Comment on "Ultrahigh Convergent Thermal Conductivity of Carbon Nanotubes from Comprehensive Atomistic Modeling"

Barbalinardo *et al.* [1] determined the thermal conductivity κ of a pristine (10,0) carbon nanotube from a numerical solution of the Boltzmann transport equation (BTE). Invoking both quantum and classical phonon statistics in the BTE, the authors reported absolute values of $\kappa_{\mathrm{quan}} = 9960\ \mathrm{Wm^{-1}K^{-1}}$ and $\kappa_{\mathrm{clas}} = 3190\ \mathrm{Wm^{-1}K^{-1}}$ for infinitely long tubes at room temperature. The latter prediction in particular was found to compare well with predictions from molecular dynamics simulations (MD), which led the authors to conclude that the two rather different approaches, BTE and MD, draw a coherent picture of heat transport in nanotubes. In the following, we demonstrate that the BTE computation as detailed in footnote 53 of Ref. [1] entails systematic errors that emanate from the usage of numerical nonsymmetrized force constants.

Low-frequency three-phonon scattering rates Γ (or, equivalently, anharmonic lifetimes $\tau_{3\mathrm{ph}} = 1/\Gamma$) of acoustic longitudinal (LA), flexural (FA), and twisting (TW) modes represent an important metric pointing towards a convergence or divergence of κ with tube length. As we showed recently [2], irrespective of the choice of phonon statistics, stress-free nanotubes under the harmonic lattice approximation give rise to power-law dependencies $\Gamma_{\mathrm{LA}} \sim |q|^{-1/2}$, $\Gamma_{\mathrm{FA}} \sim q^0$, and $\Gamma_{\mathrm{TW}} \sim |q|^{1/2}$ in the limit of small wave numbers $|q| \to 0$, which provide a rigorous benchmark for numerical calculations in the framework of the BTE. Performing conductivity computations with the software κALDo [3], which was also used in Ref. [1], we showcase in Fig. 1 numerical data of acoustic phonon lifetimes under the assumption of quantum statistics by treating third order force constants (3rdFCs) at different levels of accuracy. Here, it becomes evident that numerical 3rdFCs obtained via finite differencing, as in Ref. [1], lead to an incorrect, overly rapid decrease of lifetimes in the $|q| \to 0$ limit. Such behavior can be attributed to the fact that numerical 3rdFCs do not perfectly obey translational and rotational sum rules, which require a prior symmetrization of numerically obtained 3rdFCs, as mentioned elsewhere [4,5]. Taking as input analytical 3rdFCs determined via symbolic differentiation, which fulfill sum rules by construction, lifetime predictions in Fig. 1 are significantly improved.

In Fig. 2, we reproduce Fig. S4 of Ref. [1] to show how the accuracy of 3rdFCs affects the solution of the BTE in the infinite-size limit. Using nonsymmetrized numerical 3rdFCs, an apparent convergence of κ with the number of q-grid points N_q is reached with limiting values that are consistent with values given in Ref. [1] for $N_q = 200$. Performing calculations with analytical 3rdFCs, however, the convergence behavior of κ changes drastically and considerably larger predictions of κ are obtained. In solving the BTE numerically, high memory requirements prevent us from going beyond $N_q = 400$ q-grid points, such that no definite statement regarding a possible saturation value of κ can be made.

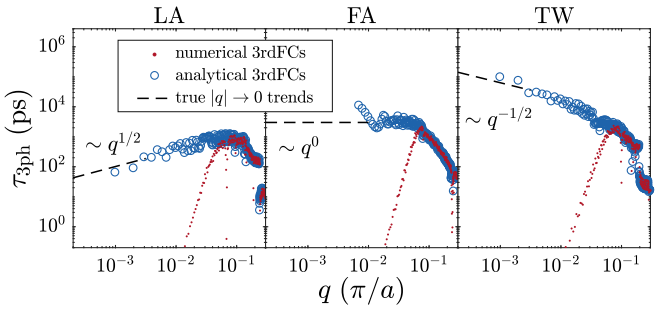

FIG. 1. Anharmonic lifetimes of acoustic modes in a (10,0) carbon nanotube at room temperature.

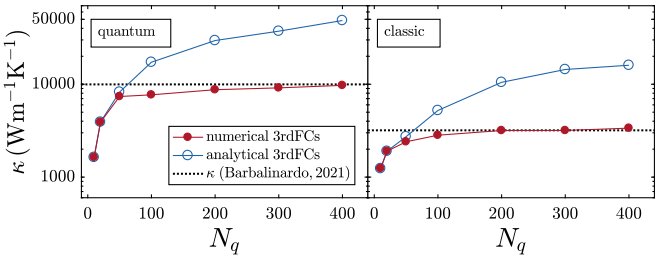

FIG. 2. Thermal conductivity of an infinite-length (10,0) carbon nanotube at room temperature vs wave number grid resolution N_q. The left (right) plot shows BTE predictions based on quantum (classical) phonon statistics.

Contrary to the conclusion drawn in Ref. [1], thermal transport in pristine macroscopically long nanotubes remains an open theoretical problem. Unfortunately, as the tube length goes beyond the 1-μm scale, the apparent agreement between MD and BTE results in Ref. [1] should be regarded as accidental and due to systematic errors in the BTE calculation. Our Comment does not preclude the possibility that the inclusion of additional physics in the BTE formalism, such as finite temperature effects or higher order phonon scattering, may reconcile the two approaches.

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Received 14 September 2021; accepted 23 May 2022; published 23 June 2022

DOI: 10.1103/PhysRevLett.128.259601

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