

Specific Heat by Quantum Mechanics

Thomas Prevenslik
QED Radiations
Discovery Bay, Hong Kong, China
e-mail: nanoqed@gmail.com

Introduction

Historically, the theory of the heat capacity of a crystal lattice began with phonons in Einstein's theory [1] of characteristic vibrations in 1907 followed by Debye's theory [2] of normal modes in 1912. Since then, Debye's phonon theory is not without controversy. In the 1950's, Raman argued [3] that normal vibration modes of the lattice cannot be the source of heat capacity because they cannot be sustained 'ad infinitum' in the presence of even the smallest amount of material damping. Raman stated:

"The enumeration of wave-patterns within an enclosure on a scale of wavelengths or frequencies presupposes that the waves are perfectly undamped and that the enclosure is perfectly reflecting. In any material medium, however, wave propagation is necessarily damped and such damping may be so enormous as altogether to preclude wave-propagation ... Since the specific heat theories of Debye and Born-Karman are based on such identification, they cannot be sustained."

Further, Raman stated [4] that Debye and Born-Karman misrepresented quantum theory by quantizing the normal modes of a macroscopic crystal instead of reserving quantization for the atomic level thereby being as meaningless as quantizing the frequencies of a tuning fork. Raman thought the specific heat of a crystal was given by Einstein's theory of characteristic vibration. But unlike Debye's phonons based on the large number of normal modes of the crystal, Raman limited Einstein's characteristic vibration theory [5, 6] to only those frequencies corresponding to spectral lines in the far infrared (FIR). Although Raman's interpretation of Einstein's specific heat based on FIR spectra avoids unphysical normal modes of a crystal, Debye's theory is widely accepted [7] for specific heat at the macroscale.

But there is more controversy to Debye's theory of specific heat. Specific heat is considered an *intensive* thermophysical property of a material independent of size or substance, and therefore macroscopic specific heat is thought applicable to the nanoscale. But interpretation of observations at the nanoscale based on macroscopic specific heat has led to unphysical results. Citing only a few, the thermal conductivity of thin films [8-10] is found to be reduced from bulk while nanofluids are found [11-13] to have thermal conductivity above that given by standard mixing rules. In contrast, thin film conductivity remains at bulk [14, 15] as film thickness is reduced, and nanofluids obey standard mixing rules [16, 17] by taking the specific heat to vanish at the nanoscale consistent with quantum mechanics (QM).

Purpose

To propose the photons in Planck's blackbody radiation [18] modified only by the refractive index of the crystal are the source of heat capacity at both the nano and macroscale. Planck's photons have vanishing specific heat at the nanoscale while at the macroscale behave like Debye's phonons at acoustic frequencies.

Theory

Planck's photons in the crystal lattice are identical to those in QM for blackbody radiation in an evacuated cavity except for the lower speed of light in the crystal. Each atom emits Planck photons in the manner of orthogonally disposed harmonic oscillators depicted in Fig. 1.

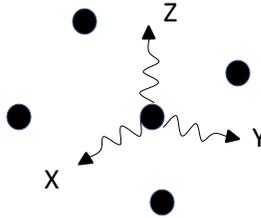


Figure 1. Planck Photons as Harmonic Oscillators

Planck's photons differ from Raman's phonons in that the inexhaustible energy source to sustain atomic vibrations at FIR frequencies is the thermal kT energy of the atom that is the source of all EM radiation. EM stands for electromagnetic. The average Planck energy $\langle E \rangle$ of Planck's photons in the lattice is,

$$\langle E \rangle = \frac{hc / n\lambda}{\exp\left(\frac{hc}{n\lambda kT}\right) - 1} \quad (1)$$

where, h is Planck's constant, c is the speed of light in a vacuum, n is the refractive index of the crystal lattice, λ is the wavelength of the Planck photon, k is Boltzmann's constant, and T is absolute temperature.

QM and Classical Oscillators. QM differs from classical physics by the heat capacity of the atom. At 300 K, the average Planck energy $\langle E \rangle$ for $n = 1$ is shown in Fig. 2

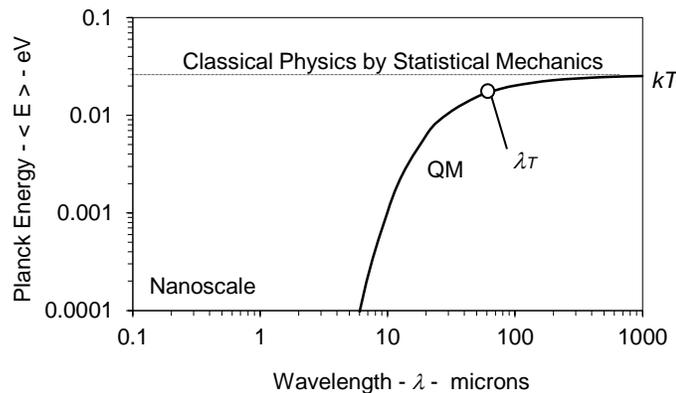


Figure 2 Classical and QM Oscillators - Heat capacity at 300 K

The thermal wavelength $\lambda_T = hc/kT$ separates classical physics from QM. Classical physics by statistical mechanics allows the atom to have heat capacity (constant kT energy) from the macroscale ($\lambda > \lambda_T$) to the nanoscale ($\lambda < 1$ microns). Hence, classical physics allows atoms at the nanoscale to have heat capacity. In contrast, QM allows the atom to have kT energy only at the macroscale ($\lambda > \lambda_T$). Alternatively, QM does not allow the atoms at the nanoscale to have heat capacity. Fig. 3 shows the effect of crystal refractive index on heat capacity for a typical range of n from 1 to 2.

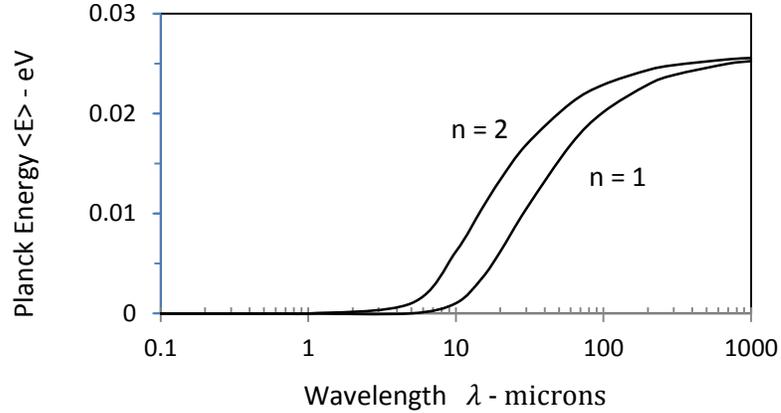


Figure 3 Heat Capacity and Wavelength

In Planck's QM, the heat capacity Q of a crystal depends [6] on the number N of atoms,

$$Q = 3N \langle E \rangle = 3N \frac{hc/n\lambda}{\exp\left(\frac{hc}{n\lambda kT}\right) - 1} \quad (2)$$

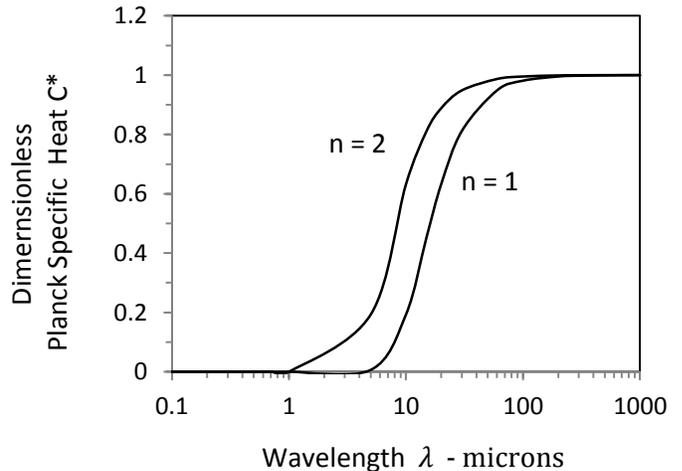
Planck's specific heat C is the thermal gradient of the heat capacity Q ,

$$C = \frac{\partial Q}{\partial T} = 3N \frac{\left(\frac{hc}{n\lambda kT}\right)^2 \exp\left(\frac{hc}{n\lambda kT}\right)}{\left[\exp\left(\frac{hc}{n\lambda kT}\right) - 1\right]^2} \quad (3)$$

The dimensionless Planck specific heat C^* is shown in Fig. 4.

$$C^* = \frac{C}{3Nk} = \frac{\left(\frac{hc}{n\lambda kT}\right)^2 \exp\left(\frac{hc}{n\lambda kT}\right)}{\left[\exp\left(\frac{hc}{n\lambda kT}\right) - 1\right]^2} \quad (4)$$

Figure 4 Dimensionless Planck Specific Heat and Wavelength



Feynman on Heat Capacity In the 1970's, Feynman described [19] 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” and which contribute to the specific heat of nanostructures have heat capacity only at temperatures > 6000 K. At 300 K, QM heat capacity is therefore “frozen out” at submicron wavelengths. Unlike statistical mechanics, QM forbids atoms at the nanoscale to have heat capacity, and therefore conservation of absorbed EM energy cannot proceed by an increase in temperature.

Conservation by QED Conservation may only proceed by the QED induced frequency up-conversion of the absorbed EM energy to the TIR confinement frequency of the nanostructure. QED stands for quantum electrodynamics and TIR for total internal reflection. At the nanoscale, almost all of absorbed EM energy is in the TIR mode because of the high surface to volume ratio, and therefore absorbed EM energy is spontaneously placed under TIR confinement. But the QED photons escape TIR confinement as random collisions with atoms redirect the QED photons to near normal incidence with the nanostructure surface. Hence, the TIR confinement is only momentary and the QED induced radiation leaks to the surroundings.

QED is highly complex process whereby electrons are created upon the absorption of EM energy. Currently, the crystal lattice is thought excited by electron-phonon coupling. However, electron-photon coupling is unlikely. In fact, the creation of QED photons is far more rapid than the phonons can respond, and therefore absorbed EM energy is conserved by Planck's photons before Debye's phonons respond. Conservation by heat conduction therefore does not occur at the nanoscale. Certainly, the lattice is excited by electron-phonon coupling, but is relatively inconsequential by the prompt conservation of absorbed EM energy by Planck's photons. Similar to creating QED photons of wavelength λ 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:

$$E = hf \quad \text{and} \quad f = c/n/\lambda \quad (5)$$

where, $\lambda = 2 D_c$. For a spherical nanoparticle of diameter D , $D_c = D$ and $\lambda = 2D$.

Summary

Comparison with Debye The Debye dimensionless C^* specific heat [3] is given in terms of the Debye temperature T_d ,

$$C^* = 3 \left(\frac{T}{T_d} \right)^3 \int_0^{T/T_d} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad (6)$$

For silver, aluminum, and lead, the Debye temperatures T_d are 225, 426, and 96 K. Planck's photons differ by depending on the refractive index. For silver, aluminum, and lead, $n = 1.35$, 1.44, and 2.01. By trial and error, FIR characteristic frequencies in the dimensionless Planck specific heat were found that best approximated the respective Debye specific heats over the temperature range 15 to 300 K. For silver, aluminum, and lead, the effective frequencies were 175, 222, and 333 cm^{-1} or wavelengths 57, 45, and 30 microns. A comparison of dimensionless Planck and Debye specific heat is shown in Fig. 5.

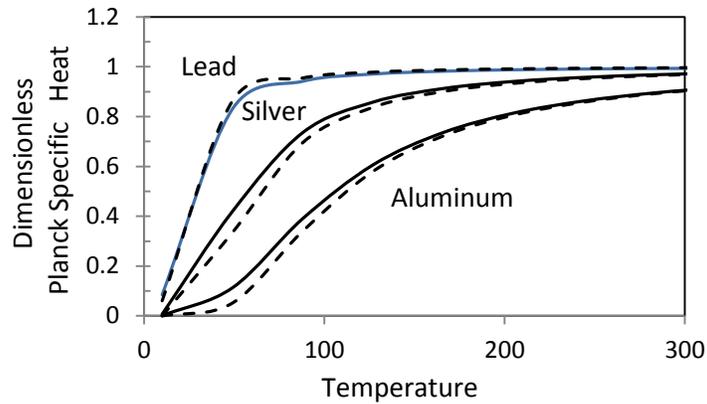


Figure 5 Dimensionless Specific Heat and Temperatures

Debye Specific Heat in Solid Lines and Planck Specific Heat in Dotted lines

Raman did not report spectroscopic frequency measurements for silver, aluminum, and lead. Instead, based on Einstein's theory the effective characteristic frequencies from the experimental [5] specific heat data over the 15 to 300 K temperature range were computed as shown in Figs 1, 3, 4 of [6]. For silver at 15, 160, and 300 K, the effective frequencies were 90, 110, and 107 cm^{-1} ; for aluminum 110, 200, and 180 cm^{-1} ; and for lead 30, 57, and 20 cm^{-1} . For silver, aluminum, and lead, Raman's average frequencies are 102, 163, and 35 cm^{-1} and generally lower than the 175, 222, and 333 cm^{-1} found for the Planck specific heat.

Specific Heat and Photon Wavelength The dimensionless Planck specific heat at 300 K for lead, silver, aluminum, and lead having $n = 1.35, 1.44,$ and 2.01 is shown in Fig.6

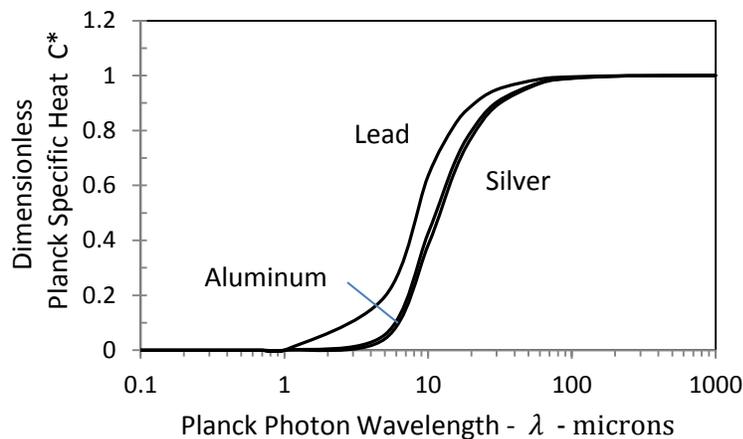


Figure 6 Dimensionless Planck Specific Heat and Wavelength at 300 K

Discussion

Raman's Argument Raman thought the heat capacity of a crystal lattice was given by Einstein's characteristic vibrations using FIR spectral lines. Debye's normal modes of vibration were refuted by Raman because of the argument that normal modes could not be sustained in the presence of material damping. Otherwise, Raman agreed with Debye that phonons were the heat carriers in the lattice. Certainly, Raman's argument that damping precludes Debye's normal modes is irrefutable, but whether Raman's notion that atomic vibration was the inexhaustible source of heat capacity driving atomic vibration is not.

Raman should have argued that thermal energy upon which Planck's formulated the QM of photons was the source of atomic vibration, but could not because then photons and not phonons would be the heat carriers in the lattice. One must understand Einstein and Debye and later Raman based their theories of heat capacity on macroscopic data and were not confronted by nanoscale observations that suggest photons and not phonons are the heat carriers in the lattice. Photon-phonon coupling induces atomic vibration, but the dominant heat carriers in a crystal lattice are photons and not phonons.

Phonon Quantization Einstein and later Debye chose to define the heat capacity of the lattice in terms of atomic vibration of phonons with the atoms vibrating at the speed of sound instead of photons at the speed of light in the lattice. Einstein quantized phonons following the QM of Planck's photons. But the QM of phonons lacks the long history of experimental support for Planck's photons, e.g. the distribution of energies in blackbody radiation embodied in the Stefan-Boltzmann equation and Wien's law. Unlike photons that are sustained 'ad infinitum' by temperature in Planck's blackbody radiation, material damping precludes phonons from sustaining atomic vibration. What this means is observed atomic vibration occurs by photon-phonon coupling.

FIR Spectral lines and Specific Heat In the 1950's, lack of experimental FIR data on metals did not allow Raman to support his argument that the specific heat of crystal lattice is determined by using IR spectral lines in Einstein's theory of characteristic vibrations. For the metals, the FIR spectra were not reported. Instead, measured specific heats were fit over the temperature range from 15 to 300 K from which an effective average characteristic vibration frequency was computed [5] based on Einstein's specific heat theory. But this methodology presupposes the characteristic vibrations based on elastic constants are correct and is inconsistent with Raman's argument that material damping precludes Debye's normal modes. ..

Today, FIR spectroscopy allows far more detail on spectral lines than available to Raman in the 1950's. Even so, data on aluminum, silver and lead used by Raman are sparse. Regardless, FIR spectra are not so simple to be represented by discrete spectral lines alone. Typical FIR spectra show spectral lines superimposed on broad backgrounds thereby holding in question Raman's notion of computing specific heat by averaging specific heat using discrete spectral lines in Einstein's theory. The complexity is illustrated in the FIR spectra [20] of silicon dioxide in Fig. 7.

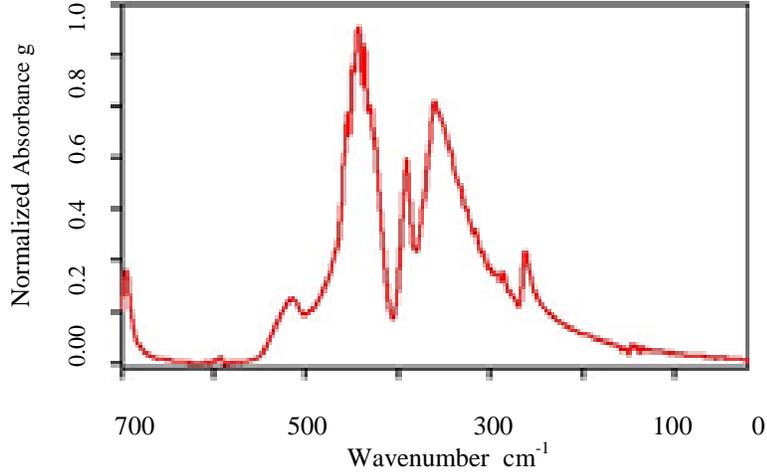


Figure 7 FIR Spectra of Silicon-Dioxide (SiO₂)

An alternative to Raman's summing the specific heat from discrete spectral lines is to compute the average Planck specific heat C_{avg} by integrating the dimensionless specific heat C^* depending on the absorbance g from the FIR spectra.

$$C_{\text{avg}} = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \frac{\left(\frac{ghc}{n\lambda kT}\right)^2 \exp\left(\frac{ghc}{n\lambda kT}\right)}{\left[\exp\left(\frac{ghc}{n\lambda kT}\right)\right]} / (\lambda_{\text{max}} - \lambda_{\text{min}}) \quad (7)$$

The absorbance g is normalized to unity at the peak. Experimentally, the specific heat of the crystal is correlated to the FIR spectra in future extensions to this paper.

Conclusions

The Planck specific heat of crystal lattice is consistent with QM in Planck's formulation of blackbody radiation in an evacuated cavity provided the velocity of light is reduced by the refractive index of the crystal.

The Planck specific heat based on photons vanishes at the nanoscale but is consistent with Debye's phonons at the macroscale.

Unphysical reductions in thermal conductivity of thin films and violations of standard mixing rules in nanofluids based on Debye's phonons is avoided with Planck specific heat based on photons that maintains bulk conductivity in thin films and obeys mixing rules in nanofluids.

Correlation of Planck specific heat with Raman's experimental data requires higher characteristic frequencies than for Raman's method of summing discrete FIR spectral lines based on phonons in Einstein's specific heat theory.

Planck specific heat is expected to correlate with experimental data if the average specific heat is computed based on the normalized absorbance given from measured FIR spectra. Correlation of the specific heat of a crystal with experimental FIR spectra is an exciting possibility, but requires more study beyond the scope of this paper.

References

- [1] Einstein, 1907, "The Planck Theory of Radiation and the Theory of Specific Heat," *Ann. der Physik*, Vol. 22, pp. 180-190.
- [2] P. Debye, 1912, "The Theory of Specific Heat," *Ann. der Physik*, Vol. 39, pp. 789- 839.
- [3] C.V. Raman, 1951, "The vibration spectra of crystals and the theory of their specific heats," *Proc. Ind. Acad. Sci.*, Vol. 34, pp. 141-151
- [4] C.V. Raman, 1957, "The specific heats of crystalline solids: Part II," *Curr. Sci.*, Vol. 36, pp. 231-234.
- [5] C.V. Raman, 1957, "The specific heats of some metallic elements: Part I. Analysis of experimental data," *Proc. Ind. Acad. Sci.*, A45, pp. 1-6.
- [6] C.V. Raman, 1957, "The specific heats of some metallic elements: Part III. The characteristic frequencies," *Proc. Ind. Acad. Sci.*, A45, pp. 59-64.
- [7] C. Kittel, 2005, *Introduction to Solid State Physics*, New York, McGraw-Hill
- [8] S. Volz, 2007, *Microscale and Nanoscale Heat Transfer* (Springer-Verlag, Berlin-Heidelberg.
- [9] M. Issa, 2006, "Nanoscale Thermal Analysis of Electronic Device," *IEEE/CCGEL*, Ottawa, pp. 2147.
- [10] W. Liu, M. Aseghi, 2006, "Thermal Conductivity Measurements of Ultra-Thin Single Crystal Silicon Layers," *J. Heat Transfer*, 128, pp. 75.
- [11] S. P. Jang and S. U. S. Choi, "Role of Brownian motion in the enhanced thermal conductivity of nanofluids," *App. Phys. Lett.*, 2004, Vol. 84, pp. 4316-8.
- [12] X. Zhang, H. Gu, and M. Fujii, "Effective thermal conductivity and thermal diffusivity of nanofluids containing spherical and cylindrical nanoparticles," *J. App. Phys.*, Vol. 100, 2006, pp. 044325.
- [13] J. Eapen, et al., "Mean-Field Versus Microconvection Effects in Nanofluid Thermal Conduction," *Phys. Rev. Lett.*, 2007, Vol. 99, pp. 095901.
- [14] T. Prevenslik, 2009, "Heat Transfer in Thin Films," Third Int. Conf. on Quantum, Nano and Micro Technologies, ICQNM 2009, February 1-6, Cancun.
- [15] T. Prevenslik, 2009, "Nanoscale Heat Transfer in Thin Films," Proceedings of MNHMT09 Micro/Nanoscale Heat and Mass Transfer International Conference, December 18-21, Shanghai.
- [16] T. Prevenslik, 2008, "Nanofluids by QED Induced Heat Transfer," IASME/WSEAS 6th Int. Conf. Heat Transfer, HTE-08, 20-22 August, Rhodes
- [17] T. Prevenslik, 2009, "Nanofluids by Quantum Mechanics," Micro/Nanoscale Heat and Mass Transfer International Conference, December 18-21, Shanghai.
- [18] M. Planck, 1900, "Entropy and Temperature of Radiant Heat," *Ann. der Physik*, Vol. 1, pp. 719-37.
- [19] R.P. Feynman, et al., 1971, *Lectures in Physics*, The Brownian Movement, Equipartition and the quantum oscillator, Vol. 1, Chp.41, pp. 6-7.
- [20] Harrick Scientific Products, "Far-IR Diamond ATR Spectroscopy," No. 080401, 141 Tompkins Ave, Pleasantville, New York.