The Second law in Near Field Radiative Heat Transfer

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Abstract: Near-field Radiative Heat Transfer (NFRHT) assumes heat Q flow across vacuum nanoscale gaps follows Rytov's theory of electrodynamic fluctuations in deriving gap surface temperatures. However, the Planck law of quantum mechanics (QM) is shown to preclude heat from producing temperature fluctuations in nanoscale gaps surfaces. Absent Brownian motion, atoms in both hot and cold gap surfaces approach absolute zero which suggests a violation of the Second law of Thermodynamics (SLT) as it is not possible to transfer heat between reservoirs having the same hot and cold temperature. Indeed, the Carnot statement of the SLT gives the efficiency of a thermodynamic cycle to depend solely on the difference between hot and cold reservoir temperatures, the efficiency vanishing for gap surfaces having the same temperature suggesting heat Q flow is not possible. In effect, the Planck law requires NFHRT theories to be independent of temperature. One such NFRHT theory is simple QED that carries heat Q flow across the gap by EM waves. Simple QED is shown to satisfy the SLT as the gap surface atoms at absolute zero create thermal gradients with adjacent atoms having finite kT energy to conduct heat from both hot and cold surfaces into the gap. But in the gap, the Fourier law is no longer valid meaning the conductive heat is conserved by creating the momenta of hot and cold EM waves, the difference in EM momenta carrying the heat Q flow across the gap. The SLT is not violated as the bulk temperatures of hot and cold EM momenta correspond to Carnot reservoirs, even though the gap surface temperatures are identical. Simple QED is illustrated for thermophotovoltaic devices having a nanoscale gap between the thermal emitter and PV cell.

Keywords: NFRHT, Second law, Planck law, simple QED, EM waves, PV cells

I. INTRODUCTION

NFRHT began a few decades ago in the search [1-3] directed to explaining why the Stefan-Boltzmann law failed to explain the heat transfer between hot and cold bodies separated by a nanoscale gap d as illustrated in Fig. 1.

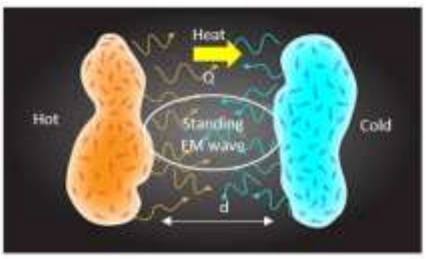

Figure 1. NFRHT

In NFRHT, the mechanisms by which heat Q flows from hot to cold bodies was extensively sought, all of which assumed surface temperatures of hot and cold bodies, the difficulty of measuring surface temperature in nanoscale gaps avoided by assuming bulk values.

Non-thermal EM waves standing across the gap do not require surface temperatures, but presumably were excluded because since Fourier, temperature differences alone were thought sufficient for describing heat Q flow. Nonetheless, Fig. 1 depicts a temperature independent EM wave transferring heat Q across the gap d.

Today, all known NFRHT mechanisms transfer heat Q by differences in gap surface temperatures. What this means is temperature dependent phonons and evanescent waves known to exist in surfaces of bodies separated by larger gaps are assumed to exist at the nanoscale.

Contrarily, the Planck law [4] of QM denies atoms in the surfaces of nanoscale gaps the heat capacity to change in temperature which may be understood by considering the average Planck energy E of the atom mediated by the Bose distribution,

$$E = \frac{\frac{hc}{\lambda}}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]} \qquad (1)$$

and at 300 K is plotted in relation to classical physics in Fig. 2.

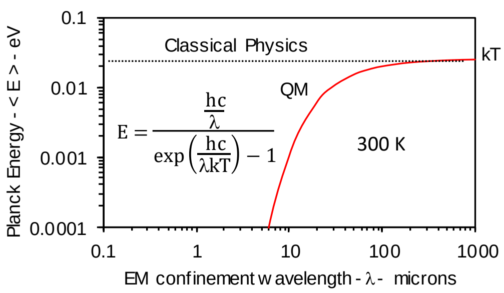

Figure. 2: Planck law of QM at 300 K
In the inset, E is Planck energy, h Planck's constant, c light speed, k Boltzmann's constant, T temperature, and λ the EM wavelength.

The Planck law at 300 K shows classical physics allows the atom to have constant thermal kT heat capacity over all EM wavelengths λ. QM differs as the kT heat capacity decreases for $\lambda < 200$ μm, and vanishes at the nanoscale for $\lambda < 0.1$ μm = 100 nm. Lacking heat capacity, atoms in nanoscale gap surfaces cannot fluctuate in temperature contrary to Rytov's theory [5] of temperature fluctuations.

Currently, nTPV devices face a dilemma in that all NFRHT theories based on phonons and evanescent waves, or variants thereof which require the atoms in the surface of nanoscale gaps to have temperature are invalid. In effect, the Planck law requires any nTPV theory to be independent of temperature.

II. PURPOSE

The purpose of this paper is to propose temperature independent simple QED heat transfer [6] by EM waves as an alternative to NFRHT theory at the nanoscale and extensions thereof to nTPV devices.

III. THEORY

Simple QED is the consequence of the Planck law denying atoms in nanostructures the heat capacity to increase in temperature upon the absorption of heat. QED stands for quantum electrodynamics, a complex theory based on *virtual* photons advanced by Feynman [7] and others. Simple QED is far simpler only requiring the heat capacity of the atoms in nanostructures to vanish allowing conservation to proceed by the creation of *real* photons comprising EM waves that stand across the nanostructures.

Similar to atomic quantum states described by electrons in discrete orbitals, simple QED quantum states are dependent on the dimension of the nanostructure over which the EM waves stand. The Planck energy E of a simple QED photon standing across a distance d is given by the time τ for light to travel across and back, $\tau = 2d/(c/n)$, where n is the index of refraction of the nanostructure material. Hence, the Planck energy E of the simple QED photons is, $E \sim h/\tau$ having wavelength $\lambda = 2nd$,

$$E = \frac{hc}{2nd} \tag{2}$$

To illustrate simple QED, consider heat flux Q having wavelength λ_o heating a nanoparticle (NP) of diameter d. For $\lambda_o >> d$, the NP is immersed in the heat flux Q as illustrated in Fig. 3.

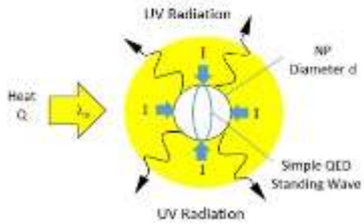

Figure 3. Heating of a NP

Importantly, heat flux Q absorbed by the NP must be placed under brief EM confinement to create the simple QED photons, the process of which depends on the Planck law denying NP atoms the heat capacity to allow the temperature changes required for Fourier heat conduction. Hence, the heat flux Q cannot penetrate the NP surface, and therefore conservation of Q at the NP surface can only proceed by creating non-thermal EM waves to carry the heat Q across and back the NP diameter d in time $\tau = 2nd/c$ as defined in Eqn. 2 for the energy E of the simple QED photon.

The EM confinement at the NP surface is caused by the brief inward spherical Poynting vector S = Q carrying momentum I (shown as blue arrows in Fig. 3). Here, U is the energy from the heat flux Q acting over an increment of time Δt, $U = QA \cdot \Delta t$, where A is the NP surface area, units of S and Q ~ Wm^{-2} and U ~ J giving momentum $I = U/c \sim Nt \cdot s$. Over time Δt, $N = U/E$ simple QED photons having momentum $I_P = h/2nd$ are created, where $NI_P < I$. Once $NI_P > I$, the simple QED photons are emitted to surroundings.

In the interest of whether simple QED photons absent a discrete heat Q may be created from the thermal surroundings alone, consider a NP in the ambient environment at temperature T. The Planck law gives the heat flux Q_T from the ambient as radiant thermal power energy density,

$$Q_T = \left(\frac{2c}{\lambda^4}\right) \frac{\frac{hc}{\lambda}}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]} \tag{3}$$

The Q_T momenta $I_T = U_T/c$ driven by the NP at absolute zero, provide the confinement of the simple QED photons, the number N_T of which at temperature T is $N_T = Q_T V/E$, where V is NP volume, and $E = hc/2nd$. For ambient at 300 K, Fig. 2 shows classical kT occurs at $\lambda > 100$ μm. Hence, $Q_T \sim 2 \times 10^4$ J/s·m^3. For Covid-19 vaccines [6] having d ~ 80 nm lipid NPs, $V = 2.68 \times 10^{-22}$ m^3. Taking n = 1.6, 2nd ~ 254 nm in the UVC with $E = 7.80 \times 10^{-19}$ J or 4.88 eV. Hence, the NPs emit $N_T \sim 7$ UVC photons/s of EM radiation to stimulate the immune system (Fig. 3). Depending on NP size, simple QED radiation from the IR to EUV may be emitted from heat Q_T in ambient surroundings, albeit at low intensity.

The EM confinement of simple QED photons in the NP by the inward spherical momenta is not applicable to NFRHT in gaps between hot and cold bodies as illustrated in Fig. 4.

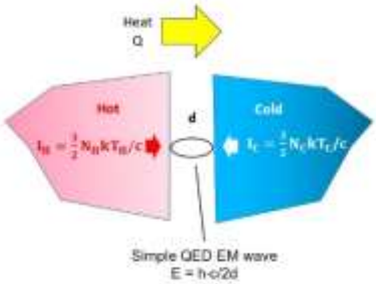

Figure 4. NFRHT.

In NFRHT, heat Q is transferred from hot to cold bodies across a nanoscale gap with vanishing thermal kT energy of atoms in hot and cold gap surfaces as required by the Planck law. To compensate for the surface atoms effectively at absolute zero, the number of adjacent atoms in hot N_H and cold N_C bodies having finite thermal kT energy $U_H = \frac{3}{2} N_H kT_H$ and $U_C = \frac{3}{2} N_C kT_C$ form the Poynting vectors of momentum $I_H = U_H/c$ and $I_C = U_C/c$ directed toward the respective gap surfaces, the momenta providing the EM confinement to form the simple QED photons.

Heat Q flows if the momentum $I_H > I_C$. In the gap, the Planck law precludes conservation of Q by a change in temperature, and instead proceeds by the creating a number N of EM waves, the heat Q/N ~ W/wave delivered to the gap d in time $\Delta t = 2d/c$ is,

$$\frac{Q}{N} = \frac{E}{\Delta t} = \frac{h}{4}\left(\frac{c}{d}\right)^2 \qquad (4)$$

The NFRHT time $\Delta t = d/2c$ is the same as the NP time $\tau = d/2nc$ having refractive index n = 1.

IV. SECOND LAW

In NFRHT, the SLT arises as the Planck law requires the gap surface to have the same temperatures which requires the heat Q flow across the gap to vanish. The efficiency η of heat engines operating between a hot T_H and cold T_C temperatures is,

$$\eta = \frac{T_H - T_C}{T_C} \qquad (5)$$

The SLT restricts T_H and T_C as first shown [8] by Carnot's hypothesis: first, that one cannot devise a process whose only result is to convert heat to work at a single temperature, and second, that one cannot make heat flow by itself from a cold to a hot place. However, simple QED avoids dependence on gap surface temperatures by the EM waves that carry heat as momentum.

Yet, controversy in SLT exists today as to whether entropy even exists in EM radiation and how the SLT restricts EM radiation. Entropy S is,

$$S = \frac{Q}{T} \qquad (6)$$

where, S is the heat Q per unit temperature in J/K.

Unlike EM radiation in simple QED which does not depend on gap surface temperatures, the literature [8-10] considers only the entropy of temperature dependent blackbody (BB) radiation.

In this regard, the thermodynamics of BB radiation [9] treated as volume of photon gas gives the entropy of radiation as $S = \frac{4}{3} aT^3V$, where T and V are the temperature and volume of a cavity at equilibrium with the radiation. However, the usual unit of entropy is J/mole-K not J/K. More importantly, entropy in matter consists atoms under endless random contact, but this is not true for photons which cease upon absorption. Experiments to measure in BB radiation are simply not available.

More recently, entropy has been related [10] to the temperature of BB radiation. A simple proof is given that EM radiation should carry entropy comprising BB reservoirs at hot T_H and cold T_C temperatures. Consider a shutter connecting the reservoirs is open for a time such that the energy of the EM radiation leaving the hot reservoir has not yet absorbed by the cold reservoir. At this time, the entropy of the hot reservoir decreases but the entropy of the cold is not yet increased. Hence, EM radiation must carry entropy equal to that removed from the hot reservoir as otherwise the SLT is violated. But this is proof is circular in that the conclusion is assumed from the beginning, as EM radiation in the hot reservoir is assumed to have entropy which would appear in the emitted EM radiation independent of the SLT.

Moreover, the energy E of a photon given in Eqn. 1 includes number n of photons/mode,

$$n = \frac{1}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} \qquad (7)$$

also known as the Bose relation. In [10], Eqn. 7 is rewritten as,

$$n\frac{hc}{\lambda} = kT\ln\left(1 + \frac{1}{n}\right)^n$$

The energy E of the mode is $n \cdot hc/\lambda$ which in the classical limit where $n \to \infty$ gives the mode temperature T = E/k and entropy S = k. For a UV photon having E = 4.88 eV, T ~ 56,000 K which does not occur in the quantum limit.

Indeed, the classical limit for mode temperature is meaningless in NFRHT. Fig. 2 shows the classical limit at 300 K has a wavelength λ ~ 200 μm or a gap d = λ/2 ~ 100 μm >> NFRHT gaps. Only modes having half-wavelengths λ/2 < 100 nm in the quantum limit in the EUV have meaning. Indeed, simple QED assumes the energy E of waves standing across the gap has vanishing heat capacity or kT energy.

In this regard, consider entropy S = Q/T, where Q = E is given in Eqn. 1. For T = 100, 300, and 500 K, the entropy S is shown in Fig. 5.

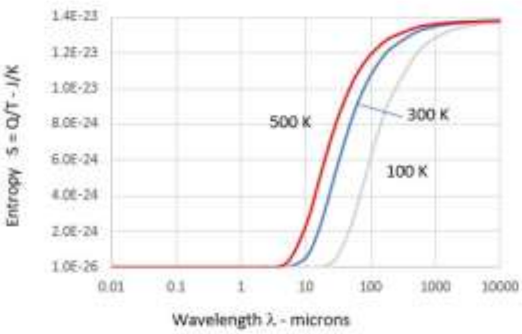

Fig. 5. Entropy of a single Photon

Fig. 5 shows S approaches the Boltzmann constant k = 1.38×10^{-23} J/K at the classical limit for all temperatures but vanishes at short wavelengths consistent with simple QED that denies temperature fluctuations in nanoscale NFRHT gaps.

Of interest, is how the EM wave acquires temperature at the quantum limit. In this regard, simple QED based on the Planck law precludes heat from producing temperature fluctuations in nanoscale gaps and surfaces. Absent Brownian motion, atoms in both hot and cold gap surfaces approach absolute zero that produce thermal ΔT_H, ΔT_C gradients toward the gap. Heat flows by Fourier conduction in both surfaces into the gap. But in the vacuum gap, the Fourier law is no longer valid and conductive heat is conserved by creating EM waves carrying the heat as momenta I_H, I_C depicted in Fig. 6.

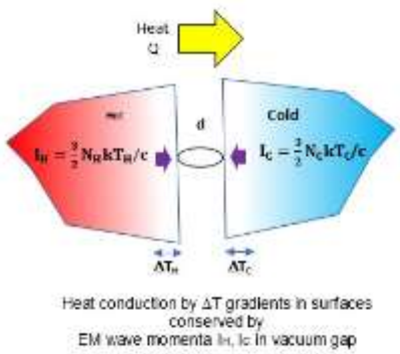

Figure 6. EM waves carry thermal momenta to gap

However, both gap surfaces at the same temperature suggests a violation of the SLT as it is not possible to transfer heat Q between reservoirs having the same hot and cold temperature.

Simple QED avoids SLT violations by transferring the heat Q across the gap by the difference in momenta (I_H - I_C) carried by photons in EM waves. The SLT is not violated as the bulk temperatures of hot T_H and cold T_C surfaces act as thermal reservoirs,

$$Q = (I_H - I_C)c = \frac{3}{2} k (N_H T_H - N_C T_C) \quad (8)$$

The heat Q transferred by EM momenta correspond to Carnot reservoirs. Hence, the SLT is not violated, even though the Planck law requires identical gap surface temperatures.

V. APPLICATION

Commercially available TPV devices [11] are thermophotovoltaic in which thermal photons at high temperatures in the NIR excite the PV cell to produce electricity, but nTPV suggests adding a nanoscale vacuum gap between emitter and PV cell somehow increases the heat Q flow that significantly enhances electrical power density.

Of relevance to nPVT devices, all known NFRHT theories are based on Rytov's fluctuation temperatures [5] that assume photon tunneling by evanescent waves. But like NFRHT, experimental verification of nTPV theory should be expected difficult as temperature differences of only a few degrees across nanoscale gaps can cause high thermal gradients and incorrect estimates of heat flow Q enhancement.

Nevertheless, a 40-fold enhancement of the nTPV output power [12] at a gap distances d = 60 nm was taken [11] as experimental proof of principal of the nTPV concept. The application of simple QED by EM waves in nTPV devices based on [12] is illustrated in Fig. 7.

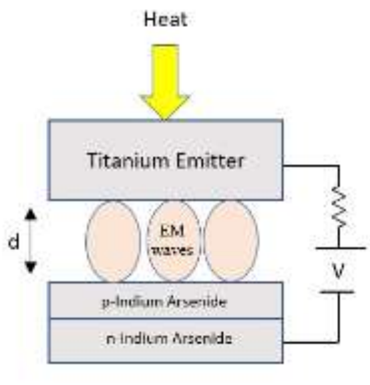

Figure 7. nTVP by EM waves

The simple QED version representative of nTVP devices comprises a titanium emitter separated by a nanoscale gap d from an InAs PV cell. EM waves travel from emitter to cell are depicted carrying heat Q across the gap.

NFRHT theory based on temperature fluctuations is shown [12] in agreement with experiment over al gap sizes and emitter temperatures from 525-665 K in Fig. 8.

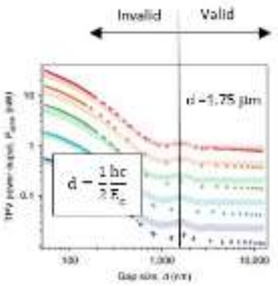

Figure 8. Simple QED vs, nPVT theory/Experiment

By simple QED, however, both NFRHT theory and experiment are invalid at gaps d < 1750 nm as noted in Fig. 8. The disparity occurs because heat Q flow by EM waves differs significantly from nPVT theory by dependence on the bandgap Eg of the InAs PV cell, $E_g = 0.354$ eV at $\lambda = 3.5$ μm.

In fact, Fig. 8 data shows small peaking of Q at all temperatures at d = λ/2 = 1.75 μm. But for d < 1.75 μm, both nPVT theory and experiment show Q increases and at 665 K is 40 nW. This is considered invalid because a decrease is expected to mirror the Q response for d > 1.75 μm, i.e., the response of an oscillator is lower both before and after bandgap resonance.

Further, NFRHT based on Rytov's temperature fluctuation theory does not answer the question of why the heat transfer Q increases and not decreases as d → 0, but in [13] surface contact is shown to transport heat Q > 0 across single-digit nanoscale gaps. This is difficult to understand as there can be no temperature difference across direct surface contact.

In this regard, simple QED differs. Eqn. 4 shows Q/N becomes large as d → 0. But the EM wave can only carry heat Q_H/N across the gap if Q_H/N > Q/N, but otherwise if Q_H/N < Q/N, the wave cannot form and Q = 0. The relation of Q_H/N and Q/N depends on gap d as shown in Fig. 9.

Now, Fig. 9 for the InAs bandgap of d = 1750 nm gives Q/N = 5 μW, but Fig. 8 for temperatures < 665 K at 1750 nm gives Q_H/N < 2 nW. Since Q/N > Q_H/N, simple QED requires heat flow Q = 0 across all gaps d < 1750 nm. Higher Q_H/N is required to enhance heat Q/N flow, say by increasing the emitter temperature.

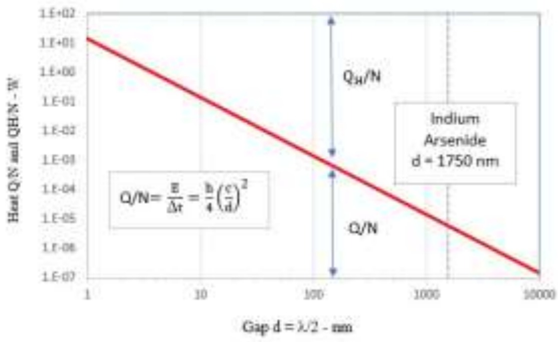

Figure 9. Q/N and QH Relation

The validity of simple QED depends on vanishing kT heat capacity in nanoscale gaps usually at wavelengths < 100 nm, but the nTPV bandgap requires the kT heat capacity to vanish at λ = 2d = 3 μm. At 300 K, Fig. 2 shows the Planck energy at λ ~ 6 μm is, E = 100 μeV, and at 3 μm, E < 100 μeV. Since the kT energy of the atom at which heat produces an increase in temperature is 0.0254 eV, the kT energy at λ = 3 μm at 3 μm is > 250 times more likely to produce NIR radiation in the 1.75 μm gap than increase in temperature upon absorbing heat. At 300 K, simple QED is indeed valid in d = 1.75 μm gaps.

VI. CONCLUSIONS

The SLT is not violated in nanoscale gaps even though gap surfaces have identical temperatures approaching absolute zero as required by the Planck law.

Carnot's hypothesis on the impossibility of converting heat to work at a single temperature, and that heat flow requires to have thermal reservoirs with different temperature are both based on the classical limit that does not apply to the nanoscale at the quantum limit.

Heat is transferred by Fourier conduction from both hot and cold atoms having finite kT energy along thermal gradients with gap surface temperatures approaching absolute zero.

At the gap surface, the hot and cold conductive heat is conserved with the momenta of hot and cold EM waves, the difference of which carries the heat across the gap, thereby satisfying the SLT even though gap surface temperatures are identical.

PVT devices comprising nanoscale vacuum gaps between the emitter and PV cell producing enhanced heat Q flow based on NFRHT theory of temperature fluctuations is invalid by the Planck law which denies gap surface atoms the heat capacity necessary for temperature fluctuations.

Experiments to verify NFRHT in nPVT based on temperature fluctuations are perhaps near impossible as the Planck law denies temperatures to fluctuate in nanoscale gaps. Measurements reported in the literature of temperature differences across nanoscale gaps are fraught with error as the difference in gap surface temperatures sought simply do not exist.

Only temperature independent NFRHT theories for nTPV devices are valid in nanoscale gaps, one of which is simple QED based on the Planck law itself.

Simple QED applied to experimental data of an InAs nPVT device shows a slight peaking in heat Q flow at temperatures < 665 K at the 3.5 μm bandgap wavelength λ of the PV cell, but for λ < 3.5 μm, the heat Q flow increases 40-fold, the latter considered invalid.

NFRHT based on Rytov's fluctuation theory does not predict zero heat Q flow, and therefore contact of gap surfaces is used. But then, the Q flow is thought to increase by conduction even though the temperatures are the same.

Unlike NFRHT, simple QED allows zero heat Q/N flow without contact at the same gap surface temperatures. Based on EM waves, the heat Q_H/N supplied to a gap d is required to satisfy $Q_H/N > Q/N = h(c/d)^2/4$ as otherwise the wave cannot form and Q = 0.

By simple QED, zero nTPV heat flow Q in vacuum gaps between emitter and PV cell may be assumed up to peaking at the bandgap wavelength λ of the PV cell. Hence, simple QED suggests setting the gap d = λ/2.

Since nTPV bandgaps are in the NIR, 60 nm gaps producing λ = 2d = 120 nm EM radiation in the EUV is not expected to enhance efficiency above that of NIR nTPV devices.

Simple QED usually applied to nanoscale gaps d < 100 nm is extended to nTPV devices having gaps d < 3 μm as NIR radiation is > 250 times more likely to conserve heat Q flow than an increase in temperature.

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