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A THEORETICAL EVALUATION OF TEMPERATURE DEPENDENT THERMAL CONDUCTIVITY OF CARBON NANOTUBE

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ABSTRACT

Using the theoretical formalism of J. Hone (Dekker encyclopedia of Nano science and Nanotechnology, 2004), we have evaluated the temperature dependent thermal conductivity of isolated SWNT, 2D-graphene sheet, 3D-graphite and single MWNT. From these evaluations, it shows that the thermal properties of carbon nanotubes are dominated by phonons. The results also show 1-D quantization of phonon band structure. Our theoretical results indicate that nanotube composite materials may be useful for thermal management applications.

Key words: 1-D Quantization of phonon band structure, 2D-Graphene sheet, 3D-Graphite, Umklapp process, Nanowires, Power law, Relaxation time approximation, Ballistic 1-D channel.

INTRODUCTION

Carbon-based materials (diamond and in-plane graphite) display the highest measured thermal conductivity of any known materials at moderate temperatures[1,2]. In graphite, the thermal conductivity is generally dominated by phonons and limited by the small crystalline size within a sample. Thus the apparent long-range crystalline of nanotubes has led the speculation that the longitudinal thermal conductivity of nanotubes could possibly exceed the in-plane thermal conductivity of graphite. The thermal conductivity of graphite is generally dominated by phonons and because of long phonon mean free-path in-plane thermal conductivity of graphite together with diamond has the highest thermal conductivity of known materials. The reason for very high thermal conductivity follows from the very high velocity of sound based on kinetic theory arguments and relates to very

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high Young's modulus of carbon nanotubes. Thermal conductivity increases as the tube diameter decreases. At low temperature thermal conductance of the carbon nanotubes bundles follows the power law T^{α} where T is the temperature and α is an exponent. The value of α is 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 is true for specific heat. The measured specific heat differs from that of graphene and graphite, especially in the low temperature region, where the quantization of phonon band structure is observed.[3] The more evident property of thermal conductivity in carbon nanotube is its increase as the carbon nanotube diameter decreases. A totally different behavior is observed in nanowires, where the thermal conductivity is reduced if the wire diameter is small. In nanowires, exponential α in the power law T^{α} ranges from 1 to 3 increasing from wire sections[4].

Measurements of the temperature dependent thermal conductivity k(T) for an individual MWNTs (14 nm diameter)[5] show very high value of k(T) more than 3000 WmK^{-1} comparable to graphite (in plane). Therefore, one needs a small diameter tubes, probably individual SWNTs to exhibit thermal conductivity greater than that of graphite.

Mathematical formulae used in the evaluation

In general thermal conductivity k is a tensor quantity but one considers only the diagonal elements.

$$K_{zz} = \sum C v^2{}_z \tau \qquad \ldots(1)$$

where C is the specific heat and v_z and τ are group velocity and relaxation time of a given phonon state. At low temperature ($T << \Theta_D$), the relaxation time is determined by scattering off fixed impurities, defects, sample boundaries etc. and is roughly constant. Therefore, in ordinary materials, the low temperature thermal conductivity has the same temperature dependence as the specific heat. However, in anisotropic materials this relationship does not strictly hold. Because the concentration of each state is weighted by the scattering time and the square of velocity, the thermal conductivity preferentially sample state with high v and τ. For example, in graphite, the thermal conductivity parallel to the basal planes is only weakly dependent on the interlayer phonons. In SWNTs bundles, κ(T) depends on the on-tube phonons rather than the inter tube mode.

The thermal conductivity due to phonon is limited to the perturbed phonon distribution b given as –

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

Where b_0 is the equilibrium phonon distribution and ψ is a deviation function. The linearzied Boltzmann equation for a solid subjected to thermal gradient written in the relaxation time approximation, turns out to be[6,7] –

$$K_\beta T v \nabla T \frac{\partial b_0}{\partial T} = -\frac{1}{\tau}\psi b_0(l + b_0) \quad \ldots(3)$$

Where v is the phonon group velocity and τ is relaxation time. The heat current density U is defined for nanotube with volume Ω = SL, where S is the section and L is the length. The expression of U is given by –

$$U = -\frac{1}{2\pi S}\sum_{p,n}\int dq_z \hbar\omega v\psi \frac{\partial b_0}{\partial(\hbar\omega)} \quad \ldots(4)$$

where the sum on all the lattice wave numbers along the z-direction are evaluated with an integral. A thermal current exists along the tube z-axis, if the nanotube is subjected to a gradient $\nabla T = \frac{\partial T}{\partial z}$. V is the phonon velocity in the z-direction. The thermal conductivity is defined as the parameter κ joining the heat current with the thermal gradient

$$U = \kappa \frac{\partial T}{\partial z} \quad \ldots(5)$$

If the phonons are only subjected to boundary scattering, that is the scattering occurring at the end of the tube, the relaxation time is given by τ = L/v. the thermal conductivity turns out to be –

$$\kappa = \frac{\hbar^2 a^3 L}{2\pi K_\beta T^2 S}\left(\frac{\phi_0}{M}\right)^{\frac{3}{2}}\sum\int d\xi \bar{\omega}^2 \bar{v} b_0(l + b_0) \quad \ldots(6)$$

Where $$\omega = a\left(\frac{\phi_0}{M}\right)^{\frac{1}{2}}\bar{\omega}, \xi = cq_z, \bar{v} = \left|\frac{\partial\bar{\omega}}{\partial\xi}\right| \quad \ldots(7)$$

Equation (6) is the kinetic model of thermal conductivity, if $\bar{v}$ is assumed equal to the mean value of the phonon velocity. For thermal conductivity of low-dimensional system i.e for a 1-D ballistic electronic channel, the electronic conductance is quantized with a universal value[8] of –

$$G_0 = \frac{2e^2}{h} \quad \ldots(8a)$$

Similarly for a single ballistic 1-D channel, the thermal conductance is independent of materials parameters and there exists a quantum of thermal conductance, which is linear in T.

$$G_{eh} = (\frac{\pi^2 K^2{}_\beta}{3h})T \quad \ldots(8b)$$

Conditions for observations of this quantum were first examined in detail by Rego and Kirezenow[9], using lithographically defined nano structure. Schwab et al.[10] confirmed this value experimentally.

At high temperatures three phonons Umklapp scattering begins to limit the phonon relaxation time. Therefore, the phonon thermal conductivity displays a peak and decreases with increasing temperature. Umklapp scattering requires production of phonon beyond the Brillion zone boundary: because of the high Debye temperature of diamond and graphite. The peak in the thermal conductivity of these materials is near 100 K, significantly higher than most of the materials. In less crystalline forms of graphite, such as carbon fibers a peak in κ(T) occurs at higher temperatures because defect scattering remains dominant over umklapp scattering at higher temperatures[11]. In low dimensional systems, it is difficult to conserve both energy and momentum for umklapp process[12], so it may be possible that umklapp scattering is suppressed in nanotube relative to 2D or 3D forms of carbon.

A measurement of κ(T) yields the combined contribution to the electrons and phonons. However, a simultaneous measurement of the electrical conductivity б provides a measure of electron conductivity κ_e from the Wiedemann-Franz law[11] –

$$\frac{\kappa_e}{\sigma T} = L_o = 2.45x10^{-8}(\frac{V}{K})^2 \quad \ldots(8c)$$

In this way, the phonon contributions can be deduced by subtracting the electronic contribution from the total measured thermal conductivity.

RESULTS AND DISCUSSION

In this paper, we have theoretically evaluated the temperature dependent thermal conductivity κ(T) of isolated SWNT, 2D graphene sheet, 3D-graphite and single MWNT. The evaluation has been performed by the theoretical formalism of Hone[13]. In Table 1, we

have shown the evaluated results of temperature dependent thermal conductivity of SWNT for different diameters 10 nm, 20 nm and 50 nm. The evaluated results were compared with the thermal conductivity of 14 nm diameter. In the experimental data[14], they obtained the thermal conductivity of single carbon nanotubes, integer n and put equal to 150 the armchair tube diameter is 14 nm. Now, to have an agreement with experimental data, the nanotube length L must be equal to 6.2 μm. Our results are shown in Table 1.

Table 1: An evaluated results of temperature dependent thermal conductivity κ(T) [W/mK] for a single wall nanotube of different diameter. Results were compared with nanotube of diameter 14 nm

Temperature T (K)	Thermal conductivity κ(T) [W/mK]			
	d = 10 nm	d = 20 nm	d = 50 nm	Expt. 14 nm
5	70.2	38.6	10.8	40.2
10	106.8	58.5	18.9	67.8
50	224.9	128.5	28.6	145.2
60	286.7	175.2	32.5	190.5
80	332.8	220.5	50.6	240.6
100	503.5	314.8	62.2	330.5
120	670.8	406.5	89.5	412.8
140	835.2	517.8	120.8	525.2
160	960.6	630.5	210.6	650.8
180	1010.8	810.6	296.5	830.5
200	1568.7	1020.5	360.8	1130.8
250	1930.5	1176.6	426.5	1260.9
300	2000.4	1530.7	563.2	1610.8
350	2243.9	1774.2	660.2	1987.0

The thermal conductivity κ(T) decreases with increasing diameter. In Table 2, we have shown the evaluated results of temperature dependent thermal conductivity of an isolated SWNT. In this calculation, κ(T) has a peak near 100 K and then decreases with increasing temperature.

Table 2: An evaluated results of temperature dependent thermal conductivity κ(T) [W/mK] of isolated SWNT

Temperature T (K)	κ(T) [W/mK]
10	3.7×10^4
50	4.8×10^4
100	5.6×10^4
150	6.6×10^4
200	4.5×10^4
250	3.7×10^4
270	2.8×10^4
300	2.3×10^4
320	2.0×10^4
340	1.8×10^4
350	1.6×10^4
360	1.4×10^4
370	1.2×10^4
390	0.97×10^4
400	0.95×10^4

The value of κ at the peak (6.6×10^4 W/mK) and is near the highest thermal conductivity ever measured (4.1×10^4 W/mK) for an isotopic ally pure diamond sample at 104 K. In Table 3, we have shown the calculated thermal conductivity of nanotube as a function of temperature. Results were compared with the thermal conductivity of 2D-graphene sheet and 3D graphite[15]. In graphite, the interlayer interactions quench the thermal conductivity by nearly 1 order of magnitude. It is likely that the same process occurs in nanotubes bundles. Thus, it is significant that the coupling between tubes in bundles is weaker than expected. It may be that the weak coupling which is problematic for mechanical applications of nanotubes is an advantage for thermal applications.

In Table 4, we have shown the evaluated results of temperature dependent thermal conductivity of a bulk sample of SWNTs, which has been aligned in a magnetic field. From our theoretical results, it show that κ(T) increases with the increasing temperature. It shows that in a magnetic field, the thermal conductivity is higher above 296 W/mK at 300 K, which is comparable to a good metal[16].

Table 3: An evaluated results of temperature dependent thermal conductivity κ(T) for carbon nanotube. Results were compared with 2D-graphene sheet and 3D-graphite

Temperature T (K)	Thermal conductivity κ(T) [W/mK]		
	Carbon nanotube	2D-graphene	3D- graphite
200	1.82×10^4	3.62×10^4	0.627×10^4
220	1.46×10^4	3.16×10^4	0.642×10^4
250	1.12×10^4	2.85×10^4	0.615×10^4
270	0.985×10^4	2.47×10^4	0.586×10^4
300	0.684×10^4	2.02×10^4	0.552×10^4
320	0.517×10^4	1.67×10^4	0.514×10^4
340	0.446×10^4	1.38×10^4	0.496×10^4
350	0.327×10^4	1.22×10^4	0.432×10^4
370	0.269×10^4	1.10×10^4	0.368×10^4
380	0.215×10^4	0.987×10^4	0.309×10^4
390	0.192×10^4	0.886×10^4	0.273×10^4
400	0.106×10^4	0.785×10^4	0.246×10^4

Table 4: An evaluated results of temperature dependent thermal conductivity κ(T) of bulk sample of SWNTs, which has been aligned in a high magnetic field

Temperature T (K)	Thermal conductivity κ(T) [W/mK] in H-field
10	2.863
20	8.432
50	15.258
100	35.659
120	58.147
150	79.226
200	120.49
250	167.56
270	182.46

Cont…

Temperature T (K)	Thermal conductivity κ(T) [W/mK] in H-field
290	210.16
300	226.48
320	233.78
350	247.54
400	259.15

In Table 5, we have presented the evaluated results of thermal conductivity for SWNT samples with two diameter d = 1.4 nm and d = 1.2 nm. Our theoretical results indicate that the smaller tube exhibit linear κ(T) up to higher temperature, which is consistent with quantization effects[17]. In Table 6, we have presented the evaluated results of thermal conductivity κ(T) of a single MWNT as a function of temperature. Our theoretically evaluated results indicate that κ(T) increases as T^2 up to 100 K, attains a peak at 300 K and then decreases with the increasing temperature. The quadratic temperature dependence is exactly what would be expected for large diameter nanotube, which act as 2D graphene sheet. The room temperature value of κ(T) is over 2000 W/mK. Some recent results[18-25] also reveals the same behavior.

Table 5: An evaluated results of thermal conductivity divided by temperature for SWNT sample with two diameters d = 1.4 nm and d = 1.2 nm

Temperature T (K)	(κ/T) (abs. unit)	
	d = 1.2 nm	d = 1.4 nm
10	1.127	1.148
20	1.148	1.169
30	1.162	1.185
35	1.185	1.206
40	1.193	1.225
45	1.206	1.248
50	1.217	1.267
55	1.228	1.288
60	1.239	1.305
65	1.246	1.329

Cont…

Temperature T (K)	(κ/T) (abs. unit)	
	d = 1.2 nm	**d = 1.4 nm**
70	1.257	1.344
75	1.268	1.367
80	1.279	1.385
85	1.299	1.402
90	1.306	1.422
100	1.357	1.458

Table 6: An evaluated results of thermal conductivity κ(T) of a single MWNT as a function of temperature

Temperature T (K)	Thermal conductivity κ(T) [W/mK]
10	157.9
50	567.8
100	687.7
120	880.2
140	960.7
160	1000.9
180	1100.5
200	1260.3
220	1475.8
240	1580.5
280	1779.6
300	2000.4
320	1769.2
340	1544.6
350	1200.5
370	1145.8
400	1000.6

CONCLUSION

From the above theoretical calculations, it appears that the thermal properties of carbon nanotubes are dominated by phonons. These results show a direct evidence of 1-D quantization of the phonon band width. It also suggests that the nanotube composite materials may be useful for thermal management applications.

REFERENCES

1. T. Yamamoto, S. Watanoble and K. Watanoble, Phys. Rev. Lett. (PRL), **92**, 075502 (2004).
2. R. S. Ruff and D. C. Lorentz, Carbon, **33**, 925 (1995).
3. D. T. Morelli, J. Heremans, M. Sakamoto and C. Uhelr, Phys. Rev. Lett. (PRL), **57**, 869 (1986).
4. D. Li, Y. Wu, P. Kim, L. Shi, P. Yang and A. Majumdar, Appl. Phys. Lett., **83**, 2934 (2003).
5. J. Hone, J. E. Fisher, M. C. Llaguno, N. M. Nemes, A. T. Johnson, J. Schmidt and R. E. Smalley, Appl. Phys. Lett., **77**, 666 (2000).
6. J. M. Ziman, Electrons and Phonons, The Theory of Transport Phenomenon in Solids Clarendon, Oxford (1965).
7. G. P. Srivastava, The Physics of Phonons Higler, Bristol (1960).
8. A. Sparavinga, Phys. Rev. B, **65**, 064305 (2002).
9. L. P. G. Rego and G. Kirczenow, Phys. Rev. Lett. (PRL), **81**, 232 (1998).
10. K. Schwab, E. A. Henriksen, J. M. Worlock and M. L. Roukes, Science, **404**, 974 (2000).
11. J. Heremans and C. P. Beetz, Phys. Rev., **B32**, 1981 (1985).
12. R. E. Peirls, Quantum Theory of Solids Oxford University Press, London (1955).
13. J. Hone, Carbon Nanotube, Thermal Properties, Dekker Encyclopeda of Nanoscience and Nanotechnology, **14**, 603 (2004).
14. G. D. Mahan and Jeon Gun Sang, Phys. Rev., **B70**, 075404 (2004).
15. J. Hone, M. Whitney, C. Piskoti and A. Zettle, Phys. Rev., **B59**, R2514 (1999).

16. J. Hone, M. C. Llaguno, M. J. Bircuk, A. T. Johonson, B. Batlogg, Z. Benes and J. E. Fischer, Appl. Phys. A Mater, **74**, 339 (2002).

17. M. J. Bieruk, M. C. Llegmo, M. Radosavligevic, J. K. Hyan, A. T. Johnson and J. E. Fisher, Appl. Phys. Lett., **80**, 2767 (2002).

18. Y. Xu., Y. Zhang, E. Sudher and X. Wang, J. Appl. Phys., **100**, 074302 (2006).

19. R. A. Cola, J. Xu, C. Cheng, X. Xu, H. Hu and J. E. Fisher, J. Appl. Phys., **101**, 054313 (2007).

20. K. Chu, Guo Hong, C. Jia, F. Yin, X. Zhang, X. Liang and H. Chen, Nanoscale Research Lett., **5**, 868 (2010).

21. A. L. M. Hernandez, C. V. Santos and V. M. Cestero, Current Nanoscience, **6**, 12 (2010).

22. Z. Han and A. Fina, Prog. Polym. Sci., **36**, 914 (2011).

23. X. Ni, G. Zhang and B. Li, J. Phys. Condens. Matter, **53**, 211301 (2011).

24. W. L. Song, W. Wang, L. M. Veca, M. S. Cad and G. E. Lecory, J. Mater. Chem., **22**, 17133 (2012).

25. I. A. Ventura, A. Rehaman and G. Lubineau, J. Appl. Polymer Sci., **130**, 2722 (2013).

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