PHYSICAL REVIEW LETTERS

Kwon, Berber, and Tománek Reply: In the preceding Comment [1], Keblinski and Schelling point out an apparent inconsistency between our finding of a temperature-dependent thermal expansion coefficient $\alpha(T)$ in carbon nanotubes [2] and their previous finding [3], based on Grüneisen theory, that α should be temperature independent in the classical regime.

By construction, the low-temperature Grüneisen theory considers only third-order anharmonicities in the interatomic interaction potentials. Since this approach cannot reproduce the temperature dependence of thermal expansion at higher temperatures, Keblinski and Schelling do not question the neglect of higher-order anharmonicities in the Grüneisen theory, but rather invoke quantum phenomena as the true cause of a temperature-dependent $\alpha(T)$. Most dramatic is the change from an in-plane contraction to expansion, postulated in our Letter for nanotubes at 800 K [2] and observed in graphite at 700 K [4]. If Keblinski and Schelling are correct, then classical molecular dynamics (MD) simulations should fail to reproduce the structural evolution of carbon systems at these temperatures that, according to Ref. [1], lie below the Debye temperature of carbon.

The vibration spectrum of sp^2 bonded carbon nanostructures is dominated by hard optical modes, associated with the distortion of the interatomic bonds, and by rather soft, long-wavelength acoustic modes, many of which couple to the global crystal shape. The interatomic bonds in sp^2 and sp^3 bonded carbons are similarly stiff, resulting in a formidable Debye temperature of 1860 K in diamond [5]. The long-wavelength, soft acoustic modes give rise to lower Debye temperatures, ranging from 420 K in graphite [6] down to ≈ 30 K in nanotubes [7]. Whereas a classical description of the soft transverse acoustic modes, depicted in Fig. 2 of Ref. [2], appears appropriate above room temperature, our classical description of the hard optical modes needs to be justified.

Unlike the soft transverse acoustic modes, which cause a length contraction in nanotubes and graphene monolayers even in the harmonic regime [2], the hard optical modes do not cause macroscopic length changes in the harmonic regime, whether subject to the Bose-Einstein or the Maxwell-Boltzmann statistics. In other words, our classical treatment of these modes does not affect results for $\alpha(T)$. Only at temperatures $T \gtrsim 800$ K, the increasing importance of higher-order anharmonicities in the C-C interaction eventually dominates over the contraction caused in nanotubes by transverse acoustic modes.

Having justified the neglect of quantum effects in our study, we should emphasize the advantages of classical MD simulations over a classical statistics approach in determining $\alpha(T)$ at finite temperatures. In our classical MD simulations, the amplitude of individual vibration modes is determined by Newton's laws and accurate force fields. This amplitude is generally large for soft modes and small for hard modes at a given temperature, qualitatively following the behavior of a quantum crystal. The equipartition theorem of classical statistics, which postulates equal population of all modes independent of temperature, is expected to describe structural changes at finite temperatures much less accurately.

We suspect that the temperature independence of the thermal expansion coefficient α, postulated for nanotubes in the classical regime [1,3], as well as contradictions regarding its sign [8], are to be blamed on the limitation of Grüneisen theory to third-order anharmonicities in the interaction potentials and a lack of convergence in the MD simulations [9]. We believe that converged classical MD simulations should correctly reproduce the temperature dependence of $\alpha(T)$ in nanotubes above room temperature, without taking recourse to quantum statistics.

Young-Kyun Kwon,* Savas Berber,† and David Tománek‡
Department of Physics and Astronomy
Michigan State University
East Lansing, Michigan 48824-2320, USA

*Present address: Department of Physics, University of California, Berkeley, CA 94720-7300, USA.
†Present address: Institute of Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8571, Japan.
‡Electronic address: tomanek@msu.edu

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[8] For carbon nanotubes near room temperature, Ref. [3] reports a negative value of α, based on Grüneisen theory, in Table I, and a positive value of α, based on MD simulations, in Fig. 1.
[9] Artificial constraints, including small unit cell sizes in MD simulations, suppress long-wavelength acoustic modes, which are responsible for the thermal contraction of nanotubes.