Thermophysical Properties at the Nanoscale

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Abstract Specific heat is thought to be an intensive thermophysical property independent of the dimensions of the body. Indeed, specific heat at the nanoscale is assumed the same as that of macroscopic bodies. The Debye and Einstein macroscopic theories of specific heat including modifications thereof by Raman are therefore assumed in simulating heat transfer in nanostructures. In effect, macroscopic specific of the classical statistical mechanics oscillator having the same kT energy is assumed valid at the nanoscale. Here k stands for Boltzmann's constant and T for absolute temperature. But quantum mechanics (QM) embodied in the Einstein-Hopf relation requires the oscillators do not have the same kT energy. At ambient temperature, the average Planck energy of QM oscillators is kT only at thermal wavelengths greater than about 50 microns while at shorter wavelengths is less than kT and for nanostructures at submicron wavelengths is zero. Since the Planck energy at a given wavelength is the amount of thermal energy that can be stored in the QM oscillator, and since the only thermal wavelengths that can fit in nanostructures are submicron, QM requires zero specific heat capacity at the nanoscale, the consequence of which is absorbed heat cannot be conserved in nanostructures by an increase in temperature. Conservation may only proceed by the QED induced frequency up-conversion of absorbed heat to non-thermal EM radiation at the fundamental EM confinement frequency of the nanostructure, typically in the UV and beyond. Here EM stands for electromagnetic, QED for quantum electrodynamics, and UV for ultraviolet. Subsequently, the QED induced radiation leaks from the nanostructure as EM radiation at UV levels only to be absorbed in the macroscopic surroundings. By QM, specific heat is not an intensive thermophysical property but rather an extensive property depending on the dimensions of the body. Applications of heat transfer with zero specific heat are presented for nanoparticles, thin films, and nanowires.

Keywords: specific heat, quantum mechanics, Debye, Einstein, Raman

1. Introduction

Currently, classical heat transfer is generally thought [1-3] not applicable to nanostructures having dimensions far smaller than the mean free paths of the electrons and phonons that traditionally carry heat to the surroundings. Generally, macroscopic specific heats are assumed at the nanoscale, the consequence of which has led to unphysical conclusions, e.g., the thermal conductivity of thin films [4-5] is reduced from the bulk while enhanced [6-7] in carbon nanotube (CNT) nanowires. Explanations of the unphysical conductivities at the nanoscale have prompted modifications in the Fourier heat conduction theory by complex ballistic heat transfer analysis [1-3] where phonons are treated as particles in the Boltzmann transport equation (BTE).

However, QM by the Einstein-Hopf relation for the harmonic oscillator explains the reduced conductivity in thin films [8-9] and nanostructures [10] including the enhancements for CNT nanowires in general by a zero specific heat at the nanoscale. Like other peculiarities of QM, zero specific heat places in question the classical notion that specific heat as an intensive thermodynamic property that is independent of the quantity of the substance, or equivalently by the size of a body. QM modifies our common expectation that the absorption of light and heat at the nanoscale should be accompanied by an increase in temperature.

Lacking specific heat, absorbed EM energy at the nanoscale may only be conserved by the QED induced frequency up-conversion to the fundamental EM confinement frequency of the nanostructure, typically beyond the UV. The EM confinement is quasi-bound allowing leakage of QED induced radiation from the nanostructure to be absorbed in the macroscopic surroundings. But QED emission is not readily observed – even by photomultipliers because of the UV cut-off. Therefore, heat balances of nanostructures do not include QED emissions as heat losses giving the false impression of reduced or enhanced thermal conductivity from that of the bulk. However, if QED emissions are included, the bulk conductivity may be applied at the nanoscale precluding any modification of Fourier's theory of heat conduction by the BTE *Ibid*.

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2. Background

2.1 Traditional Theories of Specific Heat

Traditional theories of specific heat were formulated based on observations of experimental data from macroscopic samples. Debye's specific heat theory based on phonons and Einstein's characteristic vibrations provide accurate fits to data [11] at high temperatures, although Debye's theory more closely follows low temperature T^3 data near absolute zero as would be expected because atomic vibrations central in Einstein's theory tend to cease.

But Debye's theory was refuted many years ago by Raman [12] who showed the thermal energy of a solid depends on *atomic* vibrations at IR frequencies - not *elastic* vibrations by phonons at acoustic frequencies. Raman showed the specific heat of a solid based on Einstein's theory accurately fit experimental data with characteristic vibrations determined from IR spectroscopy. Based on the theorem [13] by Lagrange, Raman argued the thermal energy of the solid is the sum of the IR energies of the characteristic vibrations given by Einstein's fundamental theorem [14].

Raman claimed the Debye specific heat theory [15] that determines the frequency distribution by counting the number of stationary normal modes inside a geometric solid is unphysical because the modes must continue unabated *ad infinitum* in the presence of even by the smallest amounts of damping present in real materials. Similarly, Brillouin's support [16] of Debye's normal modes was critiqued. Hence, Raman concluded the use of normal modes was an erroneous basis from which to determine the thermal energy of the solid.

Instead, Raman [12] argued that the frequencies of EM emission from atoms in the IR and not Debye's phonons based on normal modes at acoustic frequencies define the thermal energy of a solid, e.g., Raman found agreement [17] between IR spectral lines and fits to Einstein's specific heat theory. The average of 4 characteristic IR frequencies for Al, Ag, Cu, and Pb were found to be 222, 175, 121, and 53 cm^{-1}, respectively. In contrast, the elastic vibrations in a solid are the consequence of low frequency translational movements of volume; whereas, the IR emission are highly localized comprising sharply defined line spectra. Raman proposed that the line spectra from IR spectroscopy be used for determining the characteristic frequencies of a solid. Since the Debye specific heat theory is based on phonons, Raman openly stated the Debye theory cannot be correct.

Regardless, QM precludes the extension of Debye's and Einstein's macroscopic specific heat theories including modifications by Raman to the nanoscale. Both theories expressed in terms of the number N of atoms in the body [11] imply that finite specific heat exists for nanostructures of a few thousands of atoms. But there is no QM basis for finite specific heat at the nanoscale making nanoscale extensions of macroscopic specific heat highly questionable.

2.2 Specific Heat at the Nanoscale

Today, heat transfer at the nanoscale follows that in macroscopic bodies - the nanostructure is treated as a statistical mechanical collection of oscillators having the same kT energy. Classically, the energy residing in the oscillator given by the equipartition theorem is considered to be continuous—it can take on any positive value, depending on the temperature. But QM differs in that the amount of energy that may reside at a particular oscillator frequency is restricted to quantized increments [18] that may only be increased or decreased in finite amounts, and therefore QM oscillators do not all have the same kT energy as in classical mechanics.

QM as embodied in the Einstein-Hopf relation for the harmonic oscillator shows the Planck energy in the ground state is kT while oscillators in higher frequency states dispersed over shorter wavelengths have less than kT energy. The transition from classical to QM may be quantified by thermal wavelengths $\lambda_T = hc/kT$, where h is Planck's constant, and c is the speed of light. At 300 K, the Planck energy of the harmonic oscillators is kT for all wavelengths longer than $\lambda_T \sim 50$ microns, but for shorter wavelengths the Planck energy is less than kT decreasing very rapidly and is essentially zero below about $\lambda_T \sim 5$ microns.

Unlike phonons in the BTE, QM oscillators within nanostructures respond at the speed c of light reduced by the refractive index n_r of the solid. The QM wavelength λ is given by the characteristic dimensions D_C of the nanostructure, $\lambda = 2n_rD_C$. Hence, the Planck energy of the photons within the nanostructure, $E = hc/2n_rD_C$. For example, submicron nanostructures at ambient temperature having $D_C < 1$ micron with near unity refractive index, $E > 0.62$ eV that is far in excess of $kT = 0.0258$ eV, and therefore QM oscillators having wavelengths λ that can fit in the nanostructure are not populated leaving the nanostructure with zero specific heat capacity, i.e, the high frequency QM oscillators store next to no energy at all.

At ambient temperature, high frequency QM oscillators may be said [19] to be "frozen out" of the heat capacity of nanostructures. For Planck oscillators at $E > 0.62$ eV, the corresponding temperature $T > E/k = 7200$ K. Since the ambient at 300 K is well below 7200 K, oscillators that can fit in the nanostructure will be "frozen out" and contain little energy and do not contribute to the heat capacity of the nanostructure. But heat transfer at the nanoscale based on the specific heat given by Debye's phonon and Einstein's characteristic vibration frequency theories including modifications thereof by Raman omit the QM restriction on kT energy and allow nanostructures to erroneously have finite specific heat.

2.3 Molecular Dynamics Simulations of Heat Transfer in Discrete Nanostructures

Molecular Dynamics (MD) gives classical solutions of atomic motion based on Newton's equations are commonly [20, 21] used to determine bulk transport properties including thermal conductivity of bulk liquids. The MD simulations allow the atoms to have kT energy because to determine the bulk properties periodic boundary conditions are imposed on the computational box. In this regard, MD simulations were preceded by Monte Carlo (MC) simulations preceded MD simulations, e.g., the virial coefficients for the PVT equation of the liquid state [22] were derived with MC simulations of spherical particles in a submicron 2D computational square box with periodic boundaries.

In contrast, MD simulations [23-25] of heat transfer at the nanoscale are generally performed for discrete structures which are unambiguously not periodic. Today, the assumption is made that the atoms have kT energy without imposing periodic boundary conditions on the computation box. Similar to the invalidity in extending the Dulong-Petit law for specific heat from high to low temperatures, specific heat from macroscopic samples is extended to the nanoscale. Indeed, MD simulations of discrete nanostructures are displayed in the belief they provide precise atomistic explanations of conduction heat transfer when in fact they are not valid because the simulations are performed on the assumption the atoms in discrete nanostructures have finite kT energy.

3. Purpose

The purposes of this paper are to provide a QM basis to zero specific heat as an extensive thermophysical property of all materials at the nanoscale.

• Propose macroscopic specific heat theories of Debye and Einstein to include zero specific heat at the nanoscale.

• Suggest QED induced radiation as the mechanism by which absorbed EM energy is conserved at the nanoscale.

• Recommend MD and MC simulations of discrete structures at the nanoscale be based on zero kT energy.

4. Theory

Heat transfer at the nanoscale requires modification of classical methods to include non-thermal QED induced emission as illustrated in Fig. 1
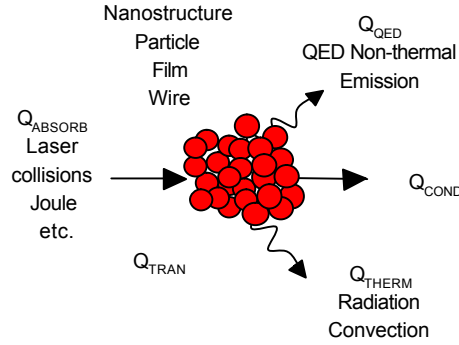
Figure 1. Heat Transfer at the Nanoscale.

Unlike thermal radiation given by the Stefan-Boltzmann law which is of importance only at high temperature, QED emission is non-thermal [10] and present at all temperatures. The heat balance at the nanoscale is,

$$Q_{ABSORB} = Q_{TRANS} + Q_{COND} + Q_{THERM} + Q_{QED} \cong Q_{COND} + Q_{QED} \qquad (1)$$

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Nanostructures (nanoparticles, thin films, nanowires) conserve Q_{ABSORB} – absorbed EM energy (lasers, molecular collisions, Joule heating) by heat losses: (1) Q_{TRANS} – transient heating of mass, (2) Q_{COND} – conduction, (3) Q_{THERM} - thermal (radiation and convection), and (4) Q_{QED} - QED induced non-thermal radiation. Lacking specific heat, Q_{TRANS} and Q_{THERM} are negligible leaving only Q_{COND} and Q_{QED} as possible heat losses.

4.1 QM Restrictions

QM restricts the allowable kT energy levels of atoms in nanostructures. At 300 K, the Einstein-Hopf relation giving the average Planck energy for the harmonic oscillator in relation to kT and thermal wavelength λ_T is shown in Fig. 2.
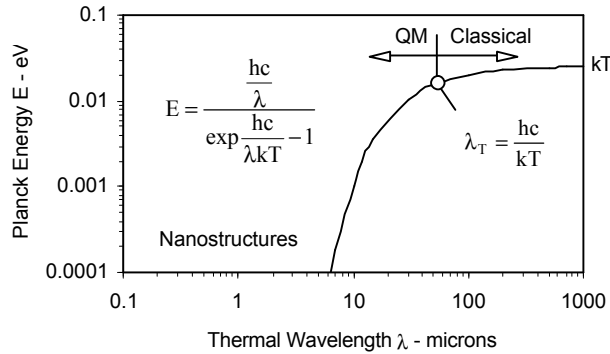

Figure 2. Harmonic Oscillator at 300 K.

Unlike classical oscillators having kT energy at all wavelengths, QM oscillators only allow classical kT energy for $\lambda > \lambda_T$, but restrict kT having $\lambda < \lambda_T$. At ambient temperature, Fig. 2 shows the Planck energy is less than kT for $\lambda < 50$ microns with kT energy available only for $\lambda > 50$ microns. In effect, classical oscillators absorb and emit in the far infrared (FIR). Hence, nanostructures having $\lambda < 1$ micron will not contribute to the absorption of any form of EM energy.

4.2 EM Confinement

Nanostructures lacking specific heat cannot conserve [8-10] absorbed EM energy by an increase in temperature. Conservation may only proceed by the QED induced frequency up-conversion of the absorbed EM energy to the confinement frequency of the nanostructure. Similar to creating QED photons of wavelength λ by supplying EM energy to a QM box with sides separated by λ/2, the low frequency absorbed EM energy is frequency up-converted to the fundamental EM resonance corresponding to the characteristic dimension D_C of the nanostructure. The QED photon energy E, frequency f, and wavelength λ are:

$$E = hf \; ; \; f = \frac{c}{\lambda} \; ; \; \text{and} \quad \lambda = 2n_r D_C \qquad (2)$$

4.3 Zero Specific Heat

Classical heat transfer conserves absorbed EM energy by an increase in temperature, but is not applicable to nanostructures because of the QM restrictions on thermal kT energy. The EM energy U absorbed in the nanostructure [24] is induced by QED to create N photons with Planck energy E,

$$U = NE \qquad (3)$$

Similarly, EM power P absorbed by a nanostructure creates QED photons at a rate dN/dt,

$$P = \frac{dU}{dt} = E\frac{dN}{dt} \qquad (4)$$

5.0 Applications

5.1 Nanoparticles

Nanofluids including NPs are found to enhance thermal conductivity in common coolants far in excess of that given by standard mixing rules. Solvent molecules have velocities depending on their kT energy; whereas, the NPs zero kT energy. In collisions with NPs, the molecules [28] transfer their kT energy to the NPs which is conserved by the emission of UV radiation as shown in Fig. 3.
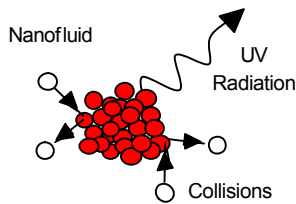

Fig. 3 Nanofluids – NPs emitting UV radiation

Classically, NPs have specific heat, and therefore the absorbed kT energy in the far IR from colliding molecules is conserved by an increase in temperature. But there is no enhancement because the absorbed FIR is also re-emitted in the FIR. QM differs in that the NPs have zero specific heat that requires the absorbed FIR to increase in frequency and be re-emitted in the UV. Hence, NPs enhance the heat transfer of coolants because the UV penetrates the solvent and transfers heat over a greater distance than that in the FIR for the solvent alone.

DNA damage induced by NPs is now considered [29] to mimic that by conventional UV ionizing radiation. Collisions of water molecules in body fluids with NPs are induced by QED to produce low-level UV. The UV forms hydroxyl radicals that act as bactericidal agents, but pose a health risk possibly leading to cancer by damaging the DNA. The NPs need not pass through the cell wall to damage the DNA by direct contact because UV radiation from extra-cellular NPs simply passes through the cell wall is illustrated in Fig. 4.
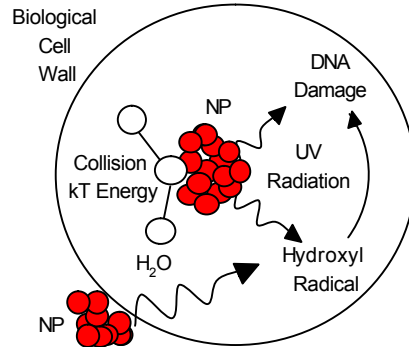
Fig. 4 DNA damage by NPs

Hubble's redshift measurement of galaxy light interpreted by the Doppler Effect showed the Universe is expanding. However, cosmic dust particles which are submicron NPs permeate space also redshift [10] absorbed galaxy light. Fig. 5 depicts a single galaxy photon of wavelength λ absorbed in a NP of diameter D that by QED creates redshift photons of wavelength $\lambda_o = 2n_rD$. The redshift $Z = (\lambda_o - \lambda) / \lambda$ occurs without the Universe expanding, thereby allowing a return to a static Universe once proposed by Einstein.
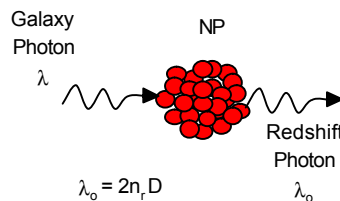

Fig. 5 Redshift in Cosmic Dust

5.2 Thin Films

QED induced heat transfer [8,9] for thin films is described for films having thickness δ, width W, and length L. Fig. 6 depicts a film conserving Joule heat by emitting QED radiation.
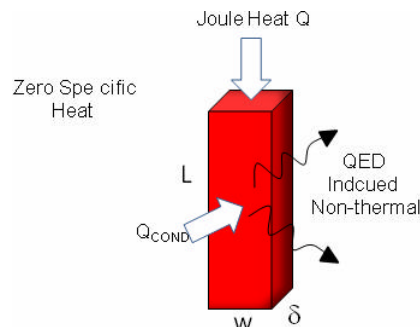

Fig. 6 Thin Film

Thin films are thought [1-3] to have large reductions in thermal conductivity through the thickness. Fig. 7 gives measured conductivity K_{eff} data for thin copper layers from (Fig. 3 of [4]). But QED induced emission is exclude. The QED emission is inferred by subtracting K_{eff} from bulk K in terms of Planck energy E and rate dN/dt of QED photons is given in Fig. 8.

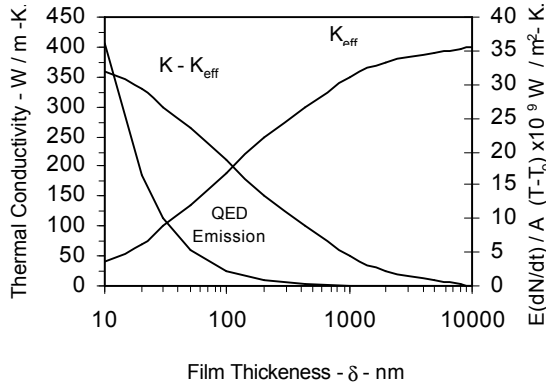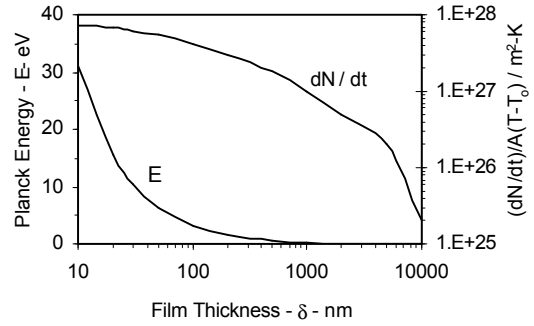Fig. 7 Thin Film – Data and QED Response   Fig. 8 Thin Film – QED Photon energy and rate

5.3 Nanowires

Nanowires differ from thin films in that EM confinement of the Joule heat occurs under orthogonal directions across the wire cross-section. The nanowire having diameter *d* and length *L* is illustrated in Fig. 9.
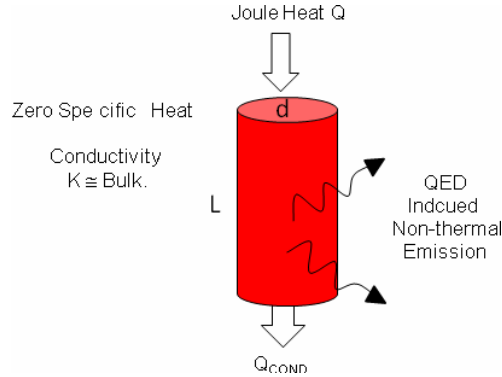

Fig. 9 Nanowire

Unlike the lower thermal conductivity than the bulk measured in thin films, the conductivity of nanowires fabricated from carbon nanotubes (CNTs) is reported [3] to be higher than the bulk. But like films, nanowires should have the same conductivity as that of the bulk. Consider nanowires of single wall carbon nanotubes (SWCNT) under Joule heating [7]. The I–V curve and power P = VI data for SWCNT having d = 1.7 nm and L = 2.6 microns at ambient temperatures of 250 and 400 K are reproduced in Fig. 10. The Joule heat Q_{ABSORB} in the wire is the sum of Q_{COND} and Q_{QED}. Equivalently, the power P = VI is,

$$VI = \frac{kA}{L}\Delta T + E\frac{dN}{dt} = G\Delta T + E\frac{dN}{dt} \qquad (6)$$

where, K is conductivity, and A and L are the wire area and length, the conductance G = KA/L. for wires, ΔT is the temperature difference across the length L. E is the Planck energy and rate dN/dt of confined QED photons confined within the wire.
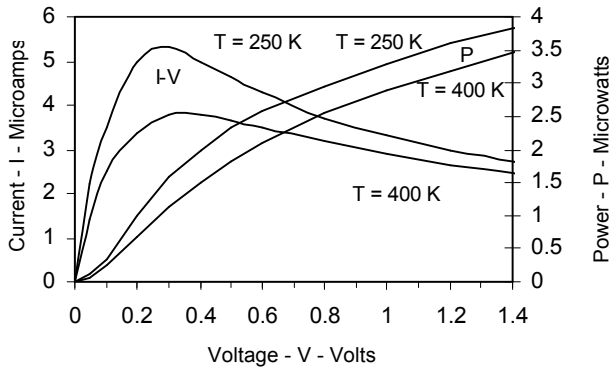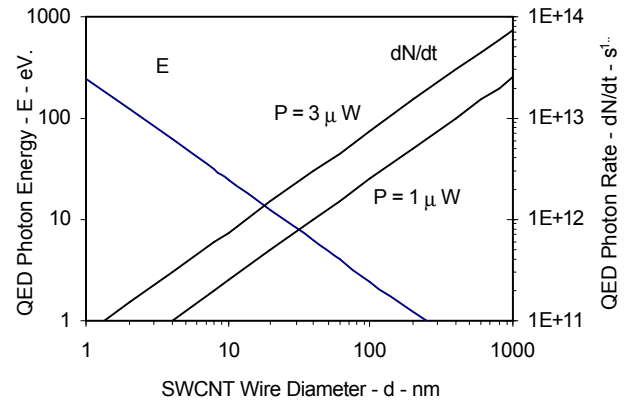
Fig. 10   I-V Curve and Power VI Data   Fig. 11 QED Photon Energy and Rate

QED induced EM radiation theory applied to the nanoscale only requires the bulk thermal conductivity K as a function of temperature which can determined in macroscopic experiments or from standard references [30]. Other parameters of nanowire area A and length L are readily measured. The Q_{QED} – QED emission is virtually the same as the Q_{ABSORB} - Joule heat, and therefore the Q_{COND} - conduction is very small. Hence, the wire conductivity K need not be enhanced from bulk to achieve the measured temperature difference ΔT over the wire length L. Fig. 11 depicts the Planck energy and rate of QED photons necessary to conserve Q_{ABSORB} - absorbed Joule heat at 1 and 3 µW in SWCNT wire of various diameters.

But temperature difference ΔT across the wire length is difficult to measure [31]. Experimental data is therefore expressed by the diameter adjusted conductivity Kd in Fig. 12
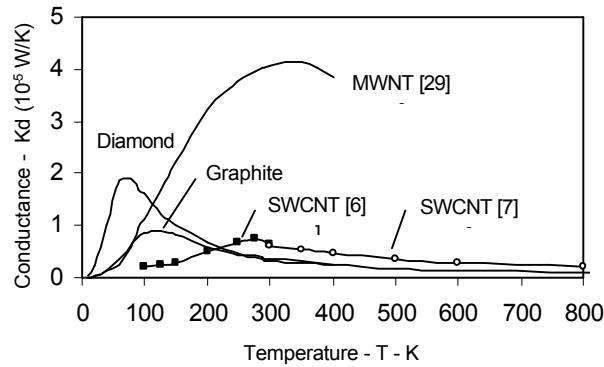

Fig. 12 SWCNT and MWNT Nanowires
Conductance G and Diameter Adjusted Conductivity Kd

Current nanoscale theory [31] for individual MWNT having d = 14 nm predicts Kd > 4. The SWCNT having d = 1.7 nm for temperatures < 300 K marked by solid squares [6] and temperatures > 300 K for open circles [7] are predicted to have Kd < 1. The spread in Kd between MWMT and SWCNT data is observed to be large. The conductance G for SWCNT and MWNT based on the bulk conductivity K for diamond and graphite differ in that the peaks are shifted to lower temperatures.

6. Summary and Conclusions

- QM requires zero specific heat capacity at the nanoscale be specified as a new thermophysical property of all materials.

- The classification of specific heat as an intensive thermophysical property should be changed to an extensive property depending on the dimensions of the body.

- Nanoscale heat transfer based on the assumption of macroscopic specific heat is likely to produce unphysical results, e.g., reduced thermal conductivity in thin films.

- There is no need for the BTE to determine the thermal conductivity in thin films as bulk conductivity may be assumed without any loss in accuracy.

- Macroscopic Debye and Einstein theories should be revised to include zero specific heat at the nanoscale.

- Lacking specific heat at the nanoscale, absorbed EM energy is not conserved by an increase in temperature, but rather by the emission of non-thermal QED induced EM radiation.

- MD and MC simulations of bulk thermal conductivity based on full kT energy of atoms in submicron computational boxes is consistent with QM provided periodic boundary conditions are imposed on the computational boxes.

- Zero specific heat is required for atoms in MD and MC simulations of discrete submicron nanostructures without periodic boundaries.

- MD and MC simulations of the heat transfer in nanostructures need not be performed as absorbed EM energy may be a priori assumed emitted as high frequency QED induced radiation that is absorbed in the macroscopic surroundings.

- Applications of the thermophysical property of zero specific heat at the nanoscale are presented.

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