

# SPECIFIC HEAT AT THE NANOSCALE

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## ABSTRACT

Specific heat is thought to be an intensive thermophysical property of a material independent of the dimensions of the body. Today, specific heat at the nanoscale is assumed the same as that of macroscopic bodies. In effect, the classical equipartition theorem is assumed valid allowing the atom to have thermal energy at all wavelengths. But quantum mechanics does not allow the atom to have the heat capacity at the submicron wavelengths necessary to store thermal energy in nanostructures, the consequence of which is absorbed energy cannot be conserved by an increase in temperature. Conservation may only proceed by the quantum electrodynamics induced frequency up-conversion of absorbed energy by non-thermal electromagnetic radiation that leaks to the surroundings. Specific heat at the nanoscale is therefore not an intensive property of a material, but rather an extensive property depending on the body dimensions.

## NOMENCLATURE

$C$	specific heat, J/kg/Kelvin
$D_c$	characteristic dimension, m
$D$	nanoparticle diameter, m
$dN/dt$	rate of QED photons, $s^{-1}$
$E$	Planck energy of QED photons, J
$G$	conductance, W/K
$I$	current, A
$K$	thermal conductivity, W/mK
$N$	number of QED photons
$P$	power, Watts
$T$	temperature, K
$U$	Planck energy, J
$V$	bias voltage, Volts
$Z$	redshift
$c$	speed of light, m/s
$d$	wire diameter, m
$f$	frequency, $s^{-1}$
$h$	Planck's constant, J s
$k$	Boltzmann's constant, J/s
$n_r$	refractive index
$\delta$	thin film thickness, m
$\lambda$	wavelength, m
$\lambda_o$	redshift wavelength, m

## INTRODUCTION

Currently, classical heat transfer is generally thought 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 (Jiji, 2009; Volz, 2007; Zhang, 2007). 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 is found reduced from the bulk (Issa, 2006; Liu and Aseghi, 2006) while increased for carbon nanotube (CNT) wires (Yu et al., 2005; Pop et al., 2006). Explanations of reduced conductivity have prompted modifications in the Fourier heat conduction theory by complex ballistic heat transfer analysis where the 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 (Prevenslik, 2009a) and nanostructures (Prevenslik, 2010) in general including CNT nanowires by a zero specific heat at the nanoscale, thereby placing in question specific heat as an intensive thermodynamic property independent of the quantity of substance, or by the size of the body. Like other peculiarities (Feynman et al., 1971) of QM, zero specific heat alters our experience in that the absorption of light and heat by a body no longer increases its temperature.

Lacking specific heat, the absorbed EM energy is conserved (Prevenslik, 2009-10) by QED induced frequency up-conversion to the fundamental EM confinement frequency of the nanostructure, typically beyond the UV. Here QED stands for quantum electrodynamics, EM for electromagnetic, and UV for ultraviolet.

Currently, QED emission is not included in the heat balance of nanostructures, and therefore the heat that has to be conserved by conduction is higher than it actually is. To satisfy measured temperature differences across the body, the conductivity therefore has to be reduced from the bulk, e.g., as in thin films. If QED emissions are included in heat balances, the bulk conductivity does not need to be reduced obviating modification of Fourier's theory of heat conduction by the BTE *Ibid.*

## BACKGROUND

### 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 (Debye, 1912) and Einstein's characteristic vibrations (Einstein, 1907) provide accurate fits to macroscopic data (Kittel, 2005) 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 Raman questioned Debye's theory (Raman, 1951) who showed the thermal energy of a solid depends on atomic vibrations at IR frequencies - not elastic vibrations by phonons at acoustic frequencies. Raman claimed the Debye specific heat theory 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 in real materials - which is not possible. Similarly, Brillouin's support (Brillouin, 1946) 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 a solid.

Instead, Raman claimed 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 (Raman, 1957). Raman found agreement 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  $\text{cm}^{-1}$ , 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 in Einstein's characteristic vibration theory to determine the specific heat of a solid. Since Debye's specific heat theory is based on phonons, Raman openly stated it 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 (Kittel, 2005) imply that finite specific heat exists for nanostructures of a few thousands of atoms. But as will be shown here there is no QM basis for finite specific heat making extensions of macroscopic specific heat to the nanoscale highly questionable.

### Specific Heat at the Nanoscale

Today, heat transfer at the nanoscale follows that in macroscopic bodies, i.e., the nanostructure is treated as a collection of statistical mechanical 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 that may only be increased or decreased in finite amounts, and therefore QM oscillators do not 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 at higher frequency dispersed over shorter wavelengths states have less than  $kT$  energy (Feynman et al., 1971). 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 rapidly and approaching zero at about  $\lambda_T < 3$  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  $\lambda$  is given by the characteristic dimensions  $D_C$  of the nanostructure,  $\lambda = 2n_r D_C$ . Hence, the Planck energy of the photons within the nanostructure,  $E = hc/2n_r D_C$ . For example, submicron nanostructures with  $D_C < 1$  micron and  $n_r = 1.2$  have  $E > 0.52$  eV far in excess of  $kT = 0.0258$  eV, and therefore QM oscillators having wavelengths  $\lambda$  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 to be "frozen out" of the heat capacity of nanostructures. *Ibid* For Planck oscillators at  $E > 0.52$  eV, the corresponding temperature  $T > E/k = 6000$  K. Since the ambient at 300 K is well below 6000 K, oscillators that can contribute to heat capacity by fitting *inside* the nanostructure contain little if any heat capacity. But heat transfer at the nanoscale based on the specific heat given by Debye and Einstein theories omit the QM restriction on  $kT$  energy and allow nanostructures to erroneously have finite specific heat.

### Molecular Dynamics of Discrete Nanostructures

Molecular Dynamics (MD) is commonly used to determine bulk transport properties including thermal conductivity of macroscopic bulk liquids (Hansen, 1986; Allen and Tildesley, 1987). MD gives the atomic response of atoms based on Newton's equations derived for ensembles of atoms in computational boxes. Even though the computation boxes are submicron that by QM requires the atoms to have zero  $kT$  energy, full  $kT$  energy is nevertheless assumed because in the bulk which is being simulated the atoms do indeed have  $kT$  energy. But this is only valid provided the MD solution is performed with periodic boundary conditions imposed on the computational box.

In this regard, MD simulations were in fact preceded by Monte Carlo (MC) simulations, e.g., the virial coefficients for the PVT equation of the liquid state were derived with MC simulations of spherical particles in a

submicron 2D computational square box with periodic boundaries (Metropolis, et al., 1953).

However, MD simulations of heat transfer at the nanoscale are also performed for discrete structures which are unambiguously not periodic (Volz and Chen, 1999; Feng et al., 2001; Akimov et al., 2008). Contrary to QM, the atoms in discrete nanostructures are erroneously assumed to have  $kT$  energy.

Indeed, MD simulations of discrete nanostructures are displayed in the belief they provide precise explanations of heat conduction when in fact they are not valid because QM precludes the atoms in discrete nanostructures to have  $kT$  energy. By assuming  $kT > 0$ , the MD simulations in effect derive the heat transfer response of the nanostructure as a macroscopic body.

## 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, and

- Propose macroscopic specific heat theories of Debye and Einstein to include zero specific heat at the nanoscale, and,
- Suggest QED induced radiation as the mechanism by which absorbed EM energy is conserved at the nanoscale, and
- Recommend MD and MC simulations of discrete structures at the nanoscale be based on zero  $kT$  energy.

## THEORY

Nanostructures (nanoparticles, thin films, nanowires, etc.) conserve absorbed  $Q_{\text{ABSORB}}$  energy from lasers, molecular collisions, and Joule heating by heat losses comprising  $Q_{\text{TRANS}}$  - transient heating of mass;  $Q_{\text{COND}}$  - conduction;  $Q_{\text{THERM}}$  - thermal radiation and convection, and  $Q_{\text{QED}}$  - QED induced emission of non-thermal radiation as illustrated in Fig. 1.

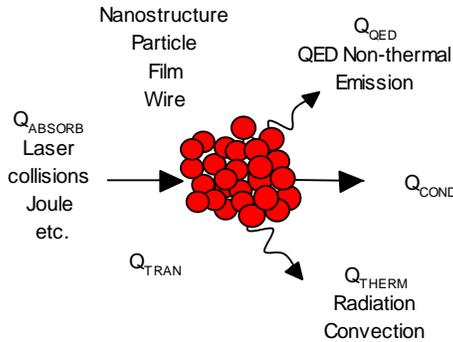


Fig. 1. Heat Transfer at the Nanoscale

Unlike thermal radiation given by the Stefan-Boltzmann law that is important only at high temperatures, QED emission is non-thermal and present at all temperatures - even in space at 2.7 K (Prevenslik, 2008). The heat balance is,

$$Q_{\text{ABSORB}} = Q_{\text{TRANS}} + Q_{\text{COND}} + Q_{\text{THERM}} + Q_{\text{QED}} \quad (1)$$

## QM Restrictions

QM restricts the  $kT$  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  $\lambda_T$  is shown in Fig. 2.

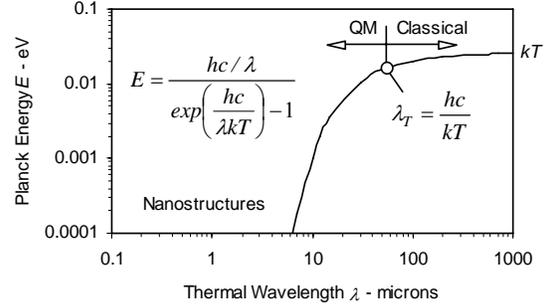


Fig. 2. Harmonic Oscillator at 300 K.

Unlike classical oscillators having  $kT$  energy at all wavelengths, QM oscillators only allow classical  $kT$  energy for  $\lambda > \lambda_T$  and restricts  $kT$  for  $\lambda < \lambda_T$ . 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. For nanostructures having  $\lambda < 1$  micron, there is no heat capacity by QM, and therefore absorbed EM energy is precluded from being conserved by an increase in temperature.

Since the nanostructures lack specific heat capacity,  $Q_{\text{TRANS}}$  may be neglected. Moreover,  $Q_{\text{THERM}}$  is neglected because high temperatures cannot occur. More importantly, there is no conductive heat flow  $Q_{\text{COND}}$  by the slow phonons because QED emission promptly conserves absorbed  $Q_{\text{ABSORB}}$  energy. Hence,

$$Q_{\text{QED}} = Q_{\text{ABSORB}} \quad (2)$$

## EM Confinement

Nanostructures lacking specific heat cannot conserve absorbed  $Q_{\text{ABSORB}}$  energy by an increase in temperature. Conservation may only proceed by the creation of QED photons *inside* the nanostructure by frequency up-conversion of the absorbed EM energy to its fundamental EM confinement frequency (Prevenslik, 2009-10).

The creation of QED photons is a complex process guided by the fact most nanostructures have an index of refraction greater than the surroundings, and therefore EM confinement is caused by total internal reflection (TIR). Similar to creating QED photons of wavelength  $\lambda$  by supplying EM energy to a QM box with sides separated by  $\lambda/2$ , TIR confines the absorbed EM energy to the characteristic dimension  $D_C$  of the nanostructure. The QED photon energy  $E$  and frequency  $f$  are:

$$E = hf \quad f = \frac{c}{\lambda} \quad \lambda = 2n_r D_C \quad (3)$$

For NPs, thin films, and nanowires, the characteristic dimensions  $D_C$  are the respective diameter  $D$ , thickness  $\delta$ , and diameter  $d$  of the nanostructure.

### QED Photon Number and Rate

Classical heat transfer conserves absorbed EM energy by an increase in temperature, but in nanostructures is negated by QM. Instead, the  $Q_{ABSORB}$  energy is conserved by creating a number  $N$  of QED photons *inside* the nanostructure having Planck energy  $E$ ,

$$Q_{ABSORB} = NE \quad (4)$$

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

$$P = \frac{dQ_{ABSORB}}{dt} = E \frac{dN}{dt} \quad (5)$$

### APPLICATIONS

#### Nanoparticles

**Nanofluid** heat transfer is enhanced by nanoparticles (NPs) because the NPs conserve absorbed  $Q_{ABSORB}$  - collision energy from solvent molecules by QED emission (Prevenslik, 2009a). Hence,

$$Q_{QED} = Q_{Collisions} \quad (6)$$

and conservation by  $Q_{QED}$  proceeds by the emission of QED induced radiation as depicted in Fig. 3.

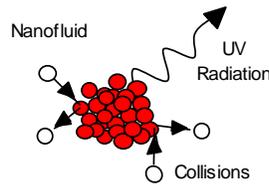


Fig. 3 Nanofluids – NPs emitting UV radiation

Classically, NPs conserve collision energy in the far IR (FIR) under local thermal equilibrium (LTE). LTE does not enhance heat transfer enhancement because re-emission also occurs in the FIR. QM differs. NPs avoid LTE by conserving the absorbed FIR by increasing its frequency with emission in the UV. Hence, NPs enhance the heat transfer because the UV penetrates the solvent a greater distance than that in the solvent alone. However, thermal conductivity itself is not enhanced beyond that given by standard mixing rules.

**DNA** damage induced by NPs is now considered to mimic that by conventional ionizing radiation. Similar to nanofluids, NPs absorb  $Q_{ABSORB}$  from collisions of water molecules in body fluids that is conserved by QED emission to produce low-level UV radiations that form hydroxyl radicals (Prevenslik, 2009b, 2010). NPs are therefore significant bactericidal agents, but on the darkside pose a health risk that by damaging the DNA may be the cause of cancer itself. NPs need not enter the cell to damage the DNA. Damage of the DNA from UV produced by extra-cellular NPs is illustrated in Fig. 4.

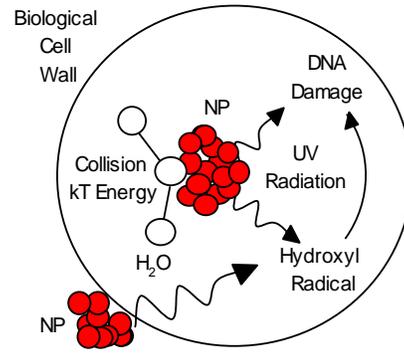


Fig. 4 DNA Damage by NPs

**Hubble** redshift measurement of galaxy light interpreted by the Doppler Effect showed the Universe is expanding. However, cosmic dust which permeates space consists of submicron NPs that also redshift absorbed galaxy light (Prevenslik, 2008).

A single galaxy photon of wavelength  $\lambda$  absorbed in a NP is depicted in Fig. 5. Only redshift QED photons are created for  $D > \lambda / 2n_r$  - blueshift is not possible in single photon absorption. The redshift  $Z = (\lambda_o - \lambda) / \lambda > 1$  occurs without the Universe expanding, thereby negating an expanding Universe and allowing a return to the infinite static Universe once proposed by Einstein.

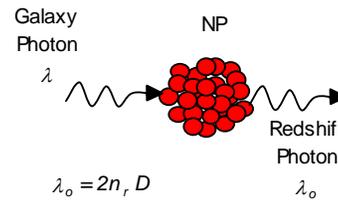


Fig. 5 Redshift in Cosmic Dust

#### Thin Films

QED induced heat transfer (Prevenslik, 2009a) for thin films of thickness  $\delta$ , width  $W$ , and length  $L$  upon the absorption of Joule heat is depicted in Fig. 6.

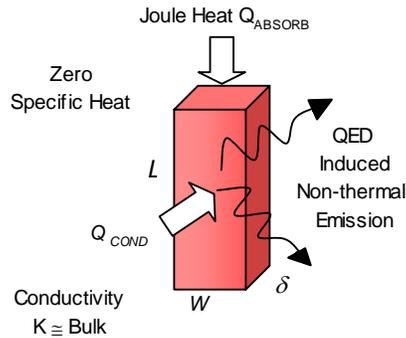


Fig. 6 Thin Film

Thin films are generally thought to have large reductions of bulk thermal conductivity  $K$  through the thickness. Experimental conductivity  $K_{eff}$  data for thin copper layers (Issa, 2006) is shown in Fig. 7

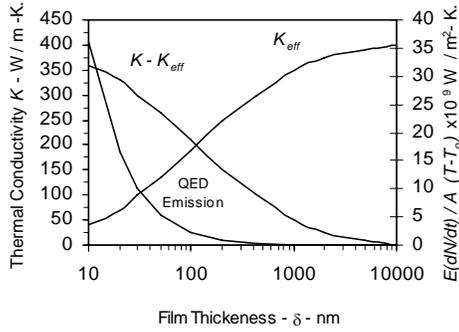


Fig. 7 Thin Film – Data and QED Response

For  $Q_{COND} \rightarrow 0$ , the QED emission is estimated from  $Q_{QED} \cong (K - K_{eff})A\Delta T / \delta$  as depicted in Fig. 7. The QED emission in terms of the Planck energy  $E$  and rate  $dN/dt$  of QED photons within the film is shown in Fig. 8.

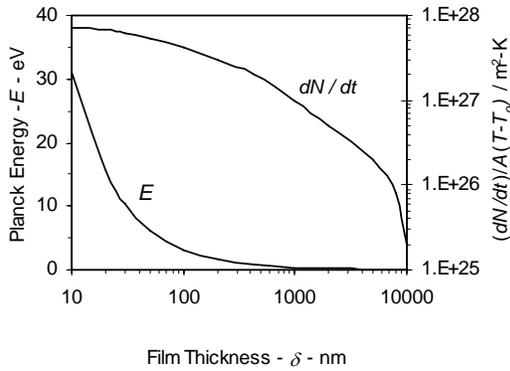


Fig. 8 Thin Film – QED Photon Energy and Rate

### Nanowires

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

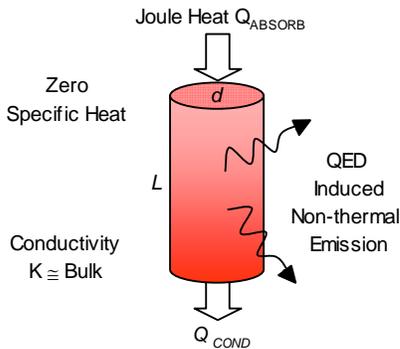


Fig. 9 Nanowire

Unlike silicon nanowires (Li, 2003) having conductivity lower than the bulk, the conductivity of nanowires of carbon nanotubes (CNTs) is found to be higher than the bulk (Jiji, 2009). But this is unlikely because nanowire conductivity cannot exceed the bulk. Consider nanowires of single wall carbon nanotubes (SWCNT) under Joule heating (Pop et al., 2006). The  $I-V$  curve and power  $P = VI$  for SWCNT having  $d = 1.7$  nm and  $L = 2.6$  microns at ambient temperatures of 250 and 400 K are shown in Fig. 10.

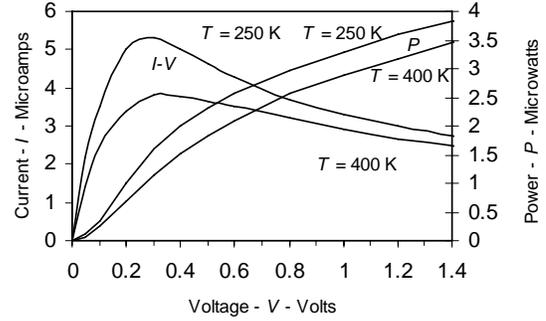


Fig. 10  $I-V$  Curve and Power  $VI$  for SWCNT Wires

The Joule heat  $Q_{ABSORB}$  in the wire is the sum of  $Q_{COND}$  and  $Q_{QED}$ . Equivalently, the power  $P$  is,

$$VI = G\Delta T + E \frac{dN}{dt} \quad (7)$$

where, the conductance  $G = KA/L$ ,  $A$  and  $L$  are the wire area and length.  $\Delta T$  is the temperature difference across the wire length.

Like NPs, thin films, and silicon wires, QED emission  $Q_{QED}$  is virtually the same as the absorbed  $Q_{ABSORB}$  energy, and therefore the conduction  $Q_{COND}$  along the wire does not exist. Hence, the wire conductivity  $K$  need not be reduced from bulk to achieve the measured temperature difference  $\Delta T$  over the wire length. Indeed, the thermal conductivity  $K$  of the nanowires at temperature may be taken as that of the bulk, and obtained from macroscopic experiments or from standard references (Touloukian et al., 1970). Fig. 11 depicts the Planck energy  $E$  and rate  $dN/dt$  of QED photons necessary to conserve  $Q_{ABSORB}$  in SWCNT wire at 1 and 3  $\mu W$ .

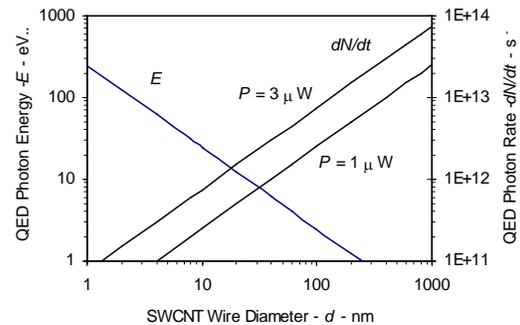


Fig. 11 SWCNT - QED Photon Energy and Rate

## DISCUSSION

### Consistency of QM with Raman

In the 1950's, Raman argued that Einstein's characteristic vibrations and not Debye's phonons define the thermal capacity of solids.

The IR lines of Al, Ag, Cu, and Pb are all greater than about  $\lambda_T \sim 50$  microns where QM and classical physics give the same heat capacity. See Fig. 2. But at the nanoscale, the wavelengths  $\lambda$  that can fit in the nanostructure of characteristic dimension  $D_C$  are,  $\lambda < 2n_r D_C$  that for  $D_C < 1$  micron and  $n_r > 1$  require  $\lambda < 2$  microns. Since  $\lambda \ll 50$  microns, the IR lines of the common metals are excluded from the nanostructure, and therefore the nanostructure by Raman's argument has no heat capacity consistent with QM. However, QM is not consistent with Debye's phonons. Normal vibration modes of classical mechanics allow the nanostructure to have heat capacity contrary to QM.

### Nanoscale Heat Transfer Mechanism

In the 1780's, Lavoisier and Laplace formed the notion of specific heat used in 1822 by Fourier in formulating the classical theory of heat conduction. At the macroscale, the Fourier theory is,

$$\nabla \cdot K \nabla T = C \frac{\partial T}{\partial t} \quad (8)$$

Conduction by phonons at the macroscale is thought to apply to the nanoscale. But this is false. Sound velocities of lead and diamond are 1300 to 12000 m/s. Conservation by phonons for lead and diamond nanostructures with  $D_C \sim 1$  micron therefore occurs at times  $D_C/V_S$  from 700 to 80 ps. But for  $n_r = 1.5$ , QED photons are created in  $n_r D_C/c \sim 5$  fs. At the nanoscale, QED emission promptly conserves absorbed EM energy thereby negating heat conduction by phonons, and therefore Fourier theory may be replaced by,

$$\nabla \cdot K \nabla T = C \frac{\partial T}{\partial t} \rightarrow \frac{d}{dt} Q_{\text{ABSORB}} = E \frac{dN}{dt} \quad (9)$$

QED radiation significantly alters classical heat transfer at the nanoscale because conduction does not occur. What this means is that the BTE and reductions in bulk conductivity based on scattering of phonons have no meaning because absorbed EM energy is conserved by QED emission well before phonons can respond.

### Feynman on Classical and QM Oscillators

In the 1970's, Feynman noted the differences between QM and classical thermal oscillators by:

- Classical physics by statistical mechanics allows the atom to have heat capacity at the nanoscale. But QM also allows atoms to have heat capacity at the nanoscale, but only at high temperature.
- Submicron wavelengths that fit into nanostructures have heat capacity only at temperatures  $> 6000$  K. At 300 K, heat capacity is therefore "frozen out" at submicron wavelengths.

Paraphrasing Feynman some 40 years later:

*QM does not allow nanostructures at ambient temperature to conserve absorbed EM energy by an increase in temperature.*

What this means is specific heat at the nanoscale vanishes, and therefore conservation of absorbed EM energy may only proceed by the prompt creation of QED photons *inside* the nanostructure.

### EM Confinement

The EM confinement of the QED photons occurs by TIR because the nanostructure is typically of a higher refractive index than the surroundings. But the TIR is only momentary. On the order of 5 fs, QED photons striking the nanostructure surface at angles greater than the critical angle are confined within the nanostructure. But because the QED photons are scattered from atoms at random, all QED photons subsequently strike the inside surface at near normal incidence and leak from the nanostructure as QED emission.

Since the QED photons are created beyond the UV, charged atoms and electrons are produced *inside* the nanostructure by the photoelectric effect. Subsequently, QED photons are created as the electrons recombine with the charged atoms at the frequency of the EM confinement prescribed by TIR.

### MD Heat Transfer of Discrete Nanostructures

MD simulations of heat transfer of absorbed EM energy in nanostructures are valid provided periodic boundary conditions (Sarkar and Selvam, 2007) are prescribed in the solution run. However, if the nanostructures are discrete, the thermal  $kT$  energy of the atoms should be set to zero.

What this means is there is no conduction at the nanoscale. MD heat transfer of discrete nanostructures is meaningless. Instead, MD simulations may be replaced by the *a priori* assumption that the nanostructure remains isothermal with the absorbed EM energy converted to QED radiation at frequencies equal to the fundamental EM resonance of the nanostructure. Typically, the QED radiation is ionizing beyond the UV and acts to charge the nanostructure by the photoelectric effect. In this arrangement, MD simulations may then be performed for the discrete nanostructures under isothermal conditions interacting with each other by electrostatic forces.

Density functional theory (DFT) calculations of minimum energy ground states of discrete nanostructures are valid only for isothermal conditions. But DFT calculations (Car and Parinello, 1985) of the bulk in combination with MD heat transfer simulations based on submicron calculation boxes having  $kT$  energy under periodic boundary conditions are certainly valid.

### Measurement of QED Emission in Thin Films

Many experimental methods have been proposed to measure the thermal properties of a material. With regard to thin films, the  $3\omega$  method (Cahill et al., 2002) is a standard procedure in the measurement of thermal conductivity and specific heat.

Although valid for macroscopic films, the  $3\omega$  method is invalid at the nanoscale because the specific heat vanishes. Instead, the  $3\omega$  method measures the QED emission  $Q_{\text{QED}} \cong (K - K_{\text{eff}})A\Delta T / \delta$  as described by the reduction of conductivity in thin films in Fig. 7.

## SUMMARY AND CONCLUSIONS

QM requires zero specific heat capacity at the nanoscale be specified as a new thermophysical property of ALL materials - both solid and liquid.

The classification of specific heat as an *intensive* thermophysical property of a body should be revised to an *extensive* property depending on body dimensions.

Nanoscale heat transfer based on zero specific heat explains reduced conductivity in thin films by QED emission without modifying bulk conductivity.

There is no heat conduction at the nanoscale. Reductions in thermal conductivity by phonons are therefore meaningless.

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 emission that may be measured by the  $3\omega$  method.

MD and MC simulations of bulk thermal conductivity based on the full  $kT$  energy of atoms are 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 QED emission that is absorbed in the surroundings.

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