{K}^{(0)} \right]^{-1},
\]

with the identity matrix \( \hat{\Sigma} \) and the mass-renormalized force constant matrix

\[
K^{(0)}_{ij} = k^{(0)}_{ij} / \sqrt{m_i m_j}.
\]

The matrix elements \( k^{(0)}_{ij} \) of the force constant matrix describe the coupling of the \( i \)-th degree of freedom in subsystem \( \alpha \) with the \( j \)-th degree of freedom in \( \beta \).

The retarded phonon Green function of the central region in the presence of electrodes reads

\[
\hat{D}_C(\omega) = \left[ (\omega + i0^+) \hat{T} - \hat{K}^{(0)} - \hat{\Pi}_L(\omega) - \hat{\Pi}_R(\omega) \right]^{-1},
\]

where the polarization operator, or phonon self-energy, due to coupling to the reservoir \( \alpha \) is

\[
\hat{\Pi}_\alpha(\omega) = \hat{K}^{(0)} D^{(0)}(\omega) \hat{K}^{(0)}. \tag{9}
\]

Here, the matrix inversion from Eq. (7) cannot be applied directly for the infinite dimensional matrices of the semi-infinite electrodes, which is overcome (equivalent to the electron case discussed above) by calculating the surface Green functions \( D^{(0)}(\omega) \) numerically using the iterative method [21, 22].

Finally, the level-width function is determined by the phonon self energies following the relation

\[
\hat{\Gamma}_{\text{ph}}^{(0)}(\omega) = i \left( \hat{\Pi}_L(\omega) - \hat{\Pi}_R(\omega) \right).
\]

The calculation of the force constant matrix can be quite demanding for large configurations because it involves \( 3N \) force calculations on the whole system (where \( N \) is total number of atoms). For this finite atomic displacement approach, the efficient DFTB framework can be used, where each atom is infinitesimally shifted in all spatial dimensions and the resulting forces on all atoms are calculated. The result is equal to the Hessian matrix of the lattice potential energy with respect to spatial displacements,

\[
k^{(0)}_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}, \tag{11}
\]

Diagonal values \( k^{(0)}_{ii} \) are obtained from the acoustic sum-rule

\[
\sum_{\nu} k^{(0)}_{\nu \nu} = 0.
\]

The here applied ballistic transport model neglects phonon–phonon and electron–phonon interactions, but the high intrinsic mean free paths for electrons and phonons at room temperature in carbon systems [34] validate this approximation. Furthermore, the model is superior to classical molecular dynamics approaches for thermal transport, as they lack quantum features like Bose–Einstein statistics. The high Debye temperature of about 2100 K in graphene systems [34] necessitates quantum calculations.

In the following, results are presented for temperatures up to 900 K. Technically, the standard argument of large mean free paths in the order of 100 nm to 1 \( \mu \)m for graphene-based systems holds for room temperature and below. However, we expect the ballistic approximation is still valid for temperatures well beyond 300 K for those systems. In the case of graphene, thermoelectric applications often involve dispersions of graphene flakes with sizes in the low nanometer range. Similarly, the characteristic grain sizes in polycrystalline nanocarbons are a few nanometers as well, which in turn legitimates the use of our approximation.
2.2 Electric properties The electron current is given by the Landauer formula

\[ I = \frac{e}{\hbar} \int_{-\infty}^{\infty} dE \, T_{el}(E, V) \cdot \left[ f_f(E - e\varphi_L, T_L) - f_f(E - e\varphi_R, T_R) \right], \]

where \( f_f(E, T) \), the Fermi–Dirac distribution, is the electron distribution function in the electrodes and \( T_{el} \) is the transmission function. From Landauer formula at small \( \Delta T \), \( e\Delta V \ll \Delta T \) the electrical conductance is given as

\[ G = \frac{2e^2}{\hbar} \int_{-\infty}^{\infty} dE \, T_{el}(E) \left( -\frac{df_f(E, T)}{dE} \right). \]  

2.3 Thermal properties For a shorthand notation for several properties, we introduce the Onsager coefficients

\[ L_{\alpha}(T) = \int_{-\infty}^{\infty} dE \, (E - E_{F})^{n} \left( -\frac{df_f(E, T)}{dE} \right) T_{el}(E), \]  

with \( n \in \mathbb{N}_0 \) and Fermi energy \( E_F \).

The heat flux

\[ Q = \kappa \Delta T = (\kappa_{el} + \kappa_{ph})(T_L - T_R) \]  

is determined by the temperature difference \( \Delta T \) and thermal conductance \( \kappa \), which can be split into electron thermal conductance \( \kappa_{el} \) and phonon thermal conductance \( \kappa_{ph} \):

\[ \kappa = \frac{2}{\hbar k_B T^2} \left( L_2 - \frac{L_1^2}{L_0} \right) + \int_{0}^{\infty} \frac{d\omega}{2\pi} \hbar \omega \frac{\partial f_{ph}(\omega, T)}{\partial T} T_{ph}(\omega), \]

Phonon heat transport in mesoscopic systems at low enough temperatures (lower than the Debye temperature \( T_D \), which is about 2100 K in graphene and is of the order of 1000 K in CNTs) is essentially quantum and at \( T \ll T_D \) the heat flow is determined by coherent transport of noninteracting phonons. In this case, the Landauer approach can be used. The thermal conductance in the limit of small temperature difference \( dT = T_L - T_R \) is defined as

\[ \kappa_{ph}(T) = \int_{0}^{\infty} \frac{d\omega}{2\pi} \hbar \omega \frac{\partial f_{ph}(\omega, T)}{\partial T} T_{ph}(\omega), \]

with the phonon transmission function \( T_{ph}(\omega) \), the Bose distribution \( f_{ph} \), the phonon frequency \( \omega \), and temperature \( T \) [35–37].

2.4 Thermoelectric properties The Seebeck coefficient \( S \), or thermopower, is the coefficient relating a temperature difference to the generated voltage (measured at zero current condition).

\[ V = -S\Delta T. \]  

The voltage is commonly defined as \( V = \varphi_L - \varphi_R \), and the temperature difference is given by \( \Delta T = T_L - T_R \). The sign convention in the formula for \( S \) implies positive values for \( S \) in the case that the voltage gradient points against the temperature gradient, and vice versa.

From Landauer formula at small \( \Delta T, e\Delta V \ll \Delta T \), we get the thermopower in the quantum limit, known as the Cutler–Mott formula [38]:

\[ S = \frac{1}{eT} \int_{-\infty}^{\infty} dE \, T_{el}(E) (E - E_F) \left( -\frac{df_f(E, T)}{dE} \right). \]

This representation for \( S \) shows clearly, that in order to generate a voltage from the temperature gradient, an asymmetry of the electron distribution around the Fermi level is required. Furthermore, the sign of \( S \) indicates the majority charge carrier, which are electrons for \( S < 0 \) and holes for \( S > 0 \). For off-resonant transport at \( T \ll E_F \) in the zero temperature limit, the thermopower \( S \) can be estimated using the Sommerfeld expansion:

\[ S \approx \frac{\pi^2 k_B^2 T}{3e} \left. \frac{d \ln(T_{el}(E))}{dE} \right|_{E=E_F}. \]

The Onsager coefficients \( L_{\alpha} \) introduced earlier in Eq. (13) allow a much shorter expression for \( S \):

\[ S(T) = -\frac{1}{eT} \frac{L_1}{L_0}. \]

The conversion efficiency of a thermoelectric device for electricity generation (\( \eta \)) is given by

\[ \eta = \frac{\text{energy provided to the load}}{\text{heat energy absorbed at hot junction}}. \]

The (maximum) efficiency at \( \Delta T \ll T \) can be represented as

\[ \eta = \frac{\Delta T}{T} \frac{\sqrt{1 + \Delta T} - 1}{\sqrt{1 + \Delta T} + 1}, \]

which is related to the quantity \( ZT \), which is called the (thermoelectric) figure of merit and defined as follows:

\[ ZT = \frac{G}{k} S^2 T. \]

Here, \( G \) is the electrical conductance and \( k = \kappa_{el} + \kappa_{ph} \) the thermal conductance. It reveals that the key strategy to
improve the thermoelectric effect in materials is to decouple electronic and thermal terms, i.e., increasing the electrical conductance and thermopower while reducing thermal conductance. Using the Onsager coefficients introduced above, one can derive an alternative expression often used in numerical implementations:

$$ZT = \frac{1}{(L_o L_2/L_1^2) - \frac{1}{\kappa_{el}}}.$$  \hfill (22)

3 Pristine nanocarbons

First of all, we present results on electron and thermal transport in pristine nanocarbon structures without defects. Specifically, the dependence of the Seebeck effect on temperature (from 100 to 900 K) and on gate voltage or doping in those systems. For the latter, the results are represented as a function of the effective Fermi level position (\(eV_G\)) which can be changed by applying a gate voltage \(V_G\) or by doping realized using atom substitution or chemical functionalization. For simplicity, we refer to all of the described Fermi level shifting events as doping.

We show that the doping dependence plays an important role in nanocarbons, which is different from classical materials. Initially the Seebeck coefficient of undoped structures is very small because of electron–hole symmetry, but the doping-introduced asymmetry significantly boosts the thermopower. Our results confirm the high values of Seebeck coefficient in doped pristine graphene and metallic nanocarbons of up to 0.1 mV K\(^{-1}\), see Fig. 2 (top) and even larger values in semiconductor CNTs of up to 2 mV K\(^{-1}\), Fig. 3 (top). Furthermore, results on heat transport, i.e., the calculated thermal conductivity of an infinite graphene sheet and thermal conductance of a semiconductor (7, 0)-CNT are shown in Figs. 2 and 3 (center). These figures show that for thermal conduction, the lattice dominates the electronic part at small dopings by over three orders of magnitude. However, at large doping levels, the electronic contribution can surpass the phononic part at least for low temperatures. Combined with the electrical properties of the system, we obtain the thermoelectric figure of merit \(ZT\), see Figs. 2 and 3 (bottom). The doping dependencies of \(S\) and \(ZT\) appear symmetric with respect to the sign of Fermi level shift due to the symmetry of the electron transmission spectrum in the pristine system. Accordingly, a slight asymmetry in the CNTs spectrum gives rise to slightly asymmetric \(S\) and \(ZT\). The analysis draws the conclusion that both Seebeck coefficient and figure of merit are much larger for semiconductor nanocarbons than for metallic ones, including graphene, when large doping is considered.

However, the doping effect required to achieve high thermoelectric parameters is certainly difficult to realize in real materials. For this reason, we further investigated the effect of defects in the following section. First, we focus on vacancies [39] and subsequently on grain boundaries [40] because these types of defects are always present in synthesized nanocarbon materials and their concentration can be artificially tuned with special treatment at the stage of production (growth) as well as by different types of post-processing methods.

4 Defected nanocarbons with vacancies

For the study on carbon nanostructures with vacancy defects, we chose as our system setup a long and narrow graphene nanoribbon with dimensions of approximately 11 nm in width and 220 nm in length. The nanoribbon is of armchair-edge type and displays metallic behavior in the defect-free case. Metallic wide-band leads have been modeled as contacts to the high aspect ratio ribbon in a side-contacted
configuration, with contact lengths of about 3.3 nm at each end. This contact-ribbon overlap is large enough to rule out any length-dependent contact effects. Several defect types, such as Stone–Wales, single vacancies, and double vacancies, were included and randomly distributed. Together with a random orientation, it accounts for a nonideal, realistic geometry (see Fig. 4). The contact areas remain undefected and can be described by a repeating unit cell. In contrast to the single/double vacancies, the Stone–Wales defect is actually not a vacancy defect, but a 90°-rotated carbon–carbon bonds producing two pentagon-heptagon pairs. However, as it has been often identified in TEM images [41], we included it here. For the double vacancies, there exist three different typical configurations: V₂(5–8–5), V₂(555–777), and V₂(5555–6–7777), all emerging from each other by bond rotation. As experimental values for the concentrations of the individual defect types are still missing, we use equal probabilities for all varieties.

Furthermore, we apply a modular approach. Using various kinds of small and equally-sized graphene patches, which include one of the defect types described above (see Fig. 5), we construct a large, high aspect ratio ribbon. This technique based on small blocks allowed us to investigate defected structures very large in dimension, lifting the constrain by computationally expensive geometry optimizations. The small graphene patches have been obtained from geometry optimizations after incorporating one of the above-mentioned defect types, while fixing the boundaries to maintain appropriate boundary conditions to allow for seamless segment joining. The patch size has been chosen large enough that those boundary conditions do not perturb the defect geometry. The relaxed defect structures strongly resemble those found in TEM images [41], validating the structural results. Finally, nearly 1000 of randomly selected fragments, pure and defected, were used to construct the system of about 220 nm in length. The influence of edge vacancies has not been studied in particular, but edge effects do not play any significant role in AGNRs compared to ZGNRs. Further it has been shown, that in AGNRs transmission is nearly independent by the depth of edge defects [42], verifying the validity of our approach.

To investigate the electronic transport properties of this very large system in the quantum coherent regime, we mapped, different to the approach used before, the structure...
The six various types of building blocks, which were used to construct a large defected GNR: (a) pure, (b) single vacancy $V_1(5–9)$, (c) Stone–Wales $SW(55–77)$, (d) double vacancy $V_2(5–8–5)$, (e) double vacancy $V_2(555–777)$, (f) double vacancy $V_2(5555–6–7777)$. Additionally, all possible defect orientations have been considered. [39]

to an one-orbital tight-binding Hamiltonian to describe non-interacting $\sigma$-electrons, considering only nearest-neighbor hopping:

$$H = \varepsilon_0 \sum_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t(|r_{ij}|) c_i^\dagger c_j. \quad (23)$$

Here $\varepsilon_0$ is the on-site energy, which gives only an energy offset and thus can be set to zero, $c_i$ and $c_i^\dagger$ are the creation and annihilation operators for an electron in the $p_z$ orbital centered on the $i$-th carbon atom, and $\langle i, j \rangle$ indicates all pairs of nearest neighbors. We assume a distance-dependent hopping parameter $t$ with an exponential decay [43]

$$t(|r_{ij}|) = t_0 \exp \left( -3.37 \left( \frac{|r_{ij}|}{a} - 1 \right) \right), \quad (24)$$

where $|r_{ij}|$ is the distance between two neighboring atoms, $a = 1.428$ Å the equilibrium carbon–carbon bond length, and $t_0 = 2.7$ eV the hopping in equilibrated graphene [44]. In an atomic basis, $\hat{H}$ becomes a block-tridiagonal matrix and the standard lead-system–lead tri-partitioning scheme can be applied. A nearest-neighbor approximation has been chosen for simplicity and is found to describe low energy properties good enough for many applications.

The introduced defects, which act as scattering sites, have a strong impact on the electron transmission spectrum for nanocarbons. As an example, we present the effect of a defect concentration of 0.02%, number of vacancies relative to total atom number, for which the electron transmission function is shown in Fig. 6 (top). The data shown here have been averaged over data sets of over 20 equivalent samples to avoid artifacts and smoothen the spectra. The electron transport is significantly suppressed and near the undoped Fermi level, we observe the formation of a quasi-gap. This should not be confused with an actual spectral energy gap, but still relates to an energy gap in electron transmission. Most importantly, the electron transmission function became highly asymmetric around the undoped Fermi level. This results in the desired growth of the previously very small Seebeck coefficient even at low doping, see Fig. 6 (bottom), reaching values of up to 0.2 mV K$^{-1}$. The oscillatory behavior of $S$ in the low-temperature regime reflects the rough, unsteady behavior of the transmission spectrum, but gets smoothed out for higher temperatures. Regarding the defect concentration, we observed a reciprocal scaling behavior of the electron conductance with defect concentration. This is no surprise, as more vacancies introduce more scattering sites and lead to increasing localization, but it is a reminder that in order to achieve the best thermoelectric performance of the given structure the defect concentration has to be set at an optimum level.

**5 Polycrystalline nanocarbons** Grain boundaries (GB) are commonly observed in carbon nanostructures, but
their influence on thermal and electronic properties has not been studied until recently [40]. Polycrystallinity is an inherent structural impurity and very challenging to avoid, as it is caused by growth kinetics or substrate imperfections, resulting in different graphene domains with a variety of crystallographic orientations. In this section, quantum transport and thermoelectric properties are summarized for graphene sheets, graphene nanoribbons, and carbon nanotubes with a variety of grain boundary types in a large temperature range. Motivated by previous findings that disorder scatters phonons more effectively than electrons, a significant improvement in the thermoelectric performance for polycrystalline systems is expected. While the effect depends only marginally on the grain boundary type, grain boundaries are a viable tool to greatly enhance the thermoelectric figure of merit, paving the way for the design of new thermoelectric materials. The polycrystalline nanostructures in this study have been constructed by joining two subsystems of different chiralities or crystal orientations. Based on those initial geometries, the minimum energy configurations of the structures were then determined using molecular dynamics simulation followed by density functional geometry optimization until the force convergence criterium of 0.02 eV˚A was met. Hydrogen saturation of eventually di-coordinated carbons was neglected. In our analysis, the variety of GBs in graphene is limited by the need for a reasonable periodicity along the interface, otherwise the system size gets too large for ab initio calculations. This limitation is not apparent in the quasi-1D systems of GNRs and CNTs, but the choice of diverse chiralities is restricted by roughly matching the CNT diameters. This section is devoted only on the impact of grain boundaries on charge and head transport and did not study any doping or gating effects.

### 5.1 Graphene

We apply a common approximation of polycrystalline graphene by approximating the grain boundaries as linear periodic arrays of dislocations [45]. Grain boundaries in graphene can be classified in two distinct cases. Naturally, a mixture of all possible types is observed in real samples, but due to their distinct behavior we discuss them separately. The classification proposed by Yazyev et al. [46] separates them into two classes corresponding to their matching vectors \((n_1, m_1)\) and \((n_R, m_R)\). If exactly one matching vector fulfills the criterion \((n \cdot m) = 3q (q \in \mathbb{Z})\), the GB is of class-II type. Otherwise, it belongs to class-I. Due to a misalignment of allowed momentum-energy manifolds, class-II type boundaries introduce a transport gap, which can be approximated by \(E_G = \hbar v_F / 3d = \frac{1.38 \text{ eV}}{d \text{ nm}}\), solely depending on the periodicity \(d\) [46]. The distinct behavior of both classes can be explained by transverse momentum conservation at the interface and an effective rotation of the Brillouin zone for the charge carriers passing the interface. We concentrate on two examples, one symmetric (class-I) and one asymmetric (class-II) GB, see Fig. 7 (top). For reference, the properties of an unperturbed graphene sheet are calculated. As expected, the asymmetric class-II GB exhibits an energy gap of about 1 eV, whereas the transmission spectrum of the symmetric class-I GB in Fig. 8 A(i) is very similar to the pristine sheet. Phonon transmission shows a weak dependence on the GB type, but a slightly stronger phonon scattering can be identified for class-II GB with differences most pronounced at very low (<200 cm\(^{-1}\)) and high phonon energies (>1000 cm\(^{-1}\)), see Fig. 8 A(ii). This can be attributed to a stronger lattice deformation and buckling along the interface. The introduced asymmetry of electron and hole transmission leads to a separation of charge carriers, improving the thermopower \(S\) in those systems over ideal graphene. Electron holes account for the Seebeck effect in class-II GBs, and therefore \(S > 0\), and give rise to an improved thermopower compared to the electron-dominated symmetric GBs. For the thermoelectric figure of merit \(ZT\), an enhancement by over three orders of magnitude in Fig. 8 A(iv) is expected above
5.2 Graphene nanoribbons As the gapless nature of graphene has negative effects on its thermoelectric properties, spatial confinement leads to an intrinsic band gap which depends on size and edge structure. By parallel cutting polycrystalline graphene sheets into ribbons, one expects structures similar to those shown in Fig. 7 (center), i.e., at least two graphene nanoribbons of different crystallographic orientation with a GB at the interface. Compared to graphene sheets, those structures omit periodicity parallel to the interface and reveal hydrogen termination at the edges to saturate dangling bonds and to remove particular edge state effects. The interface in between constitutes of an array of dislocations, either pentagons, heptagons, or octagons. For one side of the sys-

Figure 8 Calculated electron transmission (i) and phonon transmission (ii) at room temperature, as well as the Seebeck coefficient (iii), and thermoelectric figure of merit (iv) as a function of temperature for graphene (A), graphene nanoribbons (B), and carbon nanotubes (C) with different GB types, see Fig. 7. Black curves represent the monocrystalline system for reference.
system, an about 1.7 nm wide armchair GNR with 15 dimer lines in width was chosen. The ribbon across is rotated respectively by an angle $\Theta$, ranging from 11° to 24°. The angles are chosen in a way that the periodic supercell of the lead does not get unnecessarily large. By cutting the ribbon to the same width as the right part, one produces irregular but periodic edge geometries. As a reference, the results for the unperturbed armchair ribbon are shown and, like all armchair-terminated ribbons, it is semiconducting with a band gap of about 0.5 eV. As shown in Fig. 8 B(i), the suppression of electron transmission is strongest in GNR1, which may be explained by the noninterrupted dislocation array, compared to the other configurations GNR2 and GNR3, where one hexagon in the interface is preserved. One also notices the electron–hole symmetry breaking, with an improved transmission for low-energy electrons compared to respective holes. Interestingly, the effect of different GBs is not apparent in the thermal conductance. As expected, phonons get scattered at the interface, effectively lowering the transmission by roughly 50%, but the spectrum is mainly independent on the exact geometry, see Fig. 8 B(ii). This results in about one-tenth of the thermal conductance of an ideal ribbon. Effects on the electronic and thermal properties combined give rise to a significantly improved thermoelectric figure of merit, shown in Fig. 8 B(iv).

At room temperature, we calculated an increase by three to four orders of magnitude, topping at around $\Phi \approx 0.1$ for GNR3 at 700 K. The zero in the $\Phi$ graph of GNR3 can be associated to a change of the majority charge carrier type from holes to electrons with increasing temperature, implying a sign change of the Seebeck coefficient $S$ at 210 K. In fact, $S$ is negative with values around $S \approx -0.4 \text{ mV}^{-1}$ for all configurations, in contrast to $S > 0$ in the ideal GNR. Those findings are particularly promising as all three samples show the same qualitative performance suggesting a robust and efficient method for enhancing the thermoelectric effect.

### 5.3 Carbon nanotubes

Next to the planar carbon structures, their rolled-up form is equally promising and the electric and thermal properties of carbon nanotube heterojunctions are presented in the following. Carbon nanotubes of different chirality but similar diameter can form a junction by exhibiting a couple of dislocation defects, see Fig. 7 (bottom). Such structures evolve if two individual tubes eventually grow together, or by a change in the growth parameters [47–50]. First interest in application of intra molecular nanotube junctions is the use as heterojunction diodes [51]. We studied four different CNT heterojunctions, each of them with a diameter of about 0.55 nm. In all samples one part is made of a (7,0)-CNT, the as discussed in Section 3, which is complemented by a second CNT with aligned tube axis, see Fig. 7 (bottom). Kinked carbon nanotube junctions were not considered here. Notice, that the structure CNT3 shows no chirality change, but a twist around the tube axis. The twisting angle is given by (or multiples of) $\phi = \frac{2\pi}{7} \approx 12.8^\circ$ due to the sevenfold symmetry. This twist deforms the lattice and increases stress at the interface, but does not lead to defect formation or reconstruction. In the remaining three structures CNT1, CNT2, and CNT4, the chirality indices (5,3), (4,4), and (6,1) have been chosen, all yielding a diameter close to its counterpart of 0.55 nm. Primarily, one observes pentagon–heptagon pairs along the circumference, and one octagon in CNT2. The properties of the ideal and semiconducting (7,0)-CNT are calculated as a reference. Figure 8 C(i) shows the energy gap in the electron transmission appearing in all of the different heterojunctions. Most notably, the twisted carbon nanotube, CNT3, shows only little change in the electron transmission where the slight lattice perturbations smear out the perfect transmission steps of an ideal nanotube. Electrons in CNT1 and CNT4 are suppressed equally and transmission is roughly cut in half. The heterojunction in CNT2 shows the strongest scattering of electrons, effectively lowering electron conductance. We attribute this to the strong deformation caused by the octagon defect. A similar picture can be drawn for phonon transport, see Fig. 8 C(ii). As no defects are formed in CNT3, lattice vibrations are weakly affected and scattering happens only for high-frequency phonons. But for heterojunctions of different chiralities, phonon transmission gets significantly suppressed at all frequencies. Interestingly, CNT4 with only one defect pair is superior to structure CNT1 in blocking phonons and the defect configuration in CNT2 scatters strongest. Consequently, thermal conductance is decreased up to a factor of five for the CNT2 structures compared to the ideal nanotube. Quantitatively, this is very similar to the case of GNRs discussed above. In terms of figure of merit, the thermoelectric properties can be significantly improved but strongly depend on the exact structure, see Fig. 8 C(iv). At room temperature, a gain in calculated $\Phi$ as high as two orders of magnitude for the structures CNT1 and CNT2 can be reported. Note that the twisted structure without chirality change, CNT3, shows a decreased $\Phi$ by a factor of 10. This is due to the loss of electron–hole asymmetry as the slight distortions smear out the sharp band edges. Thereby, the Seebeck effect is strongly reduced. With the right choice of CNT chiralities, the Seebeck effect can be increased to values around $|S| \approx 0.6 \text{ mV}^{-1}$ for a broad temperature range and a substantial enhancement of $\Phi$ is expected.

### 6 Conclusions

A material with high thermoelectric efficiency has to show properties of an electron crystal and phonon glass at the same time, i.e., blocking thermal transport while maintaining electric current. This idea of an ideal thermoelectric material, yet easily formulated, has proven to be a difficult feat. In pursuit for high-$\Phi$ materials, specifically tailored low-dimensional structures at the nanoscale show promising results. On the other hand, for large-scale power generation applications, bulk-like materials are considered to be indispensable because of very poor power factors in nanoscale systems. Consequently, a close packing of low-dimensional nanostructures in 3D volumes to profit from the advantages of both worlds, i.e., high $\Phi$ and power factor [52]. This approach should find its application for carbon nanostructures and favors the use of flat ribbons over nanotubes due to its higher packing density.
The aim of this mini review is to summarize an efficient and \textit{ab initio}-based approach to charge and heat transport and present some applications in the field of nanocarbon phonon engineering. While electron transport calculations are omnipresent nowadays, its phononic counterpart is still trailing behind, although both can be formulated equivalently in the very same framework. The findings on thermoelectric properties in carbon nanostructures presented here show the opportunities of computational materials science in the quest for higher conversion efficiencies.

For example, our results demonstrate that lattice imperfections like vacancies or interfaces of two carbon systems with different crystallographic orientations, scatter phonons stronger than charge carriers. In polycrystalline carbon structures, the odd-membered rings at the boundary break the bipartite symmetry of the lattice resulting in an electron-hole asymmetry in the electron transmission spectrum. This charge carrier separation is advantageous for the thermoelectric effect, increasing the thermopower. This, combined with suppressed thermal transport due to phonon scattering at atomic dislocations, in particular for mid- to high-energy phonons, generates a substantial improvement in the figure of merit. Our calculations further show that the right amount of doping, or deliberate introduction of impurities allow an enhancement of up to four orders of magnitude in $ZT$ at room temperature in all three carbon allotropes, i.e., graphene, GNRs, and CNTs. Conclusively, both approaches seem to be highly effective in boosting the thermoelectric performance by a factor of thousand and higher, relative to the ideal samples. The low sensitivity on those parameters heavily facilitates any experimental realization and opens up promising prospects for the use of phonon-engineered carbon nanostructures in thermoelectric applications.

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