

Quantum Corrections of Heat Capacity support the Theory of QED Radiation

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Abstract—Molecular dynamics (MD) is commonly used in computational heat transfer to derive the thermal response of nanostructures. Finding basis in statistical mechanics, MD relates the thermal energy of the atom to its momentum through the equipartition theorem that in effect requires the atom to always have heat capacity. In bulk materials, MD that assumes the atoms in a microscopic region under periodic boundary conditions have heat capacity is valid because atoms in the bulk do indeed have the heat capacity necessary to conserve absorbed EM energy by an increase in temperature. EM stands for electromagnetic. However, MD simulations of heat transfer in discrete nanostructures differ from those in the bulk because QM requires the heat capacity of the atoms in nanostructures under TIR confinement to vanish. QM stands for quantum mechanics and TIR for total internal reflection. In nanostructures, absorbed EM energy of any form (heat, light, friction) cannot be conserved by an increase in temperature. By the theory of QED radiation, the absorbed EM energy therefore is instead conserved by frequency up-conversion to the TIR resonance of the nanostructure, the consequence of which is the production of non-thermal EM radiation having sufficient Planck energy to charge the nanostructure by the photoelectric effect and if not is emitted to the surroundings. Therefore, the uncountable numbers of MD solutions of heat transfer in discrete nanostructures based on statistical mechanics abounding the literature are invalid by QM. In support of QED radiation theory, quantum corrections of classical heat capacity in MD solutions are presented that show the heat capacity of nanostructures does indeed vanish.

I. INTRODUCTION

HEAT transfer at the nanoscale is usually performed using MD simulations [1] based on statistical mechanics assuming the thermal energy of the atom is related to its momentum through the equipartition theorem. Momenta of atoms in an ensemble are determined by solving Newton's equations with inter-atomic forces derived from Lennard-Jones potentials. Statistical mechanics assumes the atom has heat capacity as otherwise the atom momentum cannot be related to its temperature.

In heat transfer simulations of bulk materials, MD assumes the atoms have heat capacity. Under periodic boundary conditions, MD simulations of the bulk are valid by QM because atoms in the bulk do indeed have heat capacity. QM stands for quantum mechanics.

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However, MD simulations of heat transfer in discrete nanostructures differ from those in the bulk. The problem is QM precludes atoms in nanostructures under TIR confinement from having the heat capacity necessary to conserve absorbed EM energy by an increase in temperature. Today, the problem is exacerbated by the fact commercially available MD computer programs follow statistical mechanics. What this means is the uncountable numbers of heat transfer solutions derived by MD that abound the literature are invalid by QM.

II. THEORY

The theory of QED radiation avoids the invalidity of MD by QM. Based on the Einstein-Hopf relation [2] of QM the heat capacity given by the thermal kT energy of the atom vanishes at the submicron TIR wavelengths of nanostructures. Lacking heat capacity, conservation of absorbed EM energy proceeds by the QED induced creation of non-thermal EM radiation inside the nanostructure at its TIR frequency – the EM radiation having the necessary Planck energy to produce charge by the photoelectric effect, or is emitted to the surroundings. In this regard, numerous papers [3] have argued that MD heat transfer simulations of discrete nanostructures based on SM are invalid by QM.

A. QM Restrictions

Unlike classical physics, QM restricts the heat capacity of nanostructures through the thermal kT energy of the atom thereby precluding conservation of any form of EM energy by an increase in temperature. A comparison of the kT energy of the atom by classical physics and QM by the Einstein-Hopf relation [2] is shown in Fig. 1.

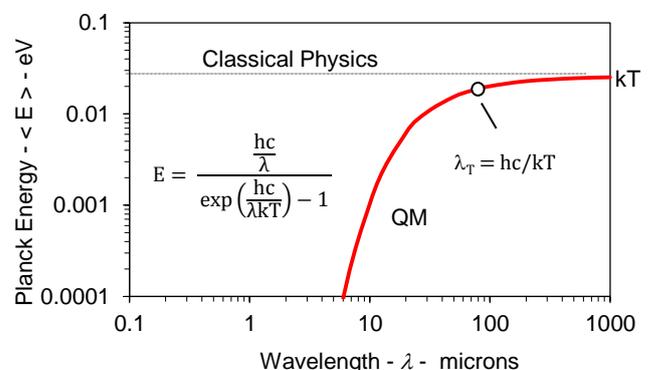


Fig. 1 Heat Capacity of the Atom at 300K
 E is Planck energy, h Planck's constant, c speed of light
 k Boltzmann's constant, T absolute temperature, and λ wavelength

Classical physics by statistical mechanics allows the atom to have the same kT energy in submicron nanostructures as in macroscopic bodies. QM differs in that kT energy is only available for $\lambda > \lambda_T$ and otherwise is $< kT$. At ambient temperature, $\lambda_T \sim 40$ microns. Fig. 1 shows the thermal energy or heat capacity of the atom is $< kT$ for $\lambda < 40$ microns. By QM, atoms under EM confinement wavelengths $\lambda < 1$ micron have virtually no heat capacity to conserve energy from any EM source by an increase in temperature.

B. TIR Confinement

Lack of heat capacity by QM precludes heat absorbed from EM sources to be conserved in nanostructures by an increase in temperature. The EM energy is proposed conserved by the creation of non-thermal EM radiation by the QED induced frequency up-conversion to the TIR resonance of the nanostructure.

In 1870, Tyndall showed light is trapped by TIR in the surface of a body if the refractive index of the body is greater than that of the surroundings. TIR has an important significance in nanostructures and need not be limited to light absorption. Unlike macroscopic bodies, nanostructures have high surface to volume ratios, and therefore EM energy from any source (lasers, mechanical and Joule heat, electron beam irradiation) is absorbed almost entirely in their surface. Since the nanostructure surface coincides with the TIR wave function, QED induces the absorbed EM energy to undergo spontaneous conversion to non-thermal EM radiation. However, TIR confinement sustains itself only during EM energy absorption, i.e., absent absorption of EM energy, there is no TIR confinement and QED radiation is not created.

QED relies on complex mathematics as described by Feynman [4] although the underlying physics is simple, i.e., photons of wavelength λ are created by supplying EM energy to a submicron QM box with sides separated by $\lambda/2$. In this way, QED frequency up-converts absorbed EM energy to the TIR resonance described by the characteristic dimension D_c of the nanostructure. The QED photon energy E and frequency ν are:

$$E = h\nu, \quad \nu = \frac{c}{\lambda}, \quad \lambda = 2nD_c \quad (1)$$

where, n is the refractive index of the nanostructure.

C. Quantum Corrections

QCs of classical thermodynamic variables support QED radiation theory that relies on a vanishing heat capacity of the atoms in nanostructures. QC stands for quantum correction. Procedures for performing QCs are not new and have been known for some time. ("Quantum Corrections" Sect. 2.9 of [1]).

QCs applied to molecules assume the atoms behave as a set of QM harmonic oscillators, the density of states given by the Fourier transform of the velocity autocorrelation function. The QC for the response of the thermodynamic variable is determined at each frequency of the density of states by the response of the QM oscillator, the total QC obtained by integrating over all frequencies. For

nanostructures, a simpler approach is to determine the QC of the thermodynamic variable at the TIR resonance.

Indeed, QCs for the water molecule [5] have been known for 30 years, the generalized expressions for the energy E , constant volume heat capacity C_v , Helmholtz free energy A , and entropy S applicable to any QM system summarized in Fig. 2.

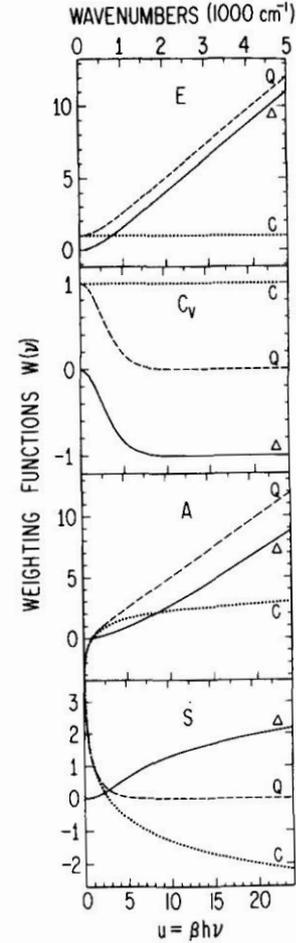


Fig. 2 Quantum Corrections

In Fig. 2, the QC weighting function $W = Q - C$ is the difference Δ between the quantum Q and classical C values of the thermodynamic variable. Extended to nanostructures, the bottom abscissa is $u = h\nu / kT$, where $\nu =$ TIR frequency of the nanostructure. The top abscissa is the wave number equivalent to the parameter u at 300 K. All W go to zero for $u < 1$ consistent with the low frequency anharmonic region of statistical mechanics where QCs are insignificant; whereas, W for $u > 1$ correspond to the harmonic approximation where QCs are significant.

D. QC of Heat Capacity

QED radiation is based on the energy E of the atom given by the Einstein-Hopf relation for the QM oscillator, the quantum Q heat capacity C_v is given by the partial derivative E / dT of the energy E with respect to temperature

T.

$$C_V = \frac{\partial E}{\partial T} = \frac{Q}{C} \frac{u^2 e^2}{[1 - e^u]^2} \quad (1)$$

The Einstein-Hopf relation does not include the ZPE in Planck's derivation, but this is inconsequential because the derivative of the ZPE with respect to temperature vanishes. ZPE stands for zero point energy. In Fig. 2, C_V shows $W < 0$ because $Q < C$ and vanishes for $u > 5$. The QC for heat capacity C_V at 300 K is shown in Fig. 3.

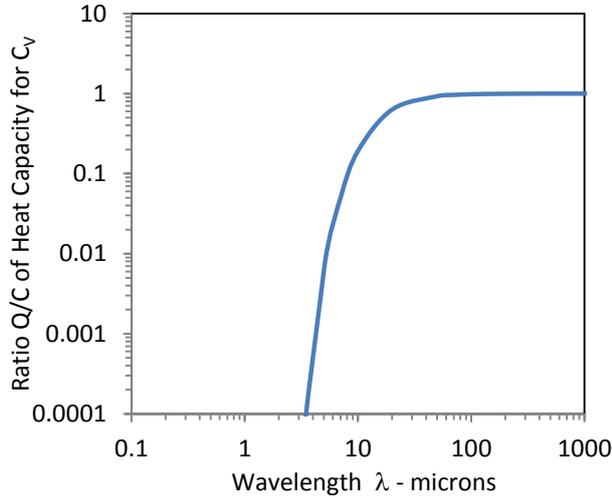


Fig. 3 QC of Heat Capacity at 300 K

Depending on TIR confinement, C_V may vanish in nanostructures at ambient temperature, i.e., vanishing heat capacity need not require temperatures at absolute zero as in statistical mechanics. Fig. 3 shows heat capacity ratio Q/C is always less than classical and vanishes under TIR confinement in nanostructures at ambient temperature thereby supporting the theory of QED radiation.

V, CONCLUSIONS

Classical physics assumes the atom always has heat capacity. QM differs by restricting the atom's heat capacity to vanishing small levels in nanostructures. Conserving absorbed EM energy by QED induced radiation in the nanostructure surface avoids unphysical findings and heat transfer anomalies.

QCs of classical thermodynamic variables for molecules shown in Fig. 2 are applicable to any QM system. However, for nanostructures there is no need to perform MD simulations to determine the heat capacity from the density of states by the Fourier transform of the velocity autocorrelation function as the fundamental frequency of the nanostructure may be derived from the fact nanostructures have submicron TIR wavelengths. One need not go further to conclude classical MD heat transfer of discrete nanostructures based on statistical mechanics with finite heat capacity is meaningless.

Vanishing heat capacity in nanostructures has been argued [3] as the basis for the theory of QED radiation. However, comparison of the Einstein-Hopf energy E with

C_V in Figs. 1 and 3 for the same ordinates of 0.0001 shows C_V vanishes at TIR wavelengths of about 3.5 microns while E by the same fraction occurs at about 6 microns. Therefore, the heat capacity given by C_V is more restrictive and will be used in further applications of QED theory. Regardless, the heat capacity of the atom vanishes at the submicron TIR wavelengths of nanostructures.

REFERENCES

- [1] M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids*, (Oxford: Clarendon Press: 1987).
- [2] A. Einstein and L. Hopf, "Statistische Untersuchung der Bewegung eines Resonators in einem Strahlungsfeld," *Ann. Physik*, vol. 33, pp. 1105-1120, 1910.
- [3] T. Prevenslik, "Validity of Molecular Dynamics in Heat Transfer", "Unphysical 2012" at <http://www.nanoqed.org>, 2012.
- [4] R. Feynman, *QED: The Strange Theory of Light and Matter*. Princeton University Press, 1985.
- [5] P. H. Berens, D. H. J. Mackay, G. M. White, and K. R. Wilson, "Thermodynamics and quantum corrections from molecular dynamics for liquid water," *J. Chem. Phys.*, 79, 1983.