Ab initio effective dragged thermoelectric properties in Si nanowires

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The growing interest in energy-harvesting has resulted in the research for more efficient thermoelectric systems [1]; as they not only allow to give a practical use to thermal waste of all our devices and/or buildings, but to generate energy for small wearable devices, thus removing the necessity of external batteries [2]. Unfortunately, traditionally those systems offered quite a low efficiency—i.e. they offer low figures of merit zT—, therefore creating a need to enhance their energy conversion ratio [3]. In that context, nanostructuration provides an effective way of reducing the lattice thermal conductivity without deteriorating electrical properties [2], [4], [5], thereby obtaining conversion ratios unachievable using more classical approaches [4]. A paradigmatic example of such an improvement due to nanostructuration can be found in heavily-doped Si nanowires (NWs), which have been found to offer a zT 100 times larger than their bulk counterpart [6]. The quantities necessary for the computation of this figure of merit ($\mathrm{zT} = \frac{\sigma S^2 T}{\kappa}$ [4], where σ, S, T and κ are the electrical conductivity, Seebeck coefficient, temperature, and thermal conductivity, respectively) can in principle be obtained from the solution of the mesoscopic linearized Boltzmann Transport Equation for both electrons and phonons (EPBTE). Indeed, the recent development of an iterative solution for these coupled system [7], has resulted in a step forward towards the *ab initio* computation of more accurate thermoelectric properties. Nonetheless the utility of such an approach to accurately describe thermoelectric properties, its practical usage is currently limited to homogeneous systems, namely bulk, thus preventing its use for high-zT systems, as the nanostructured ones.

In this work, we compute the effective thermoelectric properties for nanosystems, namely Si NWs, by iteratively solving the *ab initio*-informed (i.e. with scattering rates, energies, velocities,... calculated from first principles) linearized EPBTE with the appropriate boundary conditions to correctly model the effect of perfectly diffusive physical boundaries, going for the first time a step beyond the most common approach based on adding a Casimir boundary scattering through Matthiessen's rule. We demonstrate that our methodology provides a higher accuracy than Matthiessen's approach (see Table I) through comparison with recent experimental results [5]. Furthermore, we demonstrate that the effect of the use of Matthiessen's is not straightforward to translate to thermoelectric variables for NWs and that for some cases it provides qualitatively different results than our methodology (see Fig. 1), which provides an exact and physically correct treatment of boundary effects. Consequently, our results not only rise concern of Matthiessen's accuracy for nanosystems, but make it necessary to study its reliability on a case-by-case basis, rendering our approach superior for such systems. Finally, we also discuss the effect of the collision term approach has over thermoelectric properties, as well as the size effect (see Fig. 2); finding that coupling is essential to obtain the accurate dependence of zT with size, as not all radii provide enhancement as predicted by uncoupled approaches.

REFERENCES

[1] A. J. Minnich *et al.*, Energy Environ. Sci. **2**, 466 (2008).
[2] A. Shakouri, Annu. Rev. Mater. Res. **41**, 399 (2011).
[3] C. Wood, Energy Convers. Manag. **24**, 331 (1984).
[4] M. G. Kanatzidis, Chem. Mater. **22**, 648 (2010).
[5] G. Gadea Dez *et al.*, Nano Energy **67**, 104191 (2020).
[6] A. I. Boukai *et al.*, Nature **451**, 168 (2008).
[7] N. H. Protik *et al.*, Npj Comput. Mater. **8**, 28 (2022).

TABLE I

CALCULATED THERMAL CONDUCTIVITY (κ), ELECTRICAL CONDUCTIVITY (σ), SEEBECK COEFFICIENT (S) AND THERMOELECTRIC FIGURE OF MERIT (zT) AT 300 K, FOR NWS OF RADII RANGING 45-50 nm AND B-DOPINGS OF 2.0×10^{19} AND $5.0 \times 10^{19}\,\mathrm{cm}^{-3}$ USING OUR APPROACH, I.E. THE SUPPRESSED DRAGGED EPBTE (SDEPBTE), AND THE DRAGGED EPBTE WITH MATTHIESSEN'S PLUS A CASIMIR SCATTERING TERM (MDEPBTE) TO MODEL THE NW BOUNDARY EFFECT. RESULTS FROM REF. [5] ARE PROVIDED AS REFERENCE.

	κ $\left[\frac{\mathrm{W}}{\mathrm{m\cdot K}}\right]$	σ $\left[\frac{\mathrm{S}}{\mathrm{cm}}\right]$	S $\left[\frac{\mu\mathrm{V}}{\mathrm{K}}\right]$	zT $\times 10^{-2}$
Experimental	18.3±4.6 (13-25[†])	270 (247-290[†])	207±19	1.4-2.5[†]
SDEPBTE[‡]	25.8-27.3	276-280	276-277	2.4-2.3
	25.5-26.9	624-633	198-199	2.7-2.8
MDEPBTE[‡]	39.3-41.4	288-291	282-284	1.7-1.7
	39.5-41.4	652-658	207-209	2.1-2.1

[†] These values correspond to the minimum and the maximum of the value for the given temperature of all measurements, including errors.

[‡] These results correspond to the values for NWs of radius 45 (left) and 50 (right) nm, with a B-doping of $2.0 \times 10^{19}\,\mathrm{cm}^{-3}$ (top) and $5.0 \times 10^{19}\,\mathrm{cm}^{-3}$ (bottom).

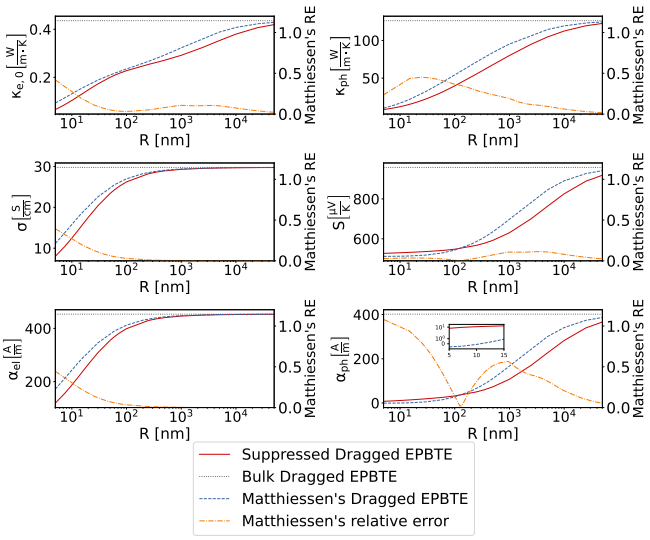

Fig. 1. Left-axis: Electronic (at 0 field; $\kappa_{\mathrm{el},0}$) and phonon (κ_{ph}) thermal conductivity, electrical conductivity, Seebeck coefficient, the electronic (α_{el}) and phonon (α_{ph}) thermal response to an electric field as a function of NW radius at 300 K and a donor concentration (P) of $1.0 \times 10^{18}\,\mathrm{cm}^{-3}$ obtained through the suppressed dragged EPBTE (red solid) and dragged EPBTE with Matthiessen's (blue dashed); bulk values (gray dotted) are given as reference. Right-axis: Relative error of Matthiessen's with respect to suppressed solution (orange dot-dash) as function of NW radii. Inset: Zoom at small radii for α_{ph}.

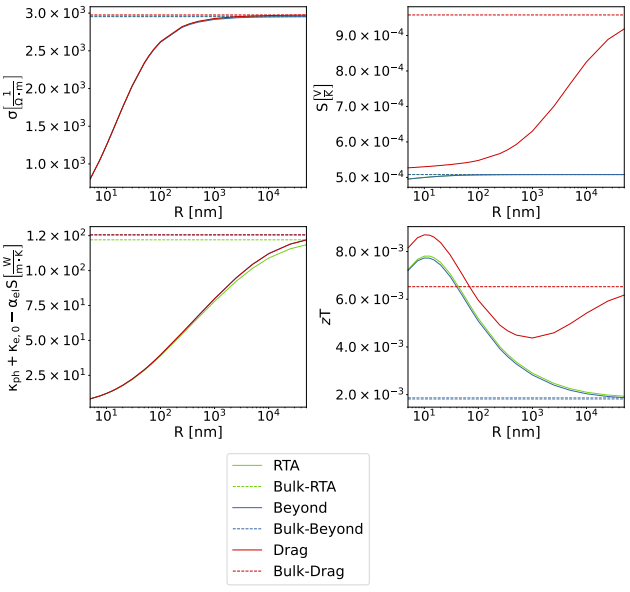

Fig. 2. Electrical conductivity, Seebeck coefficient, total thermal conductivity at zero electric current, and figure of merit as function of NW radius at 300 K and an acceptor concentration (B) of $1.0 \times 10^{18}\,\mathrm{cm}^{-3}$ for several approaches to collision operator; namely, relaxation time approximation or RTA(green), uncoupled beyond the RTA (blue), and dragged (red). Bulk values (dashed) are given as reference.