Wall “thickness” effects on Raman spectrum shift, thermal conductivity, and Young’s modulus of single walled nanotubes

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We demonstrate that at a finite temperature, an effective wall thickness of a single walled carbon nanotube (SWNT) should be $W = W_s + W_d$, where $W_s$ is the static thickness defined as the extension of the outmost electronic orbit and $W_d$ the dynamic thickness due to thermal vibration of atoms. Both molecular simulations and a theoretical analysis show that $W_d$ is proportional to $\sqrt{T}$. We find that the increase of dynamic thickness with temperature is the main mechanism of Raman spectrum shift. The introduction of the dynamic thickness changes some conclusions about the Young’s modulus and reduces the values of thermal conductivity.

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Nanotubes have attracted increasing attention in the last decade due to potential applications in nanoscale electronic, mechanical and thermal devices [1-13]. Depending on the geometrical structure, nanotubes can exhibit fascinating properties, for example, by varying the chiral index $(n,m)$, nanotubes can change from semiconductors to metals. Y-K Kwon et al. [14] studied the thermal contraction effect of fullerenes and carbon nanotube. They find that in nanotubes, the gain in entropy translates into a longitudinal contraction, which reaches a maximum at 800K. Schelling et al. [15] studied the thermal expansion coefficient of carbon nanotubes with empirical bond-order potential. These studies show that the structure of carbon nanotube depends strongly on temperature. In addition to tube radius and length, wall thickness is another important and fundamental structure parameter. It can influence the Young’s modulus and thermal conductivity, two typical physical quantities characterizing the mechanical and thermal properties of nanotubes. These two quantities depend crucially on the cross-section of the tubes. Therefore, any ambiguity in calculating the thickness will cause an error in these quantities, and might result in misleading conclusions. Unfortunately, up to now, to our best knowledge, a unified and unique way to define the thickness of nanotube does not exist even though some discussions have been made [16-17]. In the existing literature, a so called static thickness, defined as the extension of the outmost electronic orbit, is used as the wall thickness. This static thickness is temperature independent.

In this paper, we will demonstrate, with numerical evidence and theoretical arguments, that at a finite temperature the static thickness alone cannot be used as the wall thickness of SWNTs. One needs to introduce a dynamic thickness to reflect the thermal effect.

To carry out the measurement of wall thickness, a camera with resolution on the atomic scale is supposed to be put along the axis of SWNT. The wall thickness is determined by measuring the width of the wall image. If the camera shutter is in femtosecond (fs), a clear picture will be obtained, and the wall thickness from this image is the instantaneous static thickness; but if the shutter time is longer than fs, such as in picosecond (ps) scale, the effect of the thermal vibrations of atoms will appear, the wall image becomes blurry and the wall appears much thicker. We know that in most physical process such as heat conduction along the tube, the time is much longer than ps, so the widening of the wall thickness from thermal effect can not simply be ignored. We call the contribution from this part dynamic thickness and denote it as $W_d$. The wall thickness should be $W = W_s + W_d$. Thus, in calculating any relevant physical quantity, such as Young modulus and the thermal conductivity etc, one should use the effective thickness $W$ instead of the static thickness $W_s$. We will demonstrate this with numerical simulations that the dynamic thickness is a natural structure parameter and affect many physical properties such as Raman spectrum shift, Young’s modulus and thermal conductivity.

We begin our discussion by studying the radial distribution of SWNT at different temperatures. The results are obtained from molecular dynamics (MD) simulations in which the Tersoff empirical bond order potential [16] is used. The Hamiltonian of the carbon SWNT is:

$$H = \sum_i \left( \frac{p_i^2}{2m_i} + V_i \right) , \quad V_i = \frac{1}{2} \sum_{j,j\neq i} V_{ij}$$  

where $V_{ij} = f_c(r_{ij})[V_R(r_{ij}) + b_{ij}V_A(r_{ij})]$ is the Tersoff empirical bond order potential. $V_R(r_{ij})$ and $V_A(r_{ij})$ are the repulsive and attractive parts of the potential, re-
In our calculations, three armchair-type SWNTs with different diameters, (5,5), (10,10) and (15,15) are simulated, each contains 500, 1000 and 1500 atoms, respectively. For a given temperature one million steps are used for equilibration and over 30,000 simulation steps are used to calculate the radial distribution. The time step is 0.8 fs.

respectively, and \( f_c(r) \) depending on the distance between atoms. \( b_{ij} \) are the so-called bond parameters depending on the bounding environment around atoms \( i \) and \( j \) they implicitly contain many-body information. Tersoff potential has been used to study thermal properties of carbon nanotubes successfully. For detailed information, see Ref. [13].

In the MD simulations, the carbon atom is treated as a mass point of zero size. The carbon atom vibrations contain two parts: motion parallel and perpendicular to wall. The vibrations perpendicular to the tube wall will introduce a time dependent SWNT radius distribution. In our calculations, three armchair-type SWNTs with different diameters, (5,5), (10,10) and (15,15) are simulated, each contains 500, 1000 and 1500 atoms, respectively. For a given temperature one million steps are used for equilibration and over 30,000 simulation steps are used to calculate the radial distribution. The time step is 0.8 fs.

TABLE I: Dynamic thickness (second column) of three types of nanotubes at room temperature compared with different static thickness used in different models (columns 3-5).

| Tube  | \( W_d/W_s \) | \( W_s \) | \% difference | \( W_d \) | \% difference |
|-------|---------------|-----------|---------------|-----------|---------------|
| (5,5) | 0.115 Å       | 16%       | 1.44 Å        | 8%        | 3%            |
| (10,10)| 0.278 Å      | 40%       | 0.304 Å       | 20%       | 8%            |
| (15,15)| 0.304 Å      | 43%       | 0.346 Å       | 21%       | 9%            |

In Figure 1, we show the radial distribution of (5,5) SWNT, thermal expansion of the radius and the temperature dependence of dynamic thickness for (5,5) and (10,10) nanotubes, respectively. The radius distribution is well represented by a Gaussian distribution. The center of the distribution is the average radius of a carbon nanotube at the corresponding temperature, and the width of the distribution is defined as the dynamic thickness, \( W_d \), of SWNTs. From Figure 1 we can see that the dynamic thickness increases with temperature. The reason is that dynamic thickness arises from the thermal vibration of atoms. As the temperature increases, the amplitude of thermal vibration increases. \( W_d \) versus temperature is drawn in Figure 1(c) in double logarithmic scale, which indicates that \( W_d = C T^\alpha \). For both (5,5) and (10,10) SWNT, \( \alpha \approx 0.49 \), which agrees very well with the following theoretical analysis.

In a SWNT, each carbon atom has three nearest neighbor carbon atoms which are bond together by covalent bonds. The central carbon atom vibrates perpendicular to the plane determined by its three nearest neighbors (see Fig. 2). If the central atom deviates from its equilibrium position, the force arising from its nearest neighbors will drag it back. Within the first order approximation, this vibration can be treated as an harmonic one with an effective spring constant \( k_c \). If the amplitude of each oscillator is \( \Delta R \), then \( \langle \Delta R^2 \rangle \approx 2 k_B T/k_c \), where \( k_B \) is the Boltzmann constant and \( T \) temperature. \( k_c \) is the effective spring constant for the thermal vibration and can be calculated as we will show below. Thus the average width caused by the thermal vibration is

\[
W_d \approx 2 \sqrt{\langle \Delta R^2 \rangle} = 2 \sqrt{\frac{2 k_B T}{k_c}}^{1/2}. \quad (2)
\]

The calculated dynamic thickness \( W_d \), for three different nanotubes at room temperature is shown in Table I. These values are compared with the static thickness of the corresponding nanotube used in previous studies [12, 13, 17] (columns 3-5). Dynamic thickness increases as the radius increases, while the increase decreases for large tubes. This arises from their different curvatures. Fig. 2 shows the detailed structures of one carbon atom with its three nearest neighbor atoms in (5,5) and (10,10) SWNTs. The SWNT can be seen as...
a wrapped-up graphite sheet. In a graphite layer, four carbon atoms share a common plane; while in a SWNT, the central carbon atom is not in the same plane with its three nearest neighbors. The distance between the atom and the plane determined by its three nearest neighbor atoms is represented by $h$. $h$ changes with tube diameters and is proportional to the curvature of the tube wall, thus, the larger the tube radius the smaller $h$ becomes (see Fig. 2). For (5,5) SWNT, $h$ is about 0.15 Å, and for (10,10) SWNT, $h$ is about 0.07 Å. Each carbon atom in a SWNT is considered to be connected with its nearest neighbors through the covalent bond $K^c-c$. $K^c-c$ is the effective spring constant for the covalent bond. It is determined by the atomic interactions. $K^c-c$ is larger for strong covalent bond than for weak bond. It can be shown approximately that the effective spring constant for the thermal vibration is, $k_e \approx K^c-c h^2$. Therefore, at a given temperature, the SWNTs with larger radius have smaller $h$, and larger dynamic thickness.

The $\sqrt{T}$ comes from the MD simulation results. This relation can also be deduced from the simple harmonic model we describe above. The perfect consistent between the simple harmonic model and the numerical simulation demonstrate that in the temperature range we study ($< 500K$), the vibration of carbon atom in SWNT is harmonic, this is consistent with other theoretical study that only when $T > 800K$ the anharmonic effect will appear\cite{14}. The MD simulations is also performed for a zigzag tube and similar effect of dynamic thickness is found. So the dynamic thickness is a natural structure parameter to all nanotubes. In fact, from the analysis above, we can see that the dynamic thickness comes from the vibrational of atom, so it exists in all types of nanotubes.

There is not a unified view on the static thickness. For example, 0.617–0.77 Å was used in a continuum mechanics model\cite{12,16}, 1.44 Å\cite{17} was used for the diameter of carbon atom, and 3.4 Å\cite{18} the inter-layer separation of graphite, was also used as the wall thickness. These different thickness are static thickness only, while for effective thickness, one should include the dynamic thickness. From Table I, one can see that at room temperature, even for the smallest dynamic thickness of (5,5) SWNT, the dynamic thickness varies between 3% to 16% of the static thickness; while for bigger (15,15) SWNT, the dynamic thickness can be as high as 10% ~ 40% of the static thickness. Moreover, the dependence of thermal properties of SWNT on temperature are important problems in carbon nanotubes studies\cite{4,5,6,7}. Therefore, when a temperature-independent static thickness is used to calculate the thermal conductivity, the information about the temperature dependence in thermal conductivity will be lost. The high ratio and strong temperature dependence show that the dynamic thickness can not be ignored in the wall thickness calculation. Ignorance of the dynamic thickness will induce a large error in calculations of relevant properties such as Young’s modulus and thermal conductivity. In the following we shall use the increase of the wall thickness due to the thermal effect to explain the Raman spectrum shift, a correction of thermal conductivity and Young’s modulus, respectively.

**Raman spectrum shift.** In high-temperature studies of Raman-active modes in SWNTs, it is found that the Raman peak frequency shifts toward lower frequency as temperature is increased\cite{14,20}. In an attempt to describe this shift quantitatively, a temperature coefficient of Raman frequency

$$\alpha_\omega = \frac{d\omega}{dT}$$

was introduced\cite{19}. It is observed experimentally that $\alpha_\omega = -2.47 \times 10^{-5}K^{-1}$ for a SWNT with diameter of 1.34nm which is close to a (10,10) SWNT\cite{19}. This frequency shift has been explained as the diameter thermal expansion of SWNTs and the softening of the intra-tubular bonds\cite{19}. However, the molecular dynamics simulation in Ref \cite{19} gives a much larger value of $\alpha_\omega (= -5 \times 10^{-5})$. Here we attribute the Raman frequency shift to the thermal expansion of the radius, $\alpha^R_\omega$, and the increase of the thickness, $\alpha^{W_d}_\omega$. As we shall see, we obtain results which correspond more closely to experiments.

After taking into account the dynamic thickness, the Raman radial breathing frequency $\omega$ goes as $1/((R + W)/2)$, where $R$ is the radius of tube and $W$ is the wall thickness of tube. As $W$ is independent of temperature, the temperature coefficient can be written as:

$$\alpha_\omega \approx - \frac{1}{R + W/2} \left( \frac{dR}{dT} \frac{1}{2} \frac{dW}{dT} \right) = \alpha^R_\omega + \alpha^{W_d}_\omega.\quad (4)$$

Generally speaking, the contribution from thermal expansion of the radius, $\alpha^R_\omega$, is about one order of magnitude smaller than that one from the increasing thickness.
ductivity is always smaller than the experimental one. In the worst case, when $W_d/W_s \sim 0.4$, the true thermal conductivity is approximately 70% of the measured value. In other words, the thermal conductivity in SWNTs calculated by using static thickness, is somehow exaggerated. In Fig. 4 we show the thermal conductivity $\kappa$ and $\kappa_e$ for (5,5) nanotubes with different static thicknesses. Fig 4(a) corresponds to thermal conductivities calculated with $W_s = 0.7\,\text{Å}$ while Fig 4(b) with $W_s = 1.44\,\text{Å}$. These calculations clearly demonstrate that the correction of the dynamic thickness is very significant, in particular in high temperature regime.

*Young’s modulus.* Another important property of nanotubes is the Young’s modulus which determines its mechanical property. In Yakobson’s calculation with (7,7) SWNT $W_s = 0.7\,\text{Å}$ was used, the Young’s modulus calculated was 5.5 TPa; while Lu obtained 0.97 TPa with $W_s = 3.4\,\text{Å}$. The difference can be removed if they use the same wall thickness, thus these two Young’s modulus are in fact consistent with each other. One shall note that if we only discuss the Young’s modulus of the same tube, the wall thickness is not very important, but if we compare the Young’s modulus of different tubes, the effect of dynamic wall thickness will be very impor-
Young’s modulus, and thickness of both tubes at room temperature (see table 1), and \( W_s = 3.4\text{Å} \) as the static thickness, one obtains the Young’s modulus for (5,5) and (10,10) SWNT, respectively. From this result, it is concluded that the Young’s modulus is insensitive to the radius of the SWNT. However, if we notice that at the same temperature, the wall thickness is not uniform for (5,5) and (10,10) SWNT, then the conclusion is different. By using the dynamic thickness of both tubes at room temperature (see table 1), and \( W_s = 3.4\text{Å} \) as the static thickness, one obtains the Young’s modulus, 0.939TPa and 0.899 TPa for (5,5) and (10,10), respectively. The smaller SWNT has a slightly larger Young’s modulus than the larger SWNT. If the smaller \( W_s \) is used, then the dynamic thickness correction would be even more obvious.

We would like to point out that, in experiments, it is impossible to measure directly the thickness of SWNT. The thickness is indirectly inferred from the measurement of other properties, such as the Raman frequency. The wall thickness is an “effective thickness”, namely the dynamic thickness is already included. More recently, a hardness transition was observed by changing pressure on nanotube\(^21\). In this study, it is obtained, from room- temperature MD simulations, that an effective wall thickness is about 0.66Å, which should already include finite temperature effect. In the current paper, we split the effective wall thickness into static thickness and dynamic thickness so as to give the wall thickness a clear physics picture.

In summary, we have introduced a dynamic thickness, \( W_d \), to SWNTs. Unlike static thickness, which is independent of temperature, the dynamic thickness is temperature dependent and increases with temperature, \( T \), as \( \sqrt{T} \). At room temperature, \( W_d \) is comparable to the carbon atom diameter, and thus cannot be ignored in calculating the thermal conductivity or the Young’s modulus for different tubes and/or at different temperature. The introduction of dynamic thickness can alter previous conclusions wherein only static thickness is used. Moreover, we have found that the increase of dynamic thickness with temperature is the main mechanism of the Raman spectrum shift. Our numerical calculations agree very well with the experiment data. The dynamic thickness has more significant effects when the static thickness is small, such as in SWNTs. If the static thickness is large, the effects comes from dynamic thickness will decrease. And for certain measured properties, the effects of dynamic thickness will be weakened because of the time averaged in measurements. We believe that dynamic thickness is a natural structure parameter with real physical effect for nano scale systems and can be measured experimentally such as in the Raman frequency shift.

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