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LATTICE SPECIFIC HEAT OF CARBON NANOTUBES

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The lattice specific heat in carbon nanotubes is evaluated within the microscopic model proposed by Mahan and Jeon, published in the Physical Review B, in 2004. Phonons are considered for single wall carbon nanotubes in armchair configuration. As expected, low temperature and high temperature regions show different behaviour of specific heat. Carbon nanotubes are also displaying a very interesting lattice transport depending on the tube diameter, with high thermal conductivities for small diameters.

Keywords: *carbon nanotubes, phonons, specific heat*

Introduction

Carbon nanotubes are nanostructures with remarkable electronic and mechanical properties. As soon as they were discovered, their potential applications stimulated several theoretical and experimental studies. Electronic and lattice properties, such as specific heat and thermal transport coefficients, in carbon nanotubes [1–6] and nanowires [7, 8] have been deeply investigated. Measurements with microfabricated devices show very interesting thermal transport properties in nanosystems [4], in particular the possibility of a remarkably high conductance. Among the thermal properties of nanotubes, it was recently pointed out the possibility to create a device for thermal rectification. This is a nanoscale system, obtained by mass loading high-thermal-conductivity carbon and boron nitride nanotubes, which displays an asymmetric axial thermal conductance, and then a rectifying action for heat current [9, 10]. For all thermal applications, researches on stability and thermal decomposition, with thermal analytical methods such as thermo-gravimetry and differential scanning calorimetry are quite important [11–13].

Measurements show that the thermal conductivity of carbon nanotubes increases as the tube's diameter decreases. At low temperatures, the thermal conductance of carbon nanotube bundles follows the power law T^{α}, where T is the temperature, with an exponent α less than 2 (around 1.5). This fact suggested that the thermal transport in the bundles is like that of a quasi-one-dimensional system. The same for specific heat: the measured specific heat differs from that of graphene and graphite, especially in the low temperature region, where quantization of the phonon band structure is observed.

The more evident property of thermal conductivity in carbon nanotubes is its increase as the carbon nanotube diameter decreases. A totally different behaviour is observed in nanowires, where the thermal conductivity is reduced if the wire diameter is small. In nanowires, exponent α in the power law T^{α} ranges from 1 to 3, increasing with wire cross section [7].

In the framework of a recently proposed lattice model [14], we will discuss in this paper the thermal properties of the phonon system displayed by a single wall carbon nanotube in the armchair configuration. In [14], the authors deeply investigate the role of symmetry rules, pointing out that the violation of these rules destroys flexural modes. They did not discuss the lattice thermal properties of the model. The specific heat is here estimated to discuss and see if the Mahan and Jeon model is able to provide low-temperature behaviour in agreement with experimental data. A discussion on thermal conductivity is following.

Phonons

A single wall carbon nanotube is a sheet of graphene rolled up along the line connecting two lattice points, into a seamless cylinder. According to the chosen line, a carbon tube can be achiral (zig-zag or armchair) or chiral. The seamless condition brings to continuity conditions on tube surface for the phonon vibrations and for the electron distribution. Several references discuss the behaviour of electrons and electronic transport in nanotubes [15–17] and phonon dispersions [18, 19].

Here, to study the lattice thermal properties, we follow the lattice model proposed by Mahan and Jeon [14]. These authors considered a 'spring and mass'

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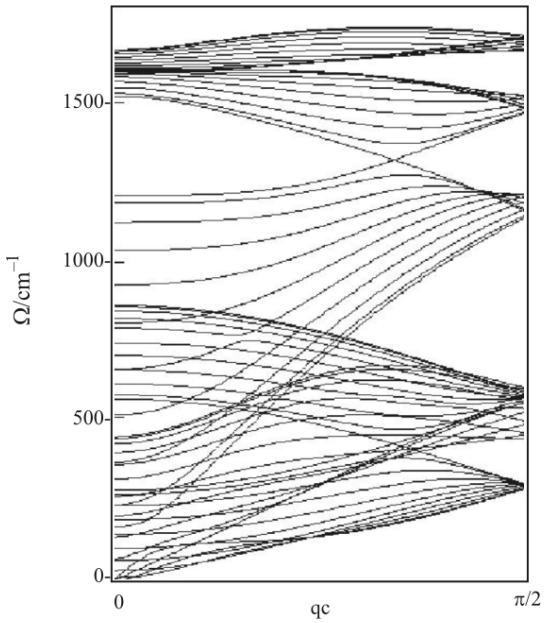

Fig. 1 Phonon frequency ω as a function of wavenumber q_z for an armchair tube (10,10). Dispersions are evaluated following [14]

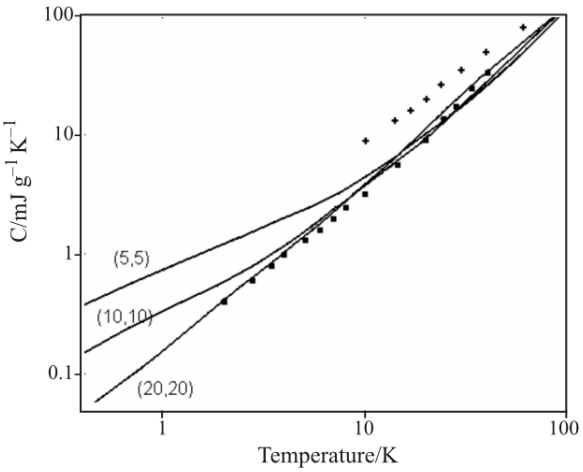

Fig. 2 Specific heat as a function of temperature for single wall armchair nanotubes (5,5), (10,10), (20,20), compared with experimental data of [1, 6]

model with first and second neighbour bonds, and introduced a radial bond bending term in the potential, to include the curvature effect of the surface. The potential they propose satisfies the symmetry rules imposed by the cylindrical geometry. For the details of armchair nanotube lattice, Figs 1 and 2 [14].

An armchair (n,n) tube with diameter R, has n atoms A and n atoms B along the circumference: each carbon atom A (or B) is connected with three nearest neighbour atoms B (A) at a distance a. Then, two integer numbers are required to describe the lattice site (l,m). l denotes the position of lattice site in the direction of nanotube axis and m, ranging from 0 to n–1, gives the position of sites A and B on the circumference. Phonons in nanotubes have then two quantum numbers, one from the quantization of wavevectors in the direction of tube axis, the other due to a quantization around the circumference.

Let us call L the length of the tube, N the total number of lattice points, M the atomic mass and ω the angular frequency for a given wave vector q_z in the axis direction, for given values of polarization p and quantum parameter n.

According to [14], phonon dispersions are evaluated. Oscillations of the lattice sites are travelling along the z-axis and, as found with the continuous models of hollow tubes, four acoustic modes are displayed. Two of them are the twist mode in tangential direction and the longitudinal stretching mode in the z-direction. The other two acoustic modes are the flexural oscillations. Flexural modes are also observed in wires [20]. The lower breathing mode in radial direction has a finite frequency for q_z=0, due to the lattice curvature, as observed [19].

Three interactions, representing first neighbour, second neighbour and radial bond-bending forces, are used in this lattice model: their contributions are weighed with relative coefficients r_j (r_1=1.0, r_2=0.06, r_3=0.024, respectively) [14]. Figure 1 shows the angular frequency for an armchair (10,10) carbon nanotube, as a function of the reduced wavenumber cq_z, where parameter c is equal to $\sqrt{3}a/2$. Here we use a scale factor Φ_0 for the potential (Φ_0=4·10^{20} g cm^{-2} s^{-2}), the value of which is chosen to give an acoustic longitudinal velocity of 16.7 km s^{-1} and acoustic twist velocity of 9.1 km s^{-1} [14]. The lattice constant is a=1.42·10^{-8} cm.

Lattice specific heat

The lattice heat capacity is then given by the following expression:

$$C=\frac{\hbar^2}{k_B T^2}\sum_{p,n}\frac{L}{2\pi}\int dq\omega^2 b_0(1+b_0) \qquad (1)$$

where b_0 is the unperturbed phonon distribution. The specific heat per atom is obtained, dividing Eq. (1) by the number of lattice sites. If we imagine a very long nanotube, integral in Eq. (1) is a very good substitute for the sum on all the values of the lattice wavenumber along the z-direction. Sums on polarization and eigenvalue number remain. Phonon frequency is according to [14].

Figure 2 shows the behaviour of specific heat as a function of the temperature for three armchair tubes, (5,5), (10,10) and (20,20), in comparison with experimental data [1, 6]. As observed by Popov [21], two distinct behaviours at low and high temperatures are clearly displayed by tube (5,5) and (10,10): they are due to phonon frequency quantization.

Heat transport

Phonon heat transport can be easily approached in the framework of the time relaxation approximation. The thermal conductivity due to phonons is linked to the perturbed phonon distribution b:

$$b-b_0=-\psi\frac{\partial b_0}{\partial(\hbar\omega)} \tag{2}$$

where b_0 is the equilibrium phonon distribution and Ψ a deviation function. The linearised Boltzmann equation for a solid subjected to a thermal gradient, written in the relaxation time approximation as [22, 23]:

$$k_B T\nu\nabla T\frac{\partial b_0}{\partial T}=-\frac{1}{\tau}\Psi b_0(1+b_0) \tag{3}$$

where ν is the phonon group velocity and τ and a phonon relaxation time. Equation (3) is a very rough estimation of Ψ.

The heat current density can be defined, for a nanotube with section S and length L, as:

$$U=-\frac{1}{2\pi S}\sum_{p,n}\int dq_z\hbar\omega\nu\Psi\frac{\partial b_0}{\partial(\hbar\omega)} \tag{4}$$

where the sum on all the lattice wavenumbers along z-direction is evaluated with the integral. A thermal current exists along the tube z-axis, if the nanotube is subjected to a gradient $\nabla T=\partial T/\partial z$. ν is the phonon velocity in the z-direction. The thermal conductivity is defined as that parameter κ joining the heat current with the thermal gradient: $U=-\kappa\partial T/\partial z$.

If the phonons are subjected to boundary scattering only, that is to the scattering occurring at the ends of the tube, the relaxation time is given by $\tau=L/\nu$ [23]. Thermal conductivity turns out to be:

$$\kappa=\frac{\hbar^2 a^3 L}{2\pi k_B T^2 S}\left(\frac{\Phi_0}{M}\right)^{3/2}\sum_{p,n}\int d\varsigma\,\overline{\omega}^2\overline{\nu}b_0(1+b_0) \tag{5}$$

where

$$\omega=a\sqrt{\frac{\Phi_0}{M}}\overline{\omega};\ \varsigma=cq_z;\ \overline{\nu}=\left|\partial\overline{\omega}/\partial\varsigma\right| \tag{6}$$

Equation (5) is the kinetic model of thermal conductivity, if $\overline{\nu}$ is assumed equal to the mean value of the phonon velocity.

To compare with experimental data reported in [5] and obtained measuring the thermal conductivity of single carbon nanotubes, the integer n is put equal to 150: then the armchair tube diameter is 14 nm, as in experiments. To have an agreement with experimental data, the nanotube length L must be equal to 6.2 μm. Thermal conductivity from Eq. (5) and experimental data are shown in Fig. 3. The three curves in this figure are given for different values of tube diameter: thermal conductivity is strongly increased by reducing the diameter. Data on the thermal conductivity of single nanotubes are rare: recent data are in [24], confirming a conductivity of the nanotube which increases as its diameter decreases.

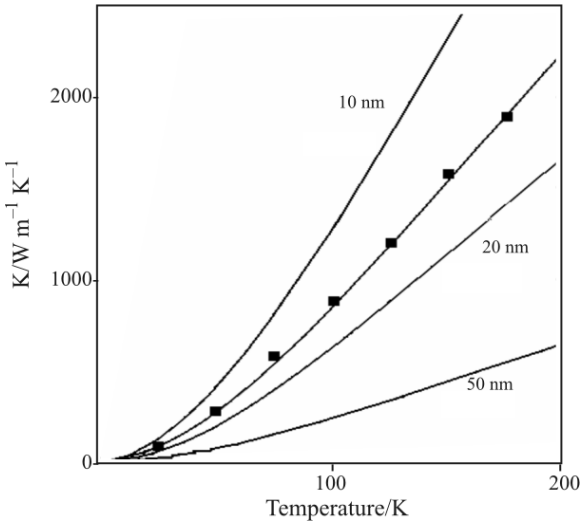

Fig. 3 Thermal conductivity as a function of temperature for a single wall nanotube with diameter 14 nm. ■ – Experimental data are from [5]. Curves refer to different values of diameter

The calculation we proposed is only a very rough estimate of thermal transport. A rigorous calculation of thermal conductivity must consider normal and umklapp three-phonon scatterings [25] and more details on phonon boundary scattering: both issues are very hard to discuss with a lattice model. Of course, Molecular Dynamics simulations can give better performances in a more rigorous framework.

Curves in Fig. 3 are following the law T^α in the temperature range between 20 and 40 K, with $\alpha=1.75$. Other experimental data have been collected from bundles containing several nanotubes, all with parallel axes, in the hexagonal packing. Two bundles formed with tubes of different diameter (10 and 148 nm) have the experimental outputs of [4]. In this reference, a behaviour T^α with $\alpha=1.5$, is deduced from the experimental points. Thermal conductivity is strongly reduced in the nanotube bundles, if compared with the values obtained in measurements on single nanotubes. With Eq. (5), to obtain the experimental values of [4], we must use a short mean free path L of about 25 nm.

Of course, if the nanotubes are packed in bundles, new phonon dispersions and phonon scattering mechanisms arise. [6] shows how the hexagonal packing provides collective vibration modes. Moreover the nanotubes in the bundle can have different diameters, and this is another source of supplementary phonon scattering processes.

A last comment on the model of Mahan and Jeong concerns the four acoustic modes that it is displaying. Below 1 K, one-dimensional phonon transport is possible, in nanowires and nanotubes. At the low temperature regime, dominated by ballistic massless phonon modes, the phonon thermal conductance of a one-dimensional quantum wire is quantized, the quantum of thermal conductance being $\pi^2 k_B^2 T/(3h)$ where h is Planck's constant [7, 26].

Following the Landauer approach, it is possible to obtain the ballistic thermal conductance G, as in [26] (the conductance G obtained for a diffusive regime fails in very low temperatures). The Landauer approach gives the thermal conductance as:

$$G=g\pi^2 k_B^2 T/(3h) \quad (7)$$

where g is the number of acoustic phonons. Acoustic modes are the channels through which the heat is transferred through a bridge (nanotube or nanowire) from a reservoir to another. Any model of the bridge, nanotube or nanowire, must then involve no less than four acoustic modes.

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