SPECIFIC HEAT AT THE NANOSCALE

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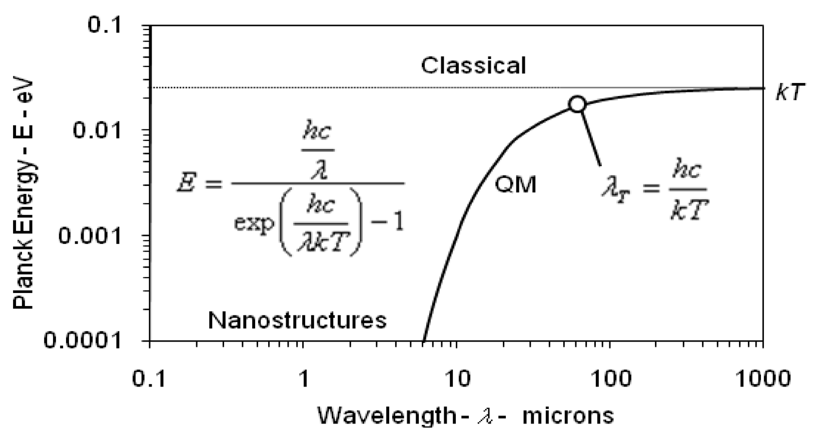
ABSTRACT

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.

BACKGROUND

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. Quantum 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 wavelength states have less than *kT* energy as shown below. 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. Hence, specific heat at the nanoscale vanishes.

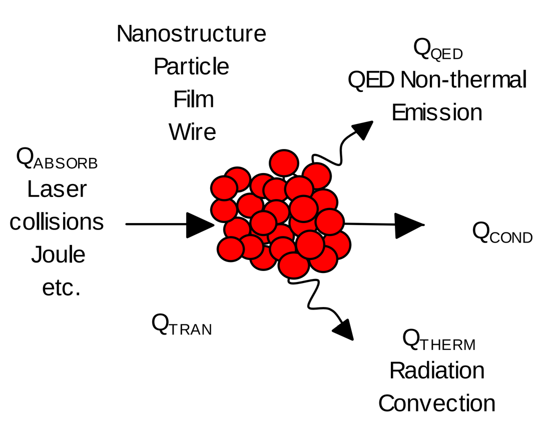


PURPOSE

The purpose of this paper is to propose that specific heat be revised from an *intensive* to an *extensive* thermophysical property depending on the quantity or size of the substance of ALL materials at the nanoscale.

THEORY

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



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. The heat balance is,

$$Q_{ABSORB} = Q_{TRANS} + Q_{COND} + Q_{THERM} + Q_{QED}$$

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

$$Q_{QED} = Q_{ABSORB}$$

EM Confinement

The creation of QED photons is a complex process guided by the fact most nanostructures have an index of refraction n_r greater than the surroundings, and therefore EM confinement is caused by total internal reflection (TIR). Similar to creating QED photons of wavelength λ 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:

$$E = hf \qquad f = \frac{c}{\lambda} \qquad \lambda = 2n_r D_C$$

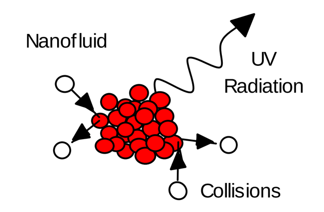
QED Photon Energy and Rate

Classical heat transfer conserves absorbed EM energy by an increase in temperature, but in nanostructures is negated by QM. Instead, the Q_{ABSORB} power is conserved by creating QED photons *inside* the nanostructure having Planck energy *E* at rate dN/dt,

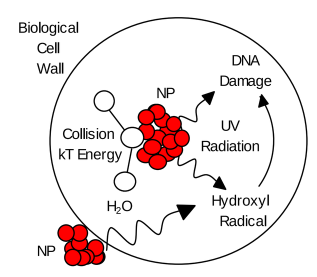
$$P = \frac{dQ_{ABSORB}}{dt} = E\,\frac{dN}{dt}$$

APPLICATIONS

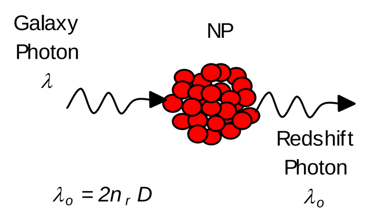
Nanofluid heat transfer is enhanced by nanoparticles (NPs) because the NPs conserve absorbed Q_{ABSORB} - collision energy from solvent molecules by QED emission,



Nanofluid



DNA damage



Hubble

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 is not enhanced beyond standard mixing rules.

DNA damage by NPs is now considered to mimic that by conventional ionizing radiation. 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 forms hydroxyl radicals. NPs are therefore significant bactericidal agents, but 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.

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. A single galaxy photon of wavelength λ absorbed in a NP is depicted. 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.

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. But at the nanoscale, the wavelengths λ that can fit in the nanostructure of characteristic dimension D_C are $\lambda < 2n_r D_C$ that for $D_C < 1$ micron and $nr > 1$ require $\lambda < 2$ microns. Since $\lambda << 50$ microns, the nanostructure excludes the IR lines of the common metals and has no heat capacity consistent with QM. The fact that NPs emit IR lines does not alter this conclusion because heat capacity requires volume and the IR emission is produced by atoms as a point source. However, QM is not consistent with Debye's phonons. Normal vibration modes of classical mechanics allow the nanostructure heat capacity contrary to QM.

Nanoscale Heat Transfer Mechanism

Today, conduction by phonons at the macroscale is thought to apply to the nanoscale. But this is false. Sound velocities may be bracketed by lead and diamond at 1300 to 12000 m/s. Conservation by phonons for general nanostructures with $D_C \sim 1$ micron therefore are bracketed by times D_C/V from 700 to 80 ps. But for $n_r = 1.5$, QED photons for 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 the far slower phonons, and therefore Fourier theory may be replaced by,

$$\nabla \bullet K\nabla T = C\,\frac{\partial T}{\partial t} \qquad \Rightarrow \qquad \frac{d}{dt} Q_{ABSORB} = E\,\frac{dN}{dt}$$

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.

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 reducng 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.

Absorbed EM energy at the nanoscale is not conserved by an increase in temperature, but rather by the emission of non-thermal QED emission that and may be measured by the 3ω 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.