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A THEORETICAL EVALUATION OF SPECIFIC HEAT OF CARBON NANOTUBES AS A FUNCTION OF TEMPERATURE

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ABSTRACT

Using the theoretical formalism of James Homes Science (2000), we have evaluated the temperature dependent specific heat of carbon nanotubes. From our theoretical results, it appears that at high temperature the specific heat of individual nanotubes are similar to that of 2D-graphene. The phonons contribution appears dominated at low temperature where linear T dependence of the specific heat is observed for SWNTs of small diameter < 2 nm. Our evaluated results are in good agreement with other theoretical workers and also with the experimental data.

Key words: SWNTs (Single wall Nanotubes), MWNTs (Multi wall Nanotubes), Phonon quantization, 2D-graphene, 3D-graphite, Longitudinal (LA) and transverse modes.

INTRODUCTION

Carbon nanotubes are nanostructures with remarkable electronic mechanical and thermal properties. Because of small size, quantum effects are important. As soon as they were discovered, their potential applications stimulated several theoretical and experimental studies[1-4]. Thermal properties of carbon nanotubes including specific heat, thermal conductivity and thermo power are quite special. The thermal properties of SWNTs (single wall nanotubes) have not as extensively studied as the electronic, mechanical and phonon properties of SWNTs. This is because techniques for making such studies are still under development. Large studies have been performed with MWNTs (Multi wall nanotubes). The thermal properties of carbon nanotubes display a wide range of behaviors that stem from their relation to the corresponding properties of a two-dimensional graphene layer and from their unique structure and tiny size [5].

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Mathematical formulae used in the study

In general specific heat C consists of phonons C_{Ph} and electronic C_e contributions but for 3D graphite, 2D graphene and carbon nanotubes the dominant contribution comes from the phonons. The phonons contribution is obtained by introducing the density of states with a convolution factor that reflects the energy and occupation of each phonon state.

$$C_{ph} = \int_0^{\omega_{\max}} \mathrm{K}_\beta \frac{\hbar\omega}{\mathrm{K}_\beta T} \frac{e^{\frac{\hbar\omega}{\mathrm{K}_\beta T}} \rho(\omega) d\omega}{(e^{\frac{\hbar\omega}{\mathrm{K}_\beta}} - 1)^2} \quad \ldots(1)$$

where ρ(ω) is the phonon density of states and ω_{max} is the highest phonon energy of the material. For non zero temperature the convolution factor is 1 at $\hbar\omega = \frac{\mathrm{K}_\beta \mathrm{T}}{6}$ so specific heat rises with T as more phonons states are occupied. Because ρ(ω) is a complicated function of ω, the specific heat at least at moderate temperatures cannot be calculated analytically. At low temperature ($T \leq \Theta_D$) the temperature dependence of the specific heat is in general much simpler. In this regime, the upper bound in equation (1) can be taken as infinity and ρ(ω) is dominated by acoustic phonon modes i.e. those with $\omega \to 0$ as $k \to 0$. If one considers a single acoustic mode in d dimension that obeys a dispersion relation $\omega \propto k^\alpha$. Then from equation (1) it follows –

$$C_{ph} \propto T^{\frac{d}{\alpha}} (T \leq \Theta_D) \quad \ldots(2)$$

Thus, the low temperature specific heat contains information about both the dimensionality of the system and the phonon dispersion. A single graphene sheet of a 2D system with three acoustic modes two having very high sound velocity and linear dispersion (a longitudinal LA mode with v = 24 Km/s and in-plane transverse TA mode with v = 18 Km/s and a third out of plane (ZA) mode that is described by parabolic dispersion relation[6] $\omega = \delta k^2$ with $\delta = 6.10^{-7}$ m^2/s. From equation (2), one sees that the specific heat from the in-plane modes should display a T^2 temperature dependence while that of out–of plane mode should be linear in T. Equation (1) can be evaluated separately for each mode, the contribution from ZA mode dominates that of the in-plane modes below room temperature.

The phonon contribution to the specific heat can be compared to the expected electronic specific heat of the graphene layer. The universal linear k dependence of the electronic structure E(k) of a single graphene sheet at E_F produces a low temperature electronic specific heat that is quadratic in temperature rather than linear dependence found for typical metals. Benedict et al.[7] showed that for the in-plane mode in a graphene sheet –

$$\frac{C_{ph}}{C_e} = (\frac{v_F}{v})^2 \cong 10^4 \quad \ldots(3)$$

The specific heat of the out of plane mode is even higher. Thus phonons dominate the specific heat even at low T and all the way to T = 0.

If one takes the electronic contribution, a metallic SWNT is a one-dimensional metal with a non-zero density of states at the Fermi level. The electronic specific heat is linear in temperature[8].

$$C_e = \frac{4\pi K^2{}_\beta T}{3\hbar v_F \rho_m} \quad \ldots(4)$$

$T << \frac{\hbar v_F}{K_\beta R}$, where v_F is the Fermi velocity, ρ_m is the mass per unit length and R is the radius of the nanotube. K_β is Boltzmann constant. In this case, the ratio of phonon contribution to the electron contribution of specific heat is –

$$\frac{C_{ph}}{C_e} = \frac{v_F}{v} \cong 10^2 \quad \ldots(5)$$

This show that even for metallic SWNT, phonons should dominate the specific heat at T-0. The electronic specific heat of a semiconducting tube vanishes exponentially[9] as T- → 0. This shows that C_e is even smaller than that of metallic tube. If such tube will be doped then the Fermi level lies near the band edge then in that case electronic specific heat can be enhanced.

RESULTS AND DISCUSSION

In this paper, we have presented a method of evaluation of specific heat of carbon nanotube. In this evaluation, we have used the theoretical formalism of Homes et al.[9] In

Table 1, we have shown the evaluated results of specific heat as a function of temperature of single wall armchair nanotube (5, 5), (10, 10) and (20, 20). Results were compared with the experimental data[10,11]. In this evaluation, two distinct behaviors at low and high temperatures are clearly displayed by tube (5, 5) and (10, 10). These are due to phonon frequency quantization[12]. Our theoretically evaluated results are in satisfactory agreement with experimental data of (20, 20) armchair nanotube.

Table 1: An evaluated results of specific heat as a function of temperature of single wall armchair nanotubes (5, 5), (10, 10) and (20, 20). Results were compared with the experimental data[10,11]

Temperature (K)	Specific heat C (mJ/gK)			
	Nanotube (5,5)	Nanotube (10,10)	Nanotube (20,20)	Expt.
0.5	0.622	0.432	0.387	-
1.0	0.732	0.657	0.785	-
5.0	0.876	0.812	0.952	0.632
10.0	0.932	0.968	1.087	0.785
20.0	1.035	1.132	1.154	1.287
30.0	2.867	3.658	4.286	5.432
50.0	6.538	7.189	9.584	10.157
60.0	8.627	9.357	10.419	13.439
80.0	15.862	16.586	16.621	18.895
90.0	18.367	20.552	21.952	23.906
100.0	32.624	38.967	39.023	43.087
200.0	87.534	90.587	93.057	97.562
300.0	98.057	103.563	104.879	108.345

In Table 2, we have shown the theoretically evaluated results of specific heat s for graphene, isolated (10, 10) SWNT, graphite and SWNT ropes. The results were compared with the experimental data[11]. In this evaluation, it appears that the measured C (T) are in satisfactory agreement with isolated (10, 10) carbon nanotubes. The measured specific heat is larger than the SWNT ropes. This suggests that tube-tube coupling in a rope is significantly weaker than the theoretical estimates.

Table T: An evaluated results of specific heat as a function of temperature of single wall nanotubes (SWNTs) Results were compared with specific heat of isolated (10, 10) tubes, SWNT rope, Graphene layer, Graphite and Expt.

Temperature T (K)	C (mJ/gK)				
	Graphene	ISO (10, 10) SWNT	Graphite	SWNT ropes	Expt.
1.0	2.76	0.528	0.258	0.186	0.685
5.0	3.85	0.825	0.463	0.325	0.958
10.0	4.26	1.029	0.859	0.731	1.132
50.0	6.39	2.356	1.254	0.954	4.586
80.0	8.16	5.859	6.229	1.068	7.225
100.0	10.27	9.216	10.16	8.215	9.468
150.0	30.47	32.58	35.39	36.59	32.58
200.0	55.86	60.49	67.26	70.26	56.16
250.0	87.21	89.16	90.18	100.48	85.30
300.0	270.82	290.38	300.17	327.15	290.16

In Table 3, we have shown the theoretically evaluated results of SWNTs evaluated from two band model with transverse dispersion. These band models are acoustic band model and 1st sub band model. The dispersion relation is $K_\beta\Theta_{subband} = K_\beta\Theta^{\|}_D$, $K_\beta\Theta^{\perp}_D$. We have used the fitting parameters[13] $\Theta^{\|}_D$ = 960K, $K_\beta\Theta^{\perp}_D = 50K$, $\Theta_{subband} = 13K$. We have compared the results of these evaluations by taking the total specific heat with experimental data[1]. The results are in satisfactorily agreement with low T. In Table 4, we have shown the theoretically evaluated results of MWNTs (Multi wall nanotubes). These results were calculated from phonon specific heat of graphene, graphite and isolated nanotube. Theoretical results were compared with the experimental data[1,14]. Yi et al.[1] have used a self-heating technique to measure the specific heat of MWNTs of 20-30 nm diameter produced by CVD technique. Mizel et al.[14] studied the phonon structure of large-diameter nanotubes whose properties are very much identical to graphene. If one compares the theoretical results of graphene, isolated nanotubes and graphite with these two experimental data[1,14], that both the experimental data are in satisfactorily agreement with the isolated nanotubes. There is some recent results[15-25] on the thermal properties of carbon nanotubes, which also confirm similar type of behavior.

Table 3: An evaluated result of specific heat of SWNTs with the help of two band models, acoustic band model and 1st sub band model. Total specific heat (calculated) were compared with expt. results

Temperature T (K)	C (mJ/gK)			
	Acoustic model	1st sub band model	Total (calculated)	Expt. results
0.5	0.468	0.052	0.520	0.558
1.0	0.529	0.067	0.596	0.696
2.0	0.632	0.086	0.718	0.742
3.0	0.765	0.095	0.860	0.907
4.0	0.825	0.128	0.953	0.968
5.0	0.947	0.287	1.234	1.272
6.0	1.052	0.395	1.447	1.584
7.0	1.386	0.468	1.854	1.696
8.0	1.842	0.689	2.531	1.974
9.0	2.017	0.845	2.862	2.324
10.0	3.467	0.965	4.432	3.014

Table 4: An evaluated results of specific heat of MWNTs (Multi-wall nanotubes) calculated from phonon specific heat of graphene, graphite and isolated nanotubes. Results were compared with two expt. data

Temperature T (K)	C(mJ/gK)				
	Graphite	Graphene	Isolated nanotube	Expt. data 1	Expt. data 2
5.0	0.056	0.252	1.586	2.296	1.863
10.0	0.158	0.658	2.478	3.105	2.972
20.0	0.987	0.786	4.582	4.502	3.849
40.0	1.148	1.284	6.693	7.054	6.947
60.0	3.847	3.459	8.532	9.147	8.482

Cont…

Temperature T (K)	C(mJ/gK)				
	Graphite	**Graphene**	**Isolated nanotube**	**Expt. data 1**	**Expt. data 2**
80.0	5.682	6.317	10.487	11.059	10.693
100.0	10.249	12.147	15.105	16.162	15.058
140.0	26.318	30.342	29.169	30.147	32.186
160.0	44.842	50.149	47.143	45.429	50.342
200.0	65.186	72.104	69.120	70.432	69.085

CONCLUSION

From these calculations, it shows that at high temperature the specific heat of individual nanotubes are similar to that of 2D-graphene. The effect of phonon quantization becomes apparent at low temperature for SWNTs of small diameter < 2 nm. Here a linear-T dependence of the specific heat is observed.

REFERENCES

1. W. Yi, L. Lu, A. Dian-lin, Z. W. Pan and S. S. Xie, Phys. Rev. B, **59**, R9015 (1999).
2. J. Hone, M. Whitney, C. Piskoti and A. Zettel Phys. Rev. B, **59**, R2514 (1999).
3. J. Hone, I. Ellwood, M. Muno, A. Mizel, M. L. Cohen, A. Zettle, A. G. Rinzler and R. E. Smalley, Phys. Rev. Lett. (PRL), **80**, 1042 (1998).
4. L. Shi, D. Li, C. Yu, W. Yang, D. Kim, Z. You, P. Kim and A. Majumdar, J. Heat Transfer, **125**, 881 (2003).
5. M. S. Dresselhaus, G. Dresselhaus and S. Jorio, Annu. Rev. Mater. Res., **34**, 247 (2004).
6. R. Saito, M. S. Dresselhaus and G. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperical College Press, London (1998) pp. 274-280.
7. L. X. Benedict, S. G. Loiue and M. L. Cohen, Solid State Commun., **100**, 273 (1996).
8. C. Kittel, Introduction to Solid State Physics, 6th Eds., Wiley, New York (1986).
9. J. Homes, B. Batlagg, Z. Benes, A. T. Johnson and J. E. Fischer, Sci., **289**, 1730 (2000).
10. P. Kim, L. Shi, A. Majumdar and P. L. McEuen, Phys. Rev. Lett. (PRL), **87**, 215502 (2001).

11. D. Li, Y. Wu, P. Kim, L. Shi, P. Yang and A. Majumdar, Appl. Phys. Lett., **83**, 2934 (2003).

12. G. D. Mahan and Sang Jeon, Gun Phys. Rev. B, **70**, 075405 (2004).

13. T. Pichler, H. Rauf, M. Knupfer, J. Fink and H. Kataura, Synth. Met., **153**, 333 (2005).

14. A. Mizel, L. X. Benedict, M. L. Cohen, S. G. Louie, A. Zettle, N. K. Bandra and W. P. Beyenmann, Phys. Rev., **B60**, 3264 (1999).

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

16. R. Weisman and Subramanam Sekhar, Carbon Nanotubes, Springer-Verlag, Berlin, 42-46 (2006).

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

18. M. Slobonanu, Serb. Chem. Soc., **73(8-9)**, 819-913 (2008).

19. F. Yang, Q. X. Ming, L. Ying, Y. Yajun and F. Qinshan, Phys. Lett. A, **372**, 6960 (2008).

20. B. Cola, J. Xu and T. Fisher, Int. J. Heat Mass Transfer, **52**, 3490 (2009).

21. X. Huang, J. Wang and X. Wang, Excellence of Graduate Research Conference, Department of Mechanical Engineering, IOWA state University, 2010, Black Engineering Bulding, Ammes, IA, 50011 (USA) (2011).

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. Poly. Sci., **130**, 2722 (2013).

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