Comment on "Thermal Contraction of Carbon Fullerenes and Nanotubes"

Using a tight-binding based energy functional parametrized to *ab initio* density-functional calculations [1], Kwon *et al.* performed classical molecular-dynamics simulations of the thermal expansion of C_{60} molecules and $(10, 10)$ single-walled carbon nanotubes. The key result reported in a recent Letter [2] is that both C_{60} and nanotubes exhibit zero thermal expansion coefficient, α, at $T = 0$, that, with increasing temperature, first becomes negative and then turns positive at higher temperatures. They noted that this temperature dependence was in agreement with the experimentally observed in-plane thermal expansion of graphite. Most of the simulation of Kwon *et al.* is for temperatures well below Debye temperatures of C_{60} and nanotubes, where the majority of the vibration modes (phonons) are quantum mechanically frozen [3,4]. This freezing is, however, not captured by classical simulations; thus the agreement of the simulation results with experimental data is accidental.

The need for a quantum mechanical approach in the description of thermal expansion can be demonstrated by the key results of the Grüneisen theory solid which, for an isotropic crystalline solid, predicts α,

$$\alpha = \frac{1}{3VB} \sum_{\lambda \mathbf{k}} \gamma_{\lambda \mathbf{k}} k_B \left(\frac{\hbar \omega_{\lambda \mathbf{k}} / k_B T}{k_B T} \right)^2$$
$$\times \frac{\exp(-\hbar \omega_{\lambda \mathbf{k}} / k_B T)}{[1 - \exp(\hbar \omega_{\lambda \mathbf{k}} / k_B T)]^2}, \tag{1}$$

where $\mathbf{k}$ is the wave vector in a phonon band labeled by λ, B is the bulk modulus, V is the system volume, T is the temperature, and $\hbar$ and k_B are the Planck and Boltzmann constants, respectively. The $\gamma_{\lambda \mathbf{k}} = \partial \ln \omega_{\lambda \mathbf{k}} / \partial \ln V$ are the mode-dependent Grüneisen parameters, which measure the sensitivity of the phonon frequencies $\omega_{\lambda \mathbf{k}}$ to changes in the system volume. The Grüneisen theory can be generalized to anisotropic structures with $\gamma_{\lambda \mathbf{k}}$ defined with respect to strain tensor rather than volume change [5], and thus is also applicable to carbon nanotubes.

The classical limit ($\hbar \omega_{\lambda \mathbf{k}} / k_B T \rightarrow 0$) of Eq. (1) predicts that each mode, regardless of its frequency, contributes to the thermal expansion with the weight proportional to its Grüneisen parameter. This is a simple consequence of the fact that within the classical description all modes are excited and have the same heat capacity, k_B. Also the temperature dependence of α comes only via rather weak and monotonic temperature variations of the modulus and the Grüneisen parameters.

Accounting for quantum effects leads to very different α. Below the Debye temperature high-frequency modes are not excited and do not contribute to thermal expansion, which is reflected by the $\exp(-\hbar \omega_{\lambda \mathbf{k}} / k_B T)$ factor in Eq. (1). In particular, the fact that α is zero at $T = 0$ for

any solid originates from the fact that all phonons are frozen at $T = 0$. Whether a solid expands or contracts upon heating depends on the balance between phonon modes with positive and negative Grüneisen parameters. Transverse acoustic (TA) modes may exhibit negative $\gamma_{\lambda \mathbf{k}}$ related to the increase of the restoring forces with increased tension [6]. Because TA modes represent the lowest frequency modes, thermal contraction is more often seen only well below the Debye temperature, where high-frequency modes with positive Grüneisen parameters are not excited and do not contribute to the sum in Eq. (1) [7]. With increasing temperature higher frequency modes are becoming excited, and α increases. We note that the Grüneisen theory is based on corrections to the harmonic theory due to the first nonharmonic (cubic) term.

While the results of Kwon *et al.* are in apparent agreement with experimental measurements, the lack of quantum statistics in the model implies that this agreement is accidental. In particular, it is likely that in the expansion of the interatomic potential used by Kwon *et al.*, higher than third order terms play an important role, thereby resulting in a temperature dependent α obtained in classical simulations. Even if higher than third order terms are, indeed, very important for carbon nanotubes, below the Debye temperature, their quantitative effects on thermal expansion will be incorrectly captured by classical simulations, as is the case with the third order terms.

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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 inter-atomic 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, 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 simulation, 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.

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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.