SPECIFIC HEAT IN NANOSTRUCTURES BY QUANTUM MECHANICS

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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 of statistical mechanics is assumed at the nanoscale allowing atoms to have heat capacity at all thermal wavelengths. Therefore, classical physics allows submicron wavelengths that can “fit inside” nanostructures to conserve electromagnetic (EM) energy by an increase in temperature. Quantum mechanics (QM) also allows the atom to have heat capacity at submicron wavelength, but only at high temperature. At ambient temperature, the high frequency modes at submicron wavelengths are therefore “frozen out” leaving nanostructures without the heat capacity to increase in temperature to conserve absorbed EM energy. By QM, specific heat vanishes at the nanoscale. Conservation may only proceed by the quantum electrodynamics (QED) induced creation of photons within the nanostructure at a frequency equal to its fundamental EM resonance. Subsequently, QED radiation 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.

1. Introduction

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 [1-3]. 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 [4-5] while increased for carbon nanotube (CNT) wires [6-7]. Explanations of reduced conductivity have prompted modifications in 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 [8] and nanostructures [9] in general including by a zero specific heat, thereby placing in question specific heat as an intensive thermophysical property independent of the size of the body. Like other peculiarities of QM, zero specific heat alters our thinking in that the absorption of EM energy by a body no longer increases its temperature.

Lacking specific heat, conservation proceeds [9] by prompt QED emission induced from frequency up-conversion of the absorbed EM energy to the fundamental EM confinement frequency of the nanostructure. Since the QED emission is prompt, absorbed EM energy is conserved well before phonons respond. QED emission therefore negates thermal conduction at the nanoscale.

Currently, QED emission is not included in the heat balance of nanostructures, and therefore conductive heat is thought higher than it actually is. To satisfy the higher implied temperature differences across the body, conductivity is then reduced from the bulk, e.g., as in thin films. With QED emissions, bulk conductivity need not be reduced obviating any modification of Fourier theory by the BTE.

2. Background

2.1 Traditional Theories of Specific Heat

Traditionally, specific heat theories were formulated based on observations of experimental data from macroscopic samples. Debye's specific heat theory based on phonons [10] and Einstein’s characteristic vibrations [11] provide accurate fits to macroscopic data [12] at high temperatures, although Debye’s theory more closely follows low temperature T³ data near absolute zero as would be expected because atomic vibrations in Einstein’s theory cease.

But Debye’s theory was questioned [13] by Raman who argued 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 the characteristic vibrations determined from IR spectroscopy.

Moreover, 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 unadulterated ad infinitum in the damping of real materials. Similarly, Brillouin’s support [14] of Debye’s normal modes was criticized. Hence, Raman concluded the use of normal modes was an erroneous basis to determine the thermal energy of a solid.
Instead, Raman proposed [15] 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 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 emissions 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 Debye’s specific heat theory is based on phonons, Raman openly stated it cannot be correct.

Raman aside, QM precludes the extension of Debye’s and Einstein’s macroscopic specific heat theories to the nanoscale. Both theories expressed in terms of the number $N$ of atoms in the body [12] 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 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, i.e., the nanostructure is treated as a collection of statistical mechanical oscillators having the same $kT$ energy. Here, $k$ is Boltzmann’s constant and $T$ is absolute temperature. Classically, the energy residing in the oscillator given by the equipartition theorem depends on temperature, but not frequency. QM differs in that the amount of energy available depends on both temperature and frequency, and therefore QM oscillators do not have the same $kT$ energy as in classical statistical mechanics.

QM as embodied in the Einstein-Hopf relation for the harmonic oscillator [16] shows the Planck energy in the ground state is $kT$ while oscillators at higher frequencies 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 rapidly and approaching zero at $\lambda_T < 3$ microns.

Unlike phonons in the BTE, QM oscillators within nanostructures respond at the speed $c$ of light reduced by the refractive index $n_0$ of the solid. The QM wavelength $\lambda$ is given by the characteristic dimensions $D_0$ of the nanostructure, $\lambda = 2n_0D_0$. Hence, the Planck energy of the photons within the nanostructure is $E = hc/2n_0D_0$. For example, submicron nanostructures with $D_0 < 1$ micron and $n_0 = 1.2$ have $E > 0.52$ eV far in excess of $kT = 0.0258$ eV, and therefore QM oscillators having wavelengths $\lambda$ that can “fit inside” the nanostructure are not populated. Hence, nanostructures have 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, QM oscillators that can “fit inside” nanostructures have no heat capacity to conserve absorbed EM energy.

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.

3. Purpose

The purpose of this paper is 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.

4. Theory

Heat transfer at the nanoscale is depicted for nanoparticles, thin films, and nanowires in Fig. 1

![Figure 1. Heat transfer at the nanoscale](image)

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

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

Nanostructures (nanoparticles, thin films, nanowires) conserve $Q_{\text{ABSORB}}$ - absorbed energy (lasers, molecular collisions, 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.
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Lacking specific heat, $Q_{\text{TRANs}}$ and $Q_{\text{THERM}}$ may be neglected leaving $Q_{\text{ABSORB}} \equiv Q_{\text{COND}} + Q_{\text{QED}}$. But $Q_{\text{COND}} \rightarrow 0$, and therefore

$$Q_{\text{ABSORB}} = Q_{\text{QED}}$$  \hspace{1cm} (2)

4.1 Quantum Mechanics 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 $\lambda_T$ is shown in Fig. 2.

![Figure 2. Harmonic Oscillator at 300 K.](image)

Unlike classical oscillators having $kT$ energy at all wavelengths, QM oscillators only allow $kT$ 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. For nanostructures having $\lambda < 1$ micron, QM by requiring specific heat to vanish precludes any increase in temperature upon the absorption of EM energy.

4.2 EM Confinement

Nanostructures lacking specific heat cannot conserve absorbed $Q_{\text{ABSORB}}$ energy by an increase in temperature. Conservation may only proceed by the QED induced frequency up-conversion of the absorbed EM energy to the confinement frequency of the nanostructure [9]. Similar to creating QED photons of wavelength $\lambda$ by supplying EM energy to a QM box with sides separated by $\lambda/2$, the absorbed EM energy is frequency up-converted to the characteristic dimension $D_C$ of the nanostructure. The QED photon energy $E$ and frequency $f$ are:

$$E = hf \quad f = \frac{c}{\lambda} \quad \lambda = 2n_cD_C$$  \hspace{1cm} (3)

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

4.3 QED Photons and Rate

Classical heat transfer conserves absorbed EM energy by an increase in temperature, but is not applicable to nanostructures because of QM restrictions on thermal $kT$ energy [9]. Instead, the $Q_{\text{ABSORB}}$ energy is conserved by creating a number $N$ of QED photons inside the nanostructure having Planck energy $E$,

$$Q_{\text{ABSORB}} = NE$$  \hspace{1cm} (4)

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

$$P = \frac{dQ_{\text{ABSORB}}}{dt} = E \frac{dN}{dt}$$  \hspace{1cm} (5)

5. Applications

5.1 Nanoparticles

5.1.1 Nanofluids

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

$$Q_{\text{QED}} = Q_{\text{Collision}}$$  \hspace{1cm} (6)

Conservation of $Q_{\text{Collision}}$ proceeds [9] by the QED emission of ultraviolet (UV) radiation shown in Fig. 3.

![Figure 3. Nanofluids – NP emitting UV radiation](image)

Classically, NPs conserve collision $Q_{\text{Collision}}$ energy in the far IR (FIR) under local thermal equilibrium (LTE). LTE does not enhance heat transfer because re-emission also occurs in the FIR. QM differs. NPs avoid LTE by conserving the absorbed FIR by increasing its frequency [17] 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. But thermal conductivity itself is not enhanced beyond that given by standard mixing rules.

5.1.2 DNA Damage

DNA damage induced by NPs is now considered to mimic that by conventional ionizing radiation. Similar to nanofluids, NPs absorb $Q_{\text{ABSORB}}$ from collisions of water molecules in body fluids that are conserved by QED emission to produce low-level UV radiation [18, 19] to form hydroxyl radicals that damage the DNA by chemical reaction.

Hydroxyl radicals produced by NPs are known to be a remarkable bactericidal agent. But on the darkside NPs pose a health risk because if DNA damage is not corrected, NPs 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 extracellular NPs is illustrated in Fig. 4.

5.1.3 Hubble Redshift

Hubble’s redshift measurement of galaxy light interpreted by the Doppler Effect showed the Universe is expanding. However, cosmic dust comprised of submicron NPs also redshift galaxy light [20].

A single galaxy photon absorbed in a NP is depicted in Fig. 5. Only redshift QED photons are created for $D > \lambda/2n_0$ - blueshift is not possible in single photon absorption. The redshift $Z = (\lambda_o - \lambda)/\lambda > 1$ occurs without the Universe expanding, thereby negating expansion and allowing a return to the infinite static Universe once proposed by Einstein.

5.2 Thin Films

QED induced heat transfer [21] for electronic films of thickness $\delta$, width $W$, and length $L$ emitting EM radiation in the absorption of Joule heat in Fig. 6.

5.3 Thermophones

Thermophones are thought to produce sound by converting AC current at audio frequencies to vibrations in thin films by rapid temperature changes. Contrary to classical physics, thermophones fabricated from nanoscale sheets of CNTs are recently shown to produce sound without vibration.

The QM explanation [22] is that sound is produced from the pressure changes that accompany the absorption of QED emission by the surrounding air as illustrated in Fig. 8.

5.4 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.
Unlike silicon nanowires [23] having conductivity lower than the bulk, the conductivity of nanowires of carbon nanotubes (CNTs) is found to be higher than the bulk [24]. But QED emission requires that neither nanowires of silicon or CNTs should be different from the respective bulk conductivities.

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

$$VI = G\Delta T + E\frac{dN}{dt}$$

(7)

where, the conductance $G = KA/L$, and $A$ and $L$ are the wire area and length. $\Delta T$ is the temperature difference across the wire length. But conduction does not occur at the nanoscale, and therefore the power $P = VI$ is conserved solely by QED emission, $P = E\frac{dN}{dt}$.

But the conductivity $K$ and specific heat $C$ cannot be extracted from the $P = VI$ curves. Instead, the power $P$ is the QED emission. For example, the QED emission for nanowires of single wall carbon nanotubes (SWCNT) under Joule heating [24] at temperatures of 250 and 400 K may be inferred from the power $P = VI$ shown in Fig. 10.

### Figure 9. Nanowire

In the 1950’s, Raman noted the IR lines of Al, Ag, Cu, and Pb are all greater than about $\lambda_F \sim 50$ microns. Fig. 2 shows QM and classical physics give the same heat capacity for $\lambda >> \lambda_F$. But at the nanoscale, the wavelengths $\lambda$ that can “fit inside” the nanostructure of characteristic dimension $D_C$ are, $\lambda < 2n_Dc$ for that for $D_C < 1$ micron and for $n_i > 1$ require $\lambda < 2$ microns. Since $\lambda << \lambda_F = 50$ microns, the IR lines of the common metals cannot “fit inside” 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 always allow the nanostructure to have heat capacity contrary to QM.

### 6. Discussion

#### 6.1 Consistency of QM with Raman

In the 1950’s, Raman noted the IR lines of Al, Ag, Cu, and Pb are all greater than about $\lambda_F \sim 50$ microns. Fig. 2 shows QM and classical physics give the same heat capacity for $\lambda >> \lambda_F$. But at the nanoscale, the wavelengths $\lambda$ that can “fit inside” the nanostructure of characteristic dimension $D_C$ are, $\lambda < 2n_Dc$ for that for $D_C < 1$ micron and for $n_i > 1$ require $\lambda < 2$ microns. Since $\lambda << \lambda_F = 50$ microns, the IR lines of the common metals cannot “fit inside” 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 always allow the nanostructure to have heat capacity contrary to QM.

#### 6.2 Nanoscale Heat Transfer Mechanism

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

$$\nabla \cdot KV = C \frac{\partial T}{\partial t}$$

(8)

Conduction by phonons at the macroscale is thought to apply to the nanoscale. But this is incorrect. Sound velocities of materials may be bracketed by lead and diamond from 1300 to 12000 m/s. Conservation by phonons by nanostructures with $D_C \sim 1$ micron therefore occurs at times $D_C/V_S$ from 700 to 80 ps. But for $n_i = 1.5$, QED photons for are created in $n_i D_C/c \sim 5$ 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,

$$\nabla \cdot KV = C \frac{\partial T}{\partial t} \rightarrow Q_{ABSORB} = E\frac{dN}{dt}$$

(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 has no meaning because absorbed EM energy is conserved by QED emission well before phonons respond.

#### 6.3 Feynman on QM Oscillators

In the 1970’s, Feynman described the differences between QM and classical thermal oscillators.

- Classical physics by statistical mechanics allows the atom to have heat capacity at the nanoscale. QM also allows atoms to have heat capacity at the nanoscale, but only at high temperature.

- Submicron wavelengths that “fit inside” the nanostructures have heat capacity only at temperatures > 6000 K. At 300 K, heat capacity is therefore “frozen out” at submicron wavelengths.
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 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 eventually strike the surface at less than the critical angle 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 upon recombination of electrons with the charged atoms. TIR assures all created QED photons are coherent at the EM confinement frequency of the nanostructure.

6.4 Measurement of QED Emission

Many experimental methods have been proposed to measure the thermophysical properties of materials. With regard to thin films, the 3ω method [26] is a standard procedure in the measurement of thermal conductivity and specific heat.

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

7. Summary and Conclusions

QM requires zero specific heat capacity at the nanoscale to 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 as QED emission without modifying bulk conductivity.

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

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 as measured by the 3ω method.

8. References