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An Atomistic Study of the Thermoelectric Signatures of CNT **Peapods**

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ABSTRACT: Carbon-based nanomaterials such as carbon nanotubes (CNTs) have a great potential for applications in the development of high performance thermoelectric (TE) materials because of their low-cost and for being environmentally friendly. Pristine nanotubes have, however, high electrical and thermal conductivities so that further nanoscale engineering is required to exploit them as TE materials. We investigate electron and phonon transport in CNT peapods to elucidate their potential advantage over pristine CNTs as basic TE elements. We show that the electron and phonon transport properties are sensitively modified by C_{60} encapsulation, when the $CNT-C_{60}$ intermolecular interaction is strong enough to produce a periodic buckling of the CNT walls. Moreover, the phonon transmission is strongly suppressed at low and



high frequencies, leading to a reduction of the phonon contribution to the overall thermal conductance. A similar effect has also been observed in the recently proposed phononic metamaterials. We obtain in general a larger TE figure of merit over a broad temperature range for the CNT peapod when compared with the pristine CNT, achieving an increase by a factor of 2.2 at 575 K. Our findings show an alternative route for the enhancement of the TE performance of CNT-based devices.

INTRODUCTION

Thermoelectric (TE) materials convert electrical energy into thermal energy and vice versa, which makes them highly attractive for a wide range of applications in various fields. This is especially the case in the search for new energy solutions as well as in the optimization of energy consumption and generation by the production of electrical power using wasted heat.² Besides this energy related aspect, TE materials possess other advantages such as being acoustically silent, lightweight, and environmentally friendly (depending of the underlying material class) and not requiring a mechanical system for their work cycle.^{3,4} Despite their great potential for an efficient energy management, there are still fundamental challenges regarding the optimization of the efficiency of TE materials. It is common to gauge it via the so-called figure of merit (ZT), a dimensionless parameter defined as⁵

$$ZT = \frac{GS^2T}{\kappa}$$
(1)

ZT involves three basic material parameters determining the efficiency of the energy conversion process: the Seebeck coefficient S, the electrical conductance G, and the thermal conductance $\kappa = \kappa_{el} + \kappa_{ph}$, the latter including both electronic $(\kappa_{\rm el})$ and phononic $(\kappa_{\rm ph})$ components. T is the absolute temperature.

Enhancing ZT implies increasing the Seebeck coefficient and the electrical conductance while minimizing the thermal conductance, reaching ideally the limit of an electron-crystal and a phonon-glass.⁶ In contrast to other efficiency measures such as the Carnot efficiency, which are bounded from above, the figure of merit can in principle become arbitrarily high. This is, however, in practical applications a very difficult issue, and values of order 1-3 are already considered as a record.⁷ In macroscopic systems, increasing ZT is a challenging task due to the Wiedemann-Franz law in metals,⁸ which correlates the electrical and thermal conductivities, or to the fact that the phonon contribution in semiconducting materials cannot be neglected and, thus, negatively affects ZT. A route pursued in the past years has been the development of high performance TE materials by producing crystal structures based on heavy metals, like BiTe, in bulk or as layered materials.⁹ Even though ZT values about 1.5 were obtained, the toxicity of some of these elements as well as their scarce availability and high production costs demands to find alternative approaches for developing efficient TE materials. The seminal work by Hicks and Dresselhaus in 1993¹⁰ suggested for the first time that dimensionality reduction toward the nanoscale could open a fully new route to optimize ZT. They predicted that ZT of nanostructured materials could become higher than that of

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their bulk counterpart, since the electrical conductance can be enhanced due to quantum confinement effects, while the phononic thermal conductance can be reduced due to boundary scattering. A typical example is silicon nanowires, where the thermal conductance is largely reduced and the obtained ZT was \sim 1 at 200 K¹¹ and \sim 0.6 at 300 K.¹² Twodimensional (2D) materials have also been found to display better thermoelectric properties than those of their bulk phases.^{13–15} For instance, it is well-known that the thermoelectric properties of SnSe bulk are limited by its poor electrical conductance at room temperature. However, Zhao et al. reported a remarkably high ZT value of 2.6 (at 923 K) and of 2.2 (at 773 K) in p-type and n-type single-crystal SnSe, respectively.¹⁶ According to experimental results, bulk black phosphorus displays a high Seebeck coefficient of 335 μ V/K and its few-layer counterpart shows an increased Seebeck coefficient up to 510 μ V/K.¹⁷ The thermal conductance of few-layer black phosphorus can also be controlled by the structural anisotropy and film thickness, influencing the thermoelectric response.^{18–20} For novel transition metal dichalchogenides like MoS_{2} , a large thermoelectric power factor has been experimentally, but the in-plane phonon conductance is still relatively large due to the strong covalent bonding, yielding a quite low in-plane ZT.^{21,22} At the molecular scale, it has been predicted that molecular junctions, which have been extensively studied in the field of molecular electronics, may also act as efficient thermal and thermoelectric elements.²³ The real challenge here remains in taking advantage of the high electronic transport properties of these materials while reducing the phonon conductance using novel physical and chemical processes (e.g., structural modifications, doping, functionalization, defects, strain).^{19,24,25}

In this regard, carbon nanotubes (CNTs), quasi onedimensional structures obtained from rolling up a graphene layer, have been at the center of experimental and theoretical research for a few decades.^{26–28} CNTs display outstanding thermal and electrical properties, which depend on their chirality, and their properties can be tuned through diverse physical and chemical routes for specific applications.²⁹⁻³¹ For instance, different guest-species like ions and molecules can be encapsulated inside CNTs,³² a particular case being the socalled CNT peapods, where CNTs with appropriate diameters host fullerene molecules distributed along the nanotube axis. Several studies have addressed the properties of CNT peapods for getting an understanding of their electronic and optical properties, $^{33-35}$ but the effect of the fullerene molecules on the thermal properties is not yet fully elucidated. Early experimental investigations of the thermal conductance of C_{60} @CNT peapods (nanotube diameter not specified)³⁶ as well as classical molecular dynamics simulations of thermal transport in a C_{60} @CNT(10,10) system³⁷ have claimed that there is an enhancement of the thermal conductance, since the C₆₀ chains provide additional transport channels by an efficient low-frequency fullerene-fullerene energy transfer in the axial direction. However, a recent experimental study at Kodama's group³⁸ addressed the thermal conductance and thermopower of bundles of CNT peapods, encapsulating C₆₀, Gd@C₈₂, and E@C₈₂, and found a suppression of the thermal conductance along the bundles of roughly 35-55% as well as an increase in thermopower by about 40% when compared with hollow CNTs (at room temperature). The authors related these results to the strong local interaction between the fullerenes and the nanotube, which caused local structural deformations

in the nanotube walls. Their interpretation does not seem, however, conclusive, since the classical MD simulations carried out to support their claim did show a sizable deformation of the CNT walls only after an artificial increase of the strength of the fullerene-CNT van der Waals interaction, although the fact that CNT bundles were investigated increases the complexity of the problem and the interpretation in terms of single peapods features. Subsequent computational studies^{39,40} showed that C₆₀ molecules are able to induce additional phonon scattering, thus reducing the phonon mean free path and the thermal conductance. The effect is most prominent in the low-frequency region, where ref 39 found that the group velocities of the acoustic branches of a CNT(9,9) peapod were considerably reduced when compared with pristine CNT, while the effect was nearly absent for CNT(10,10) peapods. Clearly, the impact of the fullerenes on the thermal conductance is sensitively dependent on the CNT radius, which controls the strength of the $CNT-C_{60}$ interaction.

In our study we will address the following issues: What are the consequences of fullerene encapsulation and strong fullerene–CNT interaction on both the electrical and thermal conductances? How are the Seebeck coefficient and the thermoelectric figure of merit modified upon fullerene encapsulation? As shown in the field of phononic metamaterials, engineering phonon scattering centers can lead to a sizable suppression of the thermal conductance.^{41,42} In particular, the proposed use of silicon nanopillars periodically arranged on a Si thin layer led to a thermal conductance suppression of ~50%.⁴³ Can we see a similar behavior in a C_{60} @CNT system, where the role of the local scattering centers ("nanopillars") will be played by the fullerenes?

For our investigation we have chosen a C_{60} @CNT(8,8) systems as reference. We are aware that experimental works carried out so far have reported that the smallest diameter of SWCNT capable of encapsulating C_{60} fullerenes is ~1.28 nm.⁴⁴ Also, diameters of 1.35 nm³⁸ and 1.37 nm⁴⁵ have been obtained after peapod synthesis, which are close to those corresponding to CNT(9,9) and CNT(10,10). Computational studies have also shown that CNT peapods with smaller CNT diameter, like the CNT(8,8), may require a larger amount of energy to encapsulate the C_{60} molecules, making them less favorable in the synthesis process.^{46,47} However, we would like to point out that our main goal is to build a minimal atomistic model where the effect of the fullerene encapsulation on the CNT is maximized in order to address the influence of the CNT surface deformation and the CNT-fullerene interaction on the thermoelectric response of the system. Encapsulating C₆₀ molecules in larger diameter nanotubes will obviously weaken the mutual interactions, but alternatively, larger fullerenes such as C_{70} or C_{82} may be used instead. Briefly, our results show that phonon transport is reduced at low frequencies due to hybridization between acoustic modes of the nanotube and local, nearly dispersionless modes, in agreement with the work of Wan and Jiang.³⁹ Additionally, phonon transport is also strongly suppressed at high frequencies, which turns out to be a result of the fullereneinduced local deformations of the CNT surface. On the other hand, the electronic conductance is enhanced around the lowest CNT conductance plateau due to the emergence of additional charge transport channels mediated by the electronic interaction between C₆₀ molecules and the carbon nanotube. The combined result of these two effects is an



Figure 1. (a) Schematic representation of the common partitioning scheme for the transport calculations. The unit cell contains four rows of carbon chains and a C_{60} . The system was built up with two unit cells per lead and three unit cells in the scattering region. (b) Cross-section perspective of the C_{60} @CNT(8,8) showing the diameters of C_{60} (0.69 nm) and the CNT (1.16 nm). This latter value corresponds to the distorted section due to the presence of the C_{60} molecule. (c) Atomic structure of C_{60} @CNT(8,8) after geometry optimization. The diameter of the CNT in the section between fullerenes is 1.09 nm, the spacing between the closest atoms of consecutive C_{60} molecules is 0.26 nm, and the diameter of the C_{60} in the axial plane is 0.72 nm. A local bulking of the CNT around the C_{60} molecules can be seen along the structure, highlighted in the zoom in the right panel. The shape of the C_{60} molecules is also modified; they acquire a slightly ellipsoidal shape with diameters of 0.69 and 0.72 nm in the axial plane and perpendicular to it, respectively.

increase of the figure of merit by a factor of 2.2 in the peapod when compared with the pristine CNT.

COMPUTATIONAL METHODOLOGY

Models of CNT Peapods. We consider an infinite (8,8) metallic single-wall carbon nanotube with C₆₀ fullerene molecules encapsulated along its inner section in a periodic array; see Figure 1a. This combined system will be denoted in what follows as C60@CNT or CNT peapod. As mentioned in the Introduction, we have selected this system to guarantee a sizable interaction between the nanotube and the encapsulated fullerene that allows the understanding of its impact on the thermoelectric transport properties. Geometry optimization of the C60@CNT was carried out by using the second-order selfconsistent charge density functional tight-binding (DFTB2) method^{48,49} as implemented in the DFTB+ code (version 1.3),⁵⁰ using the Slater-Koster parameter set matsci-0-3.⁵¹ The intermolecular interaction between C₆₀ and CNT was described by a Lennard-Jones dispersion correction,⁵² with parameters from the universal force field.53 The conjugate gradient method with a convergence threshold for the forces of 1×10^{-5} atomic units was employed to get the structure of minimal energy. The unit cell of the system consists of a C_{60} molecule encapsulated in a CNT with similar length as the diameter of the fullerene (0.71 nm); see Figure 1b for a crosssection view (188 C atoms in total). The reciprocal space was sampled by a grid of $(25 \times 1 \times 1)$ k-points. Numerical tests carried out with (9,9) and (10,10) nanotubes showed a strong suppression of the $CNT-C_{60}$ interaction due to the increased distance between the nanotube wall and the fullerenes, making them less relevant for our study (see Figure S1 of the Supporting Information for additional details). Additionally, we have performed geometry optimization of these larger peapods using more accurate implementations of van der Waals corrections like DftD4,⁵⁴ Tkatchenko–Scheffler,⁵⁵ and many-body dispersion (implemented in the DFTB+ code),⁵⁶ producing only slight modifications of the final structures but not strong enough to alter the CNT walls as observed for CNT(8,8) peapod.

Quantum Transport Methodology. The thermoelectric transport properties of the studied materials were computed in the framework of nonequilibrium thermodynamics together with the Landauer approach for transport. Thus, we do not consider phonon–phonon interactions so that all scattering processes are elastic and mediated by structural features of the system. This is in contrast to the classical MD simulations performed by Wan and Jiang,³⁹ which naturally include anharmonic effects through the force fields. We also do not address electron–phonon coupling so that we can deal separately with electronic and phononic transport channels. Upon expansion of the electrical current for small applied voltage and temperature biases, closed expressions for the electronic transport coefficients appearing in the definition of the figure of merit ZT (see eq 1) can be obtained as

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$$G = e^2 L_0 \tag{2}$$

$$S = \frac{1}{qT} \frac{L_1}{L_0} \tag{3}$$

$$\kappa_{\rm el} = \frac{1}{T} \left[L_2 - \frac{L_1^2}{L_0} \right] \tag{4}$$

Here, q is the electric charge of carriers, positive for holes and negative for electrons. The moments L_m involve the electronic transmission function $\tau_{\rm el}(E)$ as

$$L_m = \frac{2}{h} \int dE \ (E - \mu)^m \left[-\frac{\partial f(E, \mu, T)}{\partial E} \right] \tau_{\rm el}(E) \tag{5}$$

with $f(E, \mu, T)$ being the Fermi–Dirac distribution function, μ the chemical potential, and h the Planck constant. The chemical potential will be used later on as a free parameter to address the influence of doping on the system, since it can be related to the charge carrier concentration. Similarly, by linearly expanding the phononic thermal current in the applied temperature difference ΔT , the phonon thermal conductance can be obtained as

$$\kappa_{\rm ph} = \frac{1}{2\pi} \int_0^\infty \mathrm{d}\omega \ (\hbar\omega) \ \frac{\mathrm{d}N_{\rm B}}{\mathrm{d}T} \ \tau_{\rm ph}(\omega) \tag{6}$$

with $k_{\rm B}$ and $N_{\rm B}$ as the Boltzmann constant and the Bose– Einstein distribution, respectively. $\tau_{\rm ph}(\omega)$ is the phonon transmission function of the system. Unlike the L_m functions, where the effective range of integration is largely limited to a relatively narrow region around the chemical potential (due to the derivative of the Fermi distribution), the calculation of the thermal conductance involves the whole phonon spectrum. To compute both transmission coefficients $\tau_{\rm el}$ and $\tau_{\rm ph}$, we use the Green's function formalism and the common partitioning scheme in which the whole system is split into three regions, namely, left and right reservoirs (electronic and thermal) and a scattering region (see Figure 1a).^{31,57–59} Since the system is periodic, both the reservoirs and the central region have the same atomistic structure so that there is no scattering at the reservoir–central region interface. $\tau_{\rm el}$ is obtained as

$$\tau_{\rm el}(E) = \operatorname{Trace}(G^{r}\Gamma_{L}G^{a}\Gamma_{R}) \tag{7}$$

where G^r is the retarded Green's function of the central region computed as $G^r = (EI - H - \Sigma_L^r - \Sigma_R^r)^{-1}$, with H as the Hamiltonian matrix, E the energy of the electrons, and I the unit matrix. $\Gamma_{L/R} = i [\Sigma_{L/R}^r - \Sigma_{L/R}^a]$ defines the reservoir spectral densities, and $\Sigma_{L/R}^{r/a}$ are the retarded/advanced self-energies, which as usual encode the electronic structure of both the semi-infinite reservoirs and the reservoir-central region interface. The phonon transmission au_{ph} can be computed along similar lines with the replacements $H \to K$ and $EI \to \omega^2 I$, where K is the dynamical matrix.⁶⁰ Both the electronic Hamiltonian matrix and the interatomic force constants are obtained using the DFTB method. The transport calculations were performed by using the libNEGF58 and PHONON59 modules implemented in the DFTB+ code. To correctly resolve small features in the transmission functions for electrons and phonons, we have tested different energy and frequency resolutions, respectively, and we have chosen the optimal one for the further analysis of our results, as presented in the next section.

RESULTS AND DISCUSSION

Structural Properties. We first analyze the mechanical stability of the C_{60} @CNT(8,8) system. To do this, C_{60} molecules were initially placed with different intermolecular distances along the nanotube central axis. The optimized CNT(8,8) hollow structure (or pristine CNT) has a diameter of 1.09 nm, and it will be the reference system for the rest of our investigation. Upon structural relaxation, we find that the fullerenes are periodically ordered with an intermolecular distance of 0.26 nm. The C_{60} structures are modified and deviate from their spherical shape, acquiring a slightly ellipsoidal shape with diameters of 0.69 and 0.72 nm in the axial plane and perpendicular to it, respectively. The nanotube surface is locally deformed around the fullerene location due to the noncovalent C_{60} -CNT(8,8) interaction, which leads to a periodic buckling as illustrated in Figure 1c. We have also performed a stability test of the initial orientation of C_{60} fullerene with respect to the CNT walls⁶¹ by considering three different initial orientations. However, all ended in the same orientation after geometry optimization, where a hexagonhexagon pair of the C₆₀ is facing a hexagon on the CNT surface; see Figure 1b. The diameter of the CNT around the center of the fullerene becomes 1.16 nm, while the diameter in

the fullerene-free region remains 1.09 nm, implying that the local buckling is ≈ 0.07 nm. The distance between the nearest atoms of C₆₀ and CNT is 0.235 nm. At this separation, not only van der Waals interactions but also a direct, though weak, overlap of the electronic molecular orbitals of the two systems can take place. The described structural features get weaker or completely disappear for C₆₀@CNT(9,9) and C₆₀@CNT-(10,10) due to the larger separation between fullerenes and the CNT walls (see Figure S1 of the Supporting Information).

Electronic Transport. Next, the electronic transmission function τ_{el} for the optimized C_{60} @CNT(8,8) system was computed along the lines described in the previous section. Figure 2a shows τ_{el} for pristine CNT(8,8) (gray background)



Figure 2. (a) Electronic transmission function τ_{el} of C_{60} @CNT(8,8) (blue line) and of pristine CNT (gray background). (b) Projected density of states (PDOS) involving the carbon p-orbitals for CNT (black line) and fullerene (green line) atoms. The C_{60} molecules display larger contributions at lower energies (below the Fermi level). This correlates well with the energy regions where the electronic transmission is most strongly modified (see graph (a)).

and for C_{60} @CNT(8,8) system (blue solid line). As expected for a pristine metallic CNT, the transmission exhibits the typical low-energy plateau around the Fermi energy with transmission $\tau_{el} = 2$. Since we are working within the linear response regime, the corresponding electrical conductance is given by $G = G_0 \tau_{el}$ with $G_0 = e^2/h$ being the conductance quantum. Beyond the lowest conductance plateau, the transmission displays the well-known staircase behavior as additional electronic bands get involved in the transport process. On the contrary, the C_{60} @CNT(8,8) shows a substantially more irregular behavior. Although traces of the staircase behavior of the transmission are still visible over the whole energy spectrum, energy windows with smaller as well as larger transmission probability appear when compared to the pristine CNT(8,8). Interestingly, in the energy range -0.7 eV to -0.9 eV and around 0.5 eV the transmission is suppressed down to \sim 1, while within the range from -0.3 eV to -0.6 eV, it is larger than the transmission of the pristine CNT and reaches nearly a value of 4. The transmission suppression by one channel in the interval [-0.7, -0.9] eV may be related to quantum interference effects. In fact, the $C_{60} \oslash CNT(8,8)$



Figure 3. Comparison of phonon dispersion along $\Gamma \rightarrow Z$ (transport direction) of (a) pristine CNT, (b) distorted CNT, and (c) $C_{60}@$ CNT(8,8) systems at low frequencies (0–250 cm⁻¹). (d) Phonon transmission as a function of the vibrational frequency for distorted CNT (red line), $C_{60}@$ CNT(8,8) (blue line), and pristine CNT (gray background). Notice the suppression of the transmission in the low- and high-frequency ranges. (e) The function $R_X(\omega) = [\tau_{\rm ph}^{\rm CNT}(\omega) - \tau_{\rm ph}^X(\omega)]/\tau_{\rm ph}^{\rm CNT}(\omega)$, where X refers either to the full $C_{60}@$ CNT(8,8) (black line) or to the structurally distorted CNT after removing the encapsulated fullerenes (brown surface). R_X is used to help distinguish the spectral regions where the local distortions of the CNT walls dominate the conductance from those where the contributions from the C_{60} molecules have a stronger effect.

system could be ideally conceived as a conducting channel with a side dot (periodically repeating the side dot along the transport channel does not qualitatively change the picture). In such a setup, it is well-known that quantum interference can lead to different spectral features such as Fano resonances, antiresonances, etc.^{62,63} In particular, antiresonances lead to a suppression of the transmission at specific resonant energies. To check the validity of this qualitative picture, we have computed the electronic transmission of a simplified setup, where all but a single fullerene are removed from the CNT peapod (see Figure S2 of the Supporting Information). In this case, we still find a suppression of the transmission around the same energy region, with a profile similar to an antiresonance. The effect disappears, however, when only the structurally distorted (but empty) CNT is kept. To better understand now the transmission increase in the interval [-0.6, -0.3], we compute the total as well as the projected density of states (PDOS) of the system and show the results in panel b of Figure 2. Only the p-states of the carbon atoms have been included in the computation of the PDOS. It is first clearly seen that there is a strong spectral overlap of CNT and fullerene states in the range from -0.3 eV to -0.6 eV, indicating hybridization between the corresponding electronic states and hinting at a strong contribution of C_{60} atoms to the transmission probability at these energies. We therefore relate the conductance increase to nearly 4 to the emergence of additional transport pathways involving the C_{60} molecular chain. Notice also that the fullerenes possess almost zero spectral weight in the energy interval between 0 eV and +0.8 eV, and hence, the transmission probability remains at the

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Figure 4. Thermoelectric transport properties of pristine CNT (left side) and C_{60} @CNT(8,8) (right side) at 300 K (black line) and 600 K (red line). We show the variation in the (a, b) electronic contribution to the thermal conductance (k_{el}), (c, d) the Seebeck coefficient (*S*), and (e, f) the power factor (PF) as a function of the chemical potential μ . Here, one can easily see the asymmetric behavior with respect to the charge neutrality point ($\mu = 0$ eV) for the C_{60} @CNT(8,8) system.

value of the pristine CNT (=2). To further clarify the role of C_{60} in the transmission increase around -0.5 eV, we have computed τ_{el} for a case where the intermolecular distance along the C₆₀ array was fixed at a larger value of 0.49 nm and the configuration was then structurally relaxed. As a consequence, the $C_{60}-C_{60}$ electronic interactions are considerably weakened. The results presented in Figure S3 of the Supporting Information show that now only transmission suppression is visible at various energies within the region -0.3eV to -0.6 eV, i.e., no enhancement of the transmission above $\tau_{\rm el}$ = 2 of the pristine CNT is observed in that region. Notice that a similar situation with reduced transmission for larger $C_{60}-C_{60}$ separation is also found between -1.0 and -1.5 eV. These results clearly indicate that electronic coupling between the fullerenes is the major ingredient for understanding the increase in transmission probability. In general, however, it is difficult to provide an intuitive explanation for the transmission suppression/increase for all energies, since we expect a delicate interplay between the emergence of additional transport pathways and local quantum interference effects, both of which are dependent on the involved electronic states at specific energies. We also remark that the dip at 0.5 eV in Figure 2a is related to a weak reorganization of the electronic bands of the CNT around the Z-point (see Figure S5 of the Supporting Information). However, this spectral feature is not expected to play a significant role in the overall thermoelectric transport characteristics of the CNT peapod.

Further calculations using CNTs with larger diameters (see Figure S4 of the Supporting Information) prove the relevance of having strong C_{60} -CNT(8,8) interaction in order to control the electron transmission. With larger diameters the spectral features previously described progressively disappear from the transmission function and the spectrum becomes largely that of a pristine nanotube.

Phonon Transport. We now turn to the thermal transport properties of CNT peapod. The phonon dispersion along the Γ -Z path for pristine CNT, the distorted CNT (i.e., after removing the encapsulated fullerenes), and the C_{60} @CNT-(8,8) system has been first computed using the PHONON tool. Figure 3a-c shows the dispersion in the low-frequency region for these three cases. One clearly sees in Figure 3c that below 50 cm⁻¹, nearly dispersionless bands (local modes) emerge, which interact with the CNT acoustic modes and lead to a flattening of the acoustic branches and thus to a reduction of the group velocities. These modes are related to the fullerenes, since they are absent in the case of the empty, but distorted CNT; see Figure 3b. Interestingly, this low-frequency behavior has also been obtained in phononic metamaterials with engineered nanopillars,^{43,64-68} but it can also be found as a result of a substrate deposition of nanomaterials. $^{42,69-72}$ In Figure 3d, the phonon transmission $\tau_{\rm ph}$ of the C₆₀@CNT(8,8) system is shown (solid blue line) together with $\tau_{\rm ph}$ of pristine CNT (gray background) and distorted CNT (solid red line). A sizable suppression of the transmission probability for lowfrequency modes below 500 cm⁻¹ as well as (much stronger) for high-frequency modes above 1500 cm^{-1} is found, reflecting the behavior of the vibrational band structure displayed in Figure 3c. As mentioned in the Introduction, this lowfrequency transmission suppression was also obtained by Wan and Jiang³⁹ in their study of CNT peapods using classical MD simulations, although the effect in our case is eventually stronger due to the smaller nanotube diameter used in our investigation. To further quantify the influence of the fullerenes on the main features of the phonon transmission function, we have defined the following quantity: $R_X(\omega) =$ $[\tau_{\rm ph}^{\rm CNT}(\omega) - \tau_{\rm ph}^{X}(\omega)]/\tau_{\rm ph}^{\rm CNT}(\omega)$, where X refers either to the full C_{60} @CNT(8,8) or to the structurally distorted CNT (see Figure 3e). If $R_X \sim 0$ at a given frequency, then the transmission probability is similar to that of pristine CNT, while $R_{\rm X} \sim 1$ indicates a strong suppression of the transmission, eventually leading to the formation of a phonon band gap. If $R_X < 0$, then either additional phonon channels have emerged or there is a shift in the CNT transmission frequencies. Comparing the results between distorted CNT and C_{60} @CNT(8,8), one can conclude that at higher frequencies (above 1500 cm⁻¹) the local deformations in the nanotube are largely responsible for the suppression of phonon transmission, in agreement with the phonon dispersion results. Moreover, the spectral gap around 1200 cm⁻¹ also seems related to CNT deformations, although a few flat vibrational bands appear close to this spectral gap (see Figure S6 of the Supporting Information). On the contrary, in the lowfrequency range (below 500 cm^{-1}) the deviation of the transmission of the distorted CNT from that of the pristine CNT is much larger, indicating that the C₆₀ molecules are playing a stronger role in this frequency region and are thus the main source of the transmission reduction (see Figure 3d). This obviously reflects the previous discussion of the vibrational band structure in Figure 3c.

Thermoelectric Properties. After having gained a deeper insight into the electronic and vibrational transport characteristics of the CNT peapod, we proceed to discuss its thermoelectric transport properties and consider, whenever necessary, the pristine CNT as reference point. In Figure 4, the electronic contribution to the thermal conductance κ_{el} , the Seebeck coefficient *S*, and the power factor ($PF = S^2G$) of the pristine CNT and C_{60} (α CNT(8,8) are shown as a function of the chemical potential μ at 300 and 600 K. Here, μ is positive for n-type doping and negative for p-type doping. Figure 4a,b shows that κ_{el} at 300 K displays a similar behavior to the previously presented electronic transmission. At a higher temperature, the overall thermal conductance increases due to the larger broadening of the Fermi function derivative under the integrals of the L_m moments in eq 5. Regarding the Seebeck coefficient, stronger differences can be seen between both systems: S of pristine CNT shows clear electron-hole symmetry for both temperatures, the higher temperature inducing a small broadening of the peaks, only. The C_{60} CNT(8,8) displays, however, a more involved behavior, with relatively sharp changes in the sign of S on the p-type doping side (negative μ). This effect is mostly related to the strong influence of C₆₀ molecules in the electronic transmission since the distorted CNT almost keeps the same behavior as the pristine CNT (see Figure S7 of the Supporting Information). Notice also that the largest change in S occurs in an energy window around approximately -1 eV, where the influence of $C_{60}\ is$ seen most strongly in the electronic transmission spectrum. Moreover, C_{60} @CNT(8,8) possesses a larger S_{max}

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(maximum *S* value as a function of the chemical potential) compared to the pristine CNT for both temperatures, i.e., $S_{\text{max}}(\text{peapod}) \sim 8.9 \times 10^5 \text{ eV/K}$ (at $\mu = -0.86 \text{ eV}$) and $S_{\text{max}}(\text{CNT}) \sim 6.58 \times 10^5 \text{ eV/K} \text{ (at } \mu = -0.9 \text{ eV} \text{) at 600 K.}$ Similar to the Seebeck coefficient, the power factor PF for pristine CNT retains the same electron-hole symmetry. The behavior of C_{60} (\otimes CNT(8,8) is, again, asymmetric with respect to the charge neutrality point (at zero chemical potential), but more importantly, it achieves a higher PF_{max} value than the pristine system (see Figure 4e,f). Thus, at 600 K, the PF_{max} of C_{60} @CNT(8,8) is ~1.93 × 10⁻¹² AeV/K² (at $\mu = -0.88$ eV) and of pristine CNT is $\sim 1.156 \times 10^{-12} \text{ AeV/K}^2$ (at $\mu = \pm 0.91$ eV). On the basis of these analyses of the electronic contributions to the thermoelectric figure of merit, the C_{60} CNT(8,8) system has a higher efficiency in a wider range of temperatures (\in [250, 1000] K), displaying maximal efficiency at 575 K (see Figure S7 of the Supporting Information).

Figure 5a shows the electronic and the phonon contribution to the total thermal conductance for pristine CNT (red curves) and C_{60} @CNT(8,8) (black curves) as a function of the temperature. $k_{\rm el}$ for each temperature is obtained as the maximum value of the electronic thermal conductance when plotted against the chemical potential. Overall, we find that the phononic contribution $k_{\rm ph}$ dominates the thermal conductance for pristine CNT as well as for the C_{60} (\mathcal{O} CNT(8,8) system. However, both contributions become nearly the same for C_{60} @CNT(8,8) at the largest temperature considered in this study (1000 K). The impact of the C_{60} encapsulation is strongly reflected in $k_{\rm ph}$ compared to $k_{\rm el}$: whereas the latter is only weakly modified when going from the pristine CNT to the peapod, the former is progressively reduced with increasing temperature with respect to pristine CNT values. Despite the fact that there is a crossover around 650 K in the curves of $k_{\rm el}$ of both systems, the difference between them at any other temperature remains very small, below 5%. Also notice that $k_{\rm ph}$ of C_{60} @CNT(8,8) shows a tendency to saturate after 750 K, indicating that all relevant vibrational states have been already included in its computation; see eq 6. To round up this discussion, we have computed the thermoelectric transport properties for C_{60} @CNT(9,9) and C_{60} @CNT(10,10) at 200 and 600 K (see Figures S8 and S9 of Supporting Information). The choice of these temperatures is explained by the fact that the optimal results for these systems are found at lower temperatures than for C_{60} @CNT(8,8). Comparing CNT(9,9) and C₆₀@CNT(9,9), minor differences were found in κ_{el} between both systems, but when we move to S, considerable differences are found. C_{60} @CNT(9,9) displays sharper changes and a decrease of S for the p-doping region and an increase of S for n-doping. This is in contrast to C_{60} CNT(8,8), where a notorious increased was found in the pdoping side. The PF in the n-doping side at 200 K is ~ 1.2 times the PF of CNT(9,9), reaching a value of ~1.44. This increase can be correlated with the additional electronic channel that is shown in the electronic transmission of C_{60} CNT(9,9) (see Figure S4b in the Supporting Information) at ~0.8 eV, due to the incorporation of the C_{60} molecules. At this point we can see that the interaction between the C_{60} molecules and the CNT(9,9) is not as strong as it was seen in C_{60} @CNT(8,8), as expected. This becomes even more evident when dealing with C_{60} @CNT(10,10), where the two subsystems are decoupled from each other.

In Figure 5b, a heat map plot of the figure of merit ZT as a function of temperature and chemical potential μ is presented



Figure 5. (a) Thermal conductance of CNT (red circles) and C_{60} @ CNT(8,8) (black squares) as a function of temperature. The curves with filled symbols correspond to the phonon thermal conductance $\kappa_{\rm ph}$, while the empty symbols correspond to the electronic thermal conductance $\kappa_{\rm el}$ (for each temperature its maximum value when plotted as a function of the chemical potential is taken). (b) Heat map plot of the figure of merit ZT with respect to the temperature and chemical potential μ for C_{60} @CNT(8,8). (c) Temperature dependence of the maximum value of ZT for pristine CNT(n,n) (circles) and C_{60} @CNT(n,n) (squares) for different CNT diameters (n = 8 blue, n = 9 red, n = 10 green). The thermoelectric performance of C_{60} @CNT(8,8) is enhanced by a factor of 2.2 compared to pristine CNT(8,8) at 575 K, where ZT_{max} ≈ 0.12 .

for the C_{60} @CNT(8,8) system. This serves to allocate the optimal μ value (leading to a maximum ZT, ZT_{max}) for each temperature. On the basis of the behavior of the electronic contributions to ZT (see Figure 4), it is expected that the figure of merit will display a similar asymmetric behavior with

respect to charge neutrality point for different temperatures. This is indeed clearly seen in Figure 5b. The optimal μ is located around -0.9 eV, indicating a maximal performance for p-type doping. From Figure 5b, the temperature dependence of ZT_{max} can be extracted and plotted for C_{60} @CNT(8,8) system (blue solid curve with square symbols in Figure 5c). Similar to PF_{max} (shown in Figure S7 of the Supporting Information), C₆₀@CNT(8,8) also presents a larger ZT_{max} compared to pristine CNT (blue solid curve with circle symbols) over the whole temperature range studied here. The best thermoelectric performance of $\mathrm{ZT}_{\mathrm{max}}\approx 0.12$ is achieved at 575 K. This corresponds to an improvement in thermoelectric efficiency by a factor of 2.2 with respect to pristine CNT, whose ZT_{max} weakly depends on the temperature. This suggests that the fullerene encapsulation may lead to a more sensitive temperature control of the thermoelectric response. When analyzing these curves for larger CNTs, C_{60} @CNT(9,9) displays a small enhancement of ZT at low temperatures, which amounts to a factor ~ 1.3 larger than the pristine CNT(9,9) at 200 K (ZT_{max} \approx 0.074). Moreover, for the C₆₀@ CNT(10,10) system, the temperature dependence of ZT_{max} is very similar to the corresponding of the pristine CNT(10,10), coming from the negligible influence of C₆₀ molecules in their electron and phonon transport properties.

CONCLUSIONS

We have carried out a detailed computational study of the thermoelectric properties of a C_{60} @CNT(8,8) system using the DFTB-NEGF framework. Our findings indicate that the presence of C₆₀ molecules inside the CNT and the related local deformations induced by their mutual interaction play a significantly role in the electronic and thermal response of the system. In particular, a strong modification of the low-energy (around the Fermi level) electronic conductance was found, showing both conductance suppression and conductance enhancement when compared with the pristine CNT case, which shows a constant conductance plateu with $G = 2G_0$. For the phononic transmission, a reduction at low and high frequencies was found, mostly resulting from the hybridization of local, C₆₀-derived modes with acoustic modes (in the low frequency range) and from the local structural deformations of the CNT surface (at high frequencies). Despite the fact that the total thermal conductance is still dominated by the vibrational contributions, the previously mentioned suppression of the phononic transmission over various spectral windows leads to an overall reduction of the thermal conductance for C_{60} @CNT(8,8) when compared with the pristine nanotube. This, combined with a larger power factor, yields an improved thermoelectric figure of merit for the peapod. Although the obtained absolute values of ZT are still small, they nevertheless increase by a factor of 2.2 when compared with the pristine CNT at 575 K, and additionally, the ZT of the peapod displays a more pronounced temperature dependence. Our results highlight the importance of strong CNT-C₆₀ intermolecular interactions. Additional calculations for C_{60} @CNT(9,9) and C_{60} @CNT(10,10) peapods clearly demonstrated a progressive weakening of the differences between pristine nanotubes and their peapod counterpart.

Indeed, the competition between the two dominant intermolecular interactions present in this system, $C_{60}-C_{60}$ and C_{60} -CNT, offers an additional set of control variables to influence the thermoelectric transport properties of CNTbased systems. Thus, larger nanotube radii can control the

 C_{60} -CNT interaction, while the encapsulation of other (doped) fullerenes such as $Gd@C_{82}$ and $E@C_{82}$ can influence both C_{60} - C_{60} and C_{60} -CNT interactions.³⁸ Moreover, the fullerene chains in these CNTs will have a larger conformational freedom and may be able to adopt arrangements deviating from the linear chain discussed here. This will be the subject of a separate study. We expect that the insights gained in this investigation may inspire future experimental and theoretical works for the design of CNT-based thermoelectric devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c02611.

Additional results related to the electronic, thermal, and thermoelectric properties of the studied CNT peapod (PDF)

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Notes

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