

Thermal Contraction of Carbon Fullerenes and Nanotubes

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We perform molecular dynamics simulations to study shape changes of carbon fullerenes and nanotubes with increasing temperature. At moderate temperatures, these systems gain structural and vibrational entropy by exploring the configurational space at little energy cost. We find that the soft phonon modes, which couple most strongly to the shape, maintain the surface area of these hollow nanostructures. In nanotubes, the gain in entropy translates into a longitudinal contraction, which reaches a maximum at $T \approx 800$ K. Only at much higher temperatures do the anharmonicities in the vibration modes cause an overall expansion.

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There has been increasing demand for high-performance composites with near-zero thermal expansion [1]. In such composites, thermal expansion of one component may be compensated by a thermal contraction of other components [2]. Since most materials expand thermally, there has been extensive search for materials with a negative thermal expansion coefficient. Thermal contraction has been observed in quasi-one-dimensional polymers such as rubber or polyethylene [3,4], layered systems such as graphite and boron nitride [5–7], and three-dimensional covalent networks found in oxides [8,9] such as $\text{NaTi}_2\text{P}_3\text{O}_{12}$ and ZrW_2O_8 . Since carbon fullerenes and nanotubes consist of sp^2 bonded carbon networks related to graphite, we expect them to also contract at moderate temperatures.

Thermally induced contraction and expansion result from a competition between internal energy and entropy. In the harmonic regime at moderate temperatures, low-dimensional systems gain structural and vibrational entropy by exploring the voids in configurational space at relatively little energy cost. The dominating effect of entropy in this regime results in a contraction. Only at higher temperatures do the anharmonicities in the interatomic interaction play a significant role, causing an overall expansion. We expect the transition from contraction at low temperatures to expansion at high temperatures to be a universal phenomenon in low-dimensional materials, and only the crossover temperature to change from system to system. As we discuss in the following, the interplay between energy and entropy has a particularly interesting effect on the thermal behavior of nanostructures.

Following the discovery of fullerenes [10] such as C_{60} , carbon nanotubes [11,12], perfect cylinders formed of rolled graphite monolayers, are now being considered as important building blocks for nanotechnology [13]. Thermal expansion properties of carbon nanotubes are of great importance, since the electrical characteristic of complex nanotube-based circuitry will change significantly due to differential contraction imposing internal

stress [14]. Another important aspect of the thermal expansion of nanotubes is the effect on the mechanical properties of nanotube-based high-performance composites [15]. Even though the same sp^2 bonding is shared by 2D graphite, 1D nanotubes, and 0D fullerenes, we find it important to determine the effect of dimensionality on the thermal contraction at moderate temperatures and the crossover point to thermal expansion.

In this Letter, we use Nosé-Hoover molecular dynamics simulations [16] to determine how temperature affects the volume of C_{60} molecules and carbon nanotubes, and also to determine how their length changes with increasing temperature. We show that at moderate temperatures, both fullerene molecules and carbon nanotubes contract in length and volume. Only at temperatures beyond several hundred degrees Kelvin, the initial contraction changes to an overall expansion in the anharmonic regime. We determine temperature-induced structural changes by investigating the coupling between vibrational modes and the shape of fullerenes and nanotubes. We identify those vibration modes that play a dominant role in how the volume and length of fullerenes and nanotubes change with temperature.

To correctly reproduce the change in length and volume of nanostructures in response to temperature, we need to describe precisely those energy changes associated with shape deformations in the anharmonic regime. We found that the popular Tersoff potential [17] introduces a spurious soft mode that modifies the length of a straight tube. To avoid this problem, we use a parametrized linear combination of atomic orbitals formalism based on a universal parametrization of *ab initio* density functional results [18]. This energy functional is particularly suited for our purpose, as it is based on an electronic Hamiltonian that goes well beyond the nearest neighbor approximation, thus also describing anharmonic effects due to the $sp^2 \rightarrow sp^3$ rehybridization during deformation. We make use of the computationally efficient approach that has been previously used with success to describe dynamics of carbon nanostructures [19]. We focus at large

structural changes occurring at hundreds of degrees Kelvin, where a classical description is adequate, and compare to structures optimized at $T = 0$ K, ignoring the zero-point motion.

As suggested earlier, the most pronounced deviation from the thermal expansion can be expected in the zero-dimensional C_{60} molecule. To study volumetric changes with temperature, we coupled the C_{60} molecule to a thermal heat bath at temperatures ranging from $T \geq 0$ to ≤ 1000 K. Our molecular dynamics simulations indicate that the ellipsoidal deformation, with $\omega \approx 200$ cm^{-1} one of the softest vibration modes of the C_{60} molecule, depicted in Fig. 1(c), is dominating the vibrational spectrum well below room temperature. To estimate the volume at any moment in time, we first diagonalized the gyration tensor of a deformed C_{60} molecule to obtain the principal axes of the corresponding rotation ellipsoid. We changed the heat bath temperature in small steps and discarded data obtained during the first 0.2 ps following a temperature change to allow for equilibration with the heat bath. Our data for the volume change $\Delta V(T)$, shown in Fig. 1(a), represent the average over 10^4 – 10^5 time steps of $\Delta t = 5 \times 10^{-16}$ s. These results suggest that a C_{60} molecule shows a volumetric contraction, rather than an expansion, up to $T \approx 260$ K, and expands only at higher temperatures. Figure 1(b) depicts the corresponding thermal volumetric expansion coefficient, which is defined by $\beta = (1/V)(dV/dT)$.

We find that the thermal volumetric expansion coefficient starts at zero at $T = 0$ K and initially decreases linearly to $\beta \approx -1 \times 10^{-5}$ K^{-1} , which is comparable to the value of -0.9×10^{-5} K^{-1} found in ZrW_2O_8 [9]. The minimum in the $\beta(T)$ curve, corresponding to the

maximum thermal volumetric contraction, occurs at $T \approx 70$ K. Above this temperature, the volumetric contraction of C_{60} slows down. At $T \approx 150$ K, the volume of C_{60} is smallest, and its volumetric contraction turns to an expansion. Further analysis of the changes in the principal axes with temperature showed that among the soft vibration modes, it is the quadrupolar deformation, which keeps the surface area constant, that dominates the thermal contraction at low temperatures. Thermal expansion at higher temperatures results from a bond expansion, which is reflected in a radial breathing mode that changes the surface area of the fullerene.

Next, we investigate the effect of temperature on the volume and length of carbon nanotubes as model one-dimensional objects. Because of their natural abundance among single-wall carbon nanotubes grown by pulsed-laser vaporization [20], we focus on (10, 10) nanotubes [21] in our simulations. Also, nanotubes with a similar diameter are the most likely constituents of “nanotube fleece” (or “bucky paper”), for which initial experimental measurements of thermal expansion have been performed [22]. We considered 50–1500 Å long open-ended segments of an isolated (10, 10) nanotube in order to calculate the effect of temperature on its volume and total length. As in the C_{60} simulations, the nanotube was coupled to a Nosé-Hoover thermostat in our canonical molecular dynamics simulations. Considering an open-ended segment rather than an infinite nanotube with periodic boundary conditions, we avoided introduction of spurious phonon modes and problems due to a fluctuating unit cell size. Since the vibrations of an open-ended segment are altered by the presence of undercoordinated carbon atoms, we ignored the five terminating layers [23] when evaluating the total length and volume of the tube segment.

The estimation of the volume of a deformed nanotube is less trivial than for the C_{60} molecule due to the large number of relevant phonon modes, illustrated in Fig. 2(e)–2(h). We determine the volume of a deformed nanotube as a sum of partial volumes associated with each deformed layer, given by a product of its cross-section area and the distance between adjacent layers. In a deformed nanotube segment, we first determine the center of mass of the relevant layers and use the distance between them as the length. We approximate the cross-section area of each layer by that of a circle with radius r . This radius is given by the average distance of each atom from the center of mass of that layer.

Our results for the response of the nanotube to changing temperature are displayed in Fig. 2. Similar to our results for the C_{60} molecule, data points representing the volume and the length at a particular temperature have been obtained by taking a time average over 10^4 – 10^5 time steps of $\Delta t = 5 \times 10^{-16}$ s after equilibration with the heat bath. We have filtered out high-frequency noise using a simplified Fourier analysis of the total volume and length as a function of time at 0, 200, 400, 800, 1000,

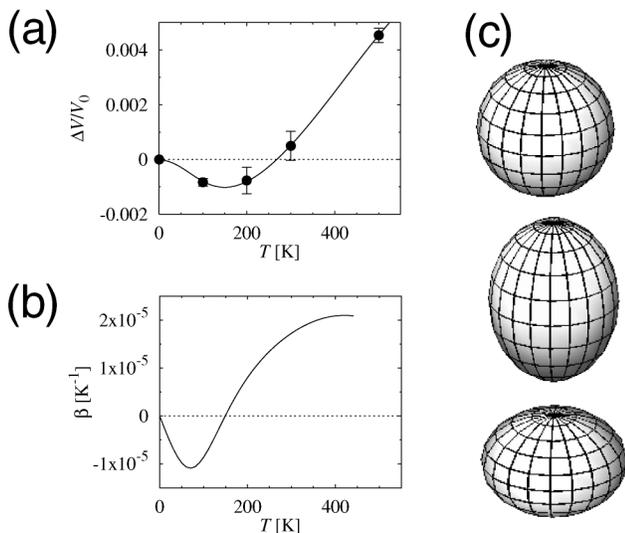


FIG. 1. (a) Relative volume change $\Delta V/V_0$ in a C_{60} molecule as a function of temperature T . (b) Temperature dependence of the thermal volumetric expansion coefficient β . (c) Schematic snapshots of the ellipsoidal deformation mode, responsible for volumetric contraction.

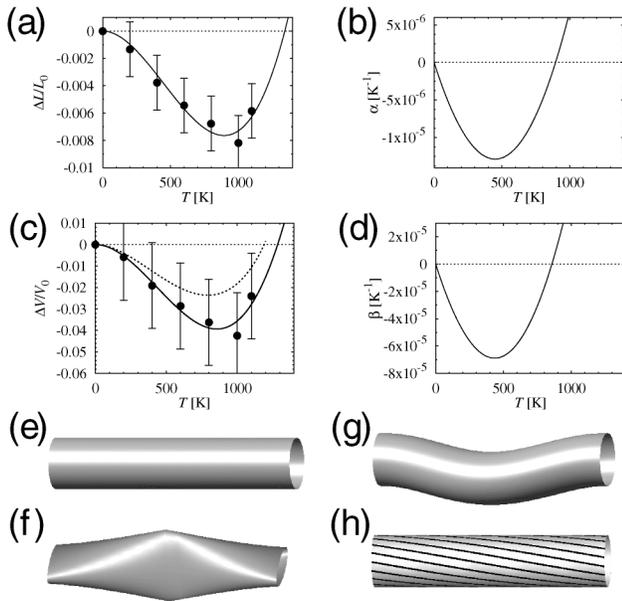


FIG. 2. (a) Relative length change $\Delta L/L_0$ in a (10, 10) carbon nanotube as a function of temperature T . (b) Temperature dependence of the thermal linear expansion coefficient α . (c) Relative volume change $\Delta V/V_0$ and (d) thermal volumetric expansion coefficient β of the (10, 10) nanotube as a function of temperature. Schematic snapshots of selected soft phonon modes that couple strongly to the length and the volume of the nanotube: (e) reference structure of the unperturbed tube, (f) optical pinch mode, (g) transverse acoustic bending mode, and (h) twist mode. The relative contribution of the pinch mode to the volume change is shown by the dashed line in (c).

and 1100 K. The error bars reflect also the additional uncertainty associated with this fitting process.

Our results for the temperature dependence of the tube length, shown in Fig. 2(a), suggest that carbon nanotubes should contract up to very high temperatures close to 1300 K. These findings are in agreement with the observed contraction in bucky paper below room temperature [22]. The solid line is a fit to the same functional form as used in the thermal expansion analysis of graphite [24], which also shows an in-plane contraction at low temperatures. In analogy to the definition of the volumetric expansion coefficient β , the linear thermal expansion coefficient α is defined as $\alpha = (1/L)(dL/dT)$.

Similar to the volumetric expansion coefficient β of C_{60} depicted in Fig. 1(b), the linear expansion coefficient α of a nanotube decreases from its initial zero value at $T = 0$ K and becomes negative. The minimum value in the $\alpha(T)$ curve, corresponding to the maximum thermal contraction, is $\alpha \approx -1.2 \times 10^{-5} \text{ K}^{-1}$ and occurs at $T \approx 400$ K. This is significantly larger than the in-plane graphite value of $-1.3 \times 10^{-6} \text{ K}^{-1}$ at 300 K [5] and comparable to the polyethylene value of $-0.8 \times 10^{-5} \text{ K}^{-1}$ at 200 K [4]. Contraction continues up to $T \approx 900$ K, where α vanishes and the tube length is minimum. Above 900 K, α becomes positive, indicating the onset of thermal expansion, as the anharmonic part of the inter-

atomic potential gains in importance. Above 1300 K, the tube should exceed its initial length at $T = 0$ K.

Our results reveal that not only do nanotubes contract axially, but they also show volumetric contraction up to very high temperatures, due to radial deformations discussed below. As shown in Fig. 2(c), the volume decreases gradually, as the temperature increases from 0 to $T \approx 800$ K. At $T \approx 800$ K, the volume starts expanding again and exceeds its original value at $T \geq 1200$ K. The larger error bars are a consequence of a combined uncertainty in the average tube radius and the length. The volumetric thermal expansion coefficient, presented in Fig. 2(d), decreases from zero to its minimum value $\beta \approx -7 \times 10^{-5}$ at $T \approx 400$ K and then increases to reach zero value at $T \approx 800$ K, corresponding to the smallest tube volume.

In order to understand the origin of thermal contraction, we analyzed our molecular dynamics simulations in terms of normal vibration modes that couple strongly to the length and the volume. In the harmonic regime, there is no change to the bond lengths and the area. Shape changes, resulting from area conserving tube deformations, reduce the mean tube radius and lead to a volumetric contraction. Similar to C_{60} , we focused on the soft modes that do not change the surface area of the reference tube, shown in Fig. 2(e). The significant modes are the pinch mode, the bending mode, and the twist mode, depicted in Figs. 2(f)–2(h), respectively. Whereas short-wavelength modes, such as the pinch mode, can be described in our atomistic molecular dynamics simulations, a description of long-wavelength modes requires long tube segments exceeding our computational resources. To describe the long-wavelength bending and twisting phonon modes, we performed molecular dynamics simulations based on a model assumption of rigid atomic layers that interact according to the energy functional described above.

Our long-wavelength calculations suggest the transverse acoustic bending mode, depicted in Fig. 2(g), to be very soft, as it involves a shear motion that requires a minimum of bond stretching and bending. Our simulations indicate that length contraction due to this mode saturates in (10, 10) tube segments with a length close to 100 Å. We find the bending mode to contribute almost one-third towards the length contraction of a (10, 10) nanotube. Also the soft twisting mode, depicted in Fig. 2(h), can be viewed as a shear mode. We found this mode to be active in the orientational melting within a nanotube rope at low temperatures [25] and to contribute up to $\approx 10\%$ towards the tube length contraction. Since none of these modes affects the tube cross section, their effect on the volumetric contraction is very small.

Our calculations suggest that an important contribution towards the longitudinal contraction, and the dominant contribution towards the volumetric contraction, comes from the optical “pinch” mode, shown in Fig. 2(f). The dashed line in Fig. 2(c) indicates the analytically calculated [26] contribution of a pure pinch

phonon mode to the total volume change. We find that the pinch mode accounts for nearly one-half of the volume change, but only one-third of the total length change.

The relative contribution of the changing cross-section area S and the length L towards the volume change is determined by the decomposition $\Delta V/V_0 = \Delta L/L_0 + \Delta S/S_0 + (\Delta L/L_0)(\Delta S/S_0)$. This expression allows us to extract additional information about the thermal behavior of nanotubes, in particular, the radial thermal expansion coefficient α_r , from the known length and volume changes, presented in Figs. 2(a)–2(d). We find that in the temperature range of interest, the average tube radius should contract. This result agrees with experimental observations [27] but contradicts simulations based on the Tersoff potential [28]. Our numerical value for the radial contraction at low temperatures $\alpha_r \approx -2 \times 10^{-5} \text{ K}^{-1}$ is about 1 order of magnitude larger than x-ray results reported for single-wall nanotube ropes [27], where the dominating pinch mode is likely to be suppressed by intertube interactions. In agreement with the experimental data [27], we expect a volumetric thermal expansion of nanotube ropes due to an increasing intertube distance, in analogy to the volumetric expansion of bulk graphite, which is dominated by the expansion along the c axis.

In summary, we investigated thermal expansion behavior of fullerenes and carbon nanotubes using molecular dynamics simulations. We showed that C_{60} molecules contract volumetrically up to $T \approx 260 \text{ K}$, whereas carbon nanotubes contract in length and volume up to $T \approx 800 \text{ K}$. Among the active vibration modes, we found the ellipsoidal deformation mode to dominate the volumetric contraction of C_{60} . In nanotubes, length contraction is shared by bending, twist, and pinch modes, whereas the volumetric contraction is dominated by the pinch mode. Combining thermal contraction of nanotubes with thermal expansion of a host material may yield composites with a negligible thermal expansion.

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- [1] H. Mavoori and S. Jin, *JOM* **50**, 70 (1998); X. C. Li, J. Stampfl, and F. B. Prinz, *Mater. Sci. Eng., A* **282**, 86 (2000).
- [2] T. Ito, T. Sugauma, and K. Wakashima, *Compos. Sci. Technol.* **60**, 1851 (2000).
- [3] Ryogo Kubo, *Rubber Elasticity* (Kawade Shobo Shinsha, Tokyo, 1946).
- [4] G. K. White and C. L. Choy, *J. Polym. Sci. Polym. Phys. Ed.* **22**, 835 (1984).
- [5] D. P. Riley, *Proc. Phys. Soc. London* **57**, 486 (1945).
- [6] W. C. Morgan, *Carbon* **10**, 73 (1972).
- [7] G. L. Belenkii *et al.*, *Solid State Commun.* **53**, 967 (1985).
- [8] R. Roy and D. Agrawal, *Nature (London)* **388**, 433 (1997).
- [9] T. A. Mary *et al.*, *Science* **272**, 90 (1996).
- [10] H. W. Kroto *et al.*, *Nature (London)* **318**, 162 (1985).
- [11] Sumio Iijima, *Nature (London)* **354**, 56 (1991).
- [12] S. Iijima and T. Ichihashi, *Nature (London)* **363**, 603 (1993).
- [13] G. Y. Tseng and J. C. Ellenbogen, *Science* **294**, 1293 (2001); J. Appenzeller *et al.*, *Microelectron. Eng.* **64**, 391 (2002).
- [14] E. D. Minot *et al.*, *Phys. Rev. Lett.* **90**, 156401 (2003).
- [15] M. Čadek *et al.*, *Appl. Phys. Lett.* **81**, 5123 (2002).
- [16] S. Nosé, *Mol. Phys.* **52**, 255 (1984); W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- [17] J. Tersoff, *Phys. Rev. Lett.* **61**, 2879 (1988).
- [18] D. Tománek and Michael A. Schluter, *Phys. Rev. Lett.* **67**, 2331 (1991).
- [19] W. Zhong, D. Tománek, and G. F. Bertsch, *Solid State Commun.* **86**, 607 (1993); Y.-K. Kwon *et al.*, *Phys. Rev. Lett.* **79**, 2065 (1997); S. Berber, Y.-K. Kwon, and D. Tománek, *Phys. Rev. Lett.* **88**, 185502 (2002); Y.-K. Kwon, D. Tománek, and S. Iijima, *Phys. Rev. Lett.* **82**, 1470 (1999); S. G. Kim and D. Tománek, *Phys. Rev. Lett.* **72**, 2418 (1994).
- [20] A. Thess *et al.*, *Science* **273**, 483 (1996).
- [21] Since the flexural rigidity of a graphene sheet is isotropic, thermal expansion of a nanotube should depend only on its diameter and not on the chiral angle. The increased flexibility of nanotubes narrower than the (10, 10) tube is expected to augment the length contraction we find. Wider nanotubes, on the other hand, cannot bend easily, but show a tendency to collapse radially, augmenting the volumetric contraction.
- [22] Ray H. Baughman and Alex Soldatov (private communication).
- [23] In achiral nanotubes aligned with the z axis, we define the ensemble of atoms with the same z coordinate as a “layer.” In the (10, 10) nanotube, a layer consists of a 20 atom ring along the tube circumference.
- [24] W. N. Reynolds, *Physical Properties of Graphite* (Elsevier, Amsterdam, 1968).
- [25] Y.-K. Kwon and D. Tománek, *Phys. Rev. Lett.* **84**, 1483 (2000).
- [26] Each tube layer in the pinch mode is subject to an elliptical deformation. To calculate the volumetric contraction in this mode, we assumed the circumference C of the elliptical cross section to be constant. In this case, the area S of the ellipse decreases monotonically with increasing eccentricity $t \equiv b/a$, defined as the ratio of its major and minor axes a and b . Making use of the complete elliptic integral of the second kind $E(x)$, the ellipse area is given by $S(t) = (\pi C^2/16)\{t/[E(1-t^2)]^2\}$. Assuming that t changes linearly between t_{\min} and 1 along the axial direction, the total volume V of the deformed nanotube segment of length L changes as $V = \int_0^L dS(t) = L\langle S \rangle$, where $\langle S \rangle = \int_{t_{\min}}^1 dt S(t)/(1-t_{\min})$.
- [27] Y. Maniwa *et al.*, *Phys. Rev. B* **64**, 241402 (2001).
- [28] N. R. Raravikar *et al.*, *Phys. Rev. B* **66**, 235424 (2002).