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Thermodynamics of Blackbody Radiation Via Classical Physics for Arbitrarily Shaped Cavities with Perfectly Conducting Walls

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An analysis is carried out involving reversible thermodynamic operations on arbitrarily shaped small cavities in perfectly conducting material. These operations consist of quasistatic deformations and displacements of cavity walls and objects within the cavity. This analysis necessarily involves the consideration of Casimir-like forces. Typically, even for the simplest of geometrical structures, such calculations become quite complex, as they need to take into account changes in singular quantities. Much of this complexity is reduced significantly here by working directly with the change in electromagnetic fields as a result of the deformation and displacement changes. A key result of this work is the derivation that for such cavity structures, classical electromagnetic zero-point radiation is the appropriate spectrum at a temperature of absolute zero to ensure that the reversible deformation operations obey both isothermal and adiabatic conditions. In addition, a generalized Wien displacement law is obtained from the demand that the change in entropy of the radiation in these arbitrarily shaped structures must be a state function of temperature and frequency.

1. INTRODUCTION

A thermodynamic analysis is carried out in the present article that involves reversible thermodynamic operations performed on electromagnetic radiation contained within closed cavity structures with perfectly conducting walls, but of arbitrary shape. Each cavity may contain an arbitrary number of perfectly conducting objects within it, such as wires, contacts, or indeed

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any arbitrarily shaped object. At the end of this article, comments are given on how the perfectly conducting restriction might be removed.

The analysis described here is carried out entirely within the realm of classical physics. Nevertheless, as will be discussed more shortly, the main points of this work hold in quantum electrodynamics (QED) as well, due to direct connections that can be made between this work and QED.

The analysis in the present article can be motivated from several viewpoints. First, it has strong connections with early classical thermodynamic analyses of blackbody radiation carried out around 1900, and illustrates how these classical physical analyses can be significantly extended in their physical applicability to describing nature accurately by simply not assuming that radiation needs to vanish at $T=0$. Second, this approach has the same physical description that scientists are used to in the macroscopic world, as opposed to the quantum mechanical description of microscopic systems, yet, a close connection exists between both descriptions. Third, since Casimir force calculations of anything but the simplest structures, and possibly related phenomena like somnoluminescence, are sufficiently complex, then related perspectives on alternative calculational methods should be welcome.

Briefly reviewing previous related work, a reinvestigation of the thermodynamics of blackbody radiation from the point of view of classical physics was carried out in 1992 in Ref. 1. This work involved the analysis of the appropriate spectrum of classical electromagnetic radiation existing between two perfectly conducting parallel plates, as deduced by imposing minimal thermodynamic demands on the system. The appendix in Ref. 1 extended this work to the consideration of the radiation within rectilinear parallel-pipeds with walls made of perfect conductors. Much of this work involved reexamining the problem of a movable piston sliding in a cylinder containing classical electromagnetic thermal radiation. This problem had initially been analyzed in the late 1800s and early 1900s by researchers such as Wien, Stéfan, Boltzmann, and Planck. The key difference between the early work on this problem and the analysis in Ref. 1 was that the latter did not make the implicit assumption that the thermal radiation spectrum reduces to zero at the temperature of $T=0$. As pointed out in Ref. 1 (i.e., see Sec. IX), this subtle, but very critical assumption, was implicitly buried in the much earlier work by researchers on blackbody radiation.

Imposing this assumption helped to contribute to a number of related problems regarding the deduced thermal radiation spectrum, such as the ultraviolet catastrophe for Rayleigh–Jeans (RJ) radiation, the infinite specific heat of RJ radiation, and the failure to satisfy the third law of thermodynamics. Sections V, VI, and VIII in Ref. 2 discussed these problems in some detail. Generalizing the classical analysis to avoid imposing this assumption was shown in Refs. 1–3 to enable these problems to be avoided. Indeed, as shown in Ref. 1, the only radiation spectrum that will yield no heat flow during isothermal quasistatic displacements of perfectly conducting parallel plates, is a spectrum with the same functional form as the classical electromagnetic ZP radiation spectrum, $\rho_{ZP}(\omega) = \hbar\omega^3/2\pi^2c^3$. This condition of no heat flow during reversible isothermal operations is precisely the one that must be satisfied in thermodynamics at temperature $T=0$.[3] Moreover, the resulting Casimir force between the plates is exactly the same result as obtained in QED.[1]

The analysis in Ref. 1 for perfectly conducting parallel plates and rectilinear parallel-pipeds will be extended in the present article to cavities of perfectly conducting materials, where now no restriction is placed on the shape of the cavity or on objects within the cavity. Quasistatic displacement and deformation operations on the cavity structure will be examined. More specifically, we will consider the following physical operations, all performed very slowly (no hard impacts): (1) physically deforming the walls of the cavity or the shapes of the objects in the cavity; (2) displacing the objects within the cavity; or (3) any combination of (1) and (2). To accomplish these tasks, external work must be performed on the system to deform the structures, or to separate objects from each other and from the walls in the cavity. In particular, Casimir-like forces must be taken into account when evaluating the work required to deform and displace objects from one other. These operations will result in changes in the internal energy of the electrodynamic system. Both of these quantities, namely, (1) average work, $\langle W \rangle$, done during these quasistatic displacement and deformation operations, and (2) average changes in internal energy, $\Delta\langle U \rangle$, will be calculated in Sec. 3.

Section 4 then ties this analysis together, by examining the average heat flow $\langle Q \rangle$ into the cavity that is given by

$$\langle Q \rangle = \Delta\langle U \rangle - \langle W \rangle \tag{1}$$

Consideration of this quantity will enable us to show that the deduction of the classical electromagnetic ZP spectrum in Ref. 1 for very specific geometry conditions (parallel plates and rectilinear parallel-pipeds), also holds here for arbitrarily shaped cavities. This result agrees with the findings in Refs. 1–5, and with the expectation that this spectral form is the correct one to be in thermodynamic equilibrium with physically realizable electrodynamic systems at $T=0$.[6, 7, 3] Perhaps the most surprising aspect of this work is that this deduction can be obtained entirely from within classical physical considerations. The present article provides yet another example of an electrodynamic system, along with Refs. 1, 3, 4, and 8, where this result is obtained.[2]

In Sec. 5, an analysis is carried out showing that the thermal radiation spectrum in these arbitrarily shaped cavities must obey a generalized Wien's displacement relationship in order for the entropy of the radiation to be a state function of temperature and frequency. Section 6 then ends with some concluding remarks and ideas for future directions.

The present analysis makes use of a mathematical framework that may be helpful for future work involving the thermodynamic and electrodynamic analysis of small structures with cavities, movable walls and structures, and changes in carrier concentration on the walls of these structures. Considerable attention has been paid in recent years to micro-electromechanical structures (MEMS).[3] Subsets of MEMS devices, such as the atomic force microscope and related measurement tools,[(9)] involve changes in van der Waals and Casimir-like energies. Moreover, another somewhat related field in physics, namely, cavity QED, involves the behavior of particles and radiation interacting within cavities.[(10–13)]

For such systems, calculations involving Casimir-like forces are notorious[(14–16)] for needing to deal with changes in infinite quantities to obtain finite measurable results, like forces and changes in energy. To emphasize this point, it is well known that calculating Casimir forces for simple structures like a spherical shell[(17)] of perfectly conducting material or conducting rectangular parallel-pipeds,[(1, 18)] are all treatable by nearly fully analytical methods. However, analyzing even these simple structures are far from trivial, as evidenced by the time delay between 1953, when Casimir published the suggestion of computing the spherical conducting shell situation,[(19)] and 1968, when Boyer solved the proposed problem.[(17)] Treatment of unusual geometries are even more difficult. Nevertheless, the present treatment applies for arbitrary geometries of cavities with conducting walls. The treatment works because it relies on a perturbation method that directly deals with the changes in the electromagnetic fields that arise due to the changes in the physical constraints of the system, namely, the deformations and displacements in the cavity structure. The method makes direct use of an approach well known in the area of resonant cavities in microwave electronics[(20, 21)] for describing classical electromagnetic field behavior. The analysis in Sec. 2 introduces this approach.

[2] See Ref. 8, Sec. 2, for a simplified proof of the classical electromagnetic ZP spectrum via considering a single harmonic electric dipole oscillator displaced within an electrostatic field.
[3] See, for example, articles published in IEEE Journal of Microelectromechanical Systems.

The treatment in this article makes use of the classical electrodynamic theory often called stochastic electrodynamics (SED).[15, 22, 5], [4] SED describes nature via Maxwell's equations, with the relativistic version of Newton's second law of motion for the trajectory of classical charged particles. The key difference of this theory versus conventional classical electrodynamics is that the restriction is not made that radiation must vanish at a temperature $T=0$. The relaxation of this subtle restriction enables the deduction to be made that classical electromagnetic ZP radiation must be present to satisfy a number of thermodynamic conditions.[1–5] The result is a more accurate description of our physical world, including a number of properties normally only attributed to quantization effects, while still retaining a classical view.[15, 22, 5]

However, a cautionary comment should certainly be made here, that is undoubtedly not a surprise to most physicists: namely, research to date has concluded that agreement between QED and SED, only holds for the situation involving linear equations of motion for the modeled atomic systems and linear equations governing the electromagnetic fields for the modeled macroscopic systems.[24, 5, 15] Thus, if one treats the macroscopic materials as being composed of a set of electric dipole oscillators, or as macroscopic bodies with linear dielectric properties, then we can have confidence in the agreement.

Of course, this situation is quite limiting in many critically important ways, but what is interesting is that even in QED, handling the general situation of nonhomogeneous, dispersive, and absorbing material has not been successfully tackled yet. The problem is far from trivial, both from the physical description point of view (i.e., appropriate quantization method for this complicated many-particle system, and relation to measurable physical quantities), as well as the mathematical complication of solving the resulting governing equations. Reference 25 summarizes much of the difficulties involved with dealing with more general nonlinear, nonhomogeneous, dispersive, and dissipative mediums. Consequently, a number of articles have appeared in the QED literature that model the medium by treating it as being composed of quantum mechanical electric dipole harmonic oscillators. These oscillators model the actual atoms existing in real materials. By placing them in varying density arrangements, and of course coupling all their interactions appropriately, one can treat the case of a nonhomogeneous material, as well as one that is dispersive and dissipative. Renne made the connection[26] between this more microscopic approach of treating a medium to the more familiar macroscopic electrodynamic treatment originally developed by Lifshitz.[27]

[4] See Ref. 23 for a brief review regarding Ref. 15.

Hence, much of the research in this area still relies on solving the problem in QED by precisely the model where QED and SED are known to agree,[24] namely, where atomic systems are treated as being composed of simple harmonic electric dipole oscillators. Fortunately, Renne's basic approach[28] involving full retarded van der Waals forces between such oscillator systems, was shown to yield identical results to those of SED[29] for the case of two oscillators, and later for an arbitrary number of oscillators.[30] Indeed, Kupiszewska's treatment of this problem in QED can be cast entirely within the description of SED, as described in Sec. 6.1 of Ref. 15.

Before beginning our analysis, a few subtle points need to be mentioned. First, no radiation can flow through the cavity walls, since the perfect conductors result in the electromagnetic fields within the walls being equal to zero. Moreover, since we are not treating the walls as possessing a specific heat themselves, but are rather treating them here as idealistic mathematical boundaries that ensure zero fields within the walls, then neither will heat flow through the conducting walls by conduction. Thus, when cavity walls are moved in and out, the work done on the walls must be exactly compensated by changes in internal electromagnetic energy within the cavity. Hence, no heat will flow, resulting in us dealing with adiabatic reversible processes.

In most cases, such adiabatic processes will result in changes in the temperature of the radiation as the walls are moved or deformed. Only in one case will the temperature not change during such an adiabatic process, namely, at absolute zero temperature.[2, 3] Section 4 covers this analysis.

A key restriction on the present analysis is that the cavity walls and the objects inside are treated as being composed of continuous medium. Thus, if comparisons were to be made with experiment, we would expect the analysis to break down when trying to compare with real structures with dimensions approaching molecular and atomic sizes for the cavity, objects, and distances between cavity walls. The continuous medium approach would be suspect then, and the restriction to perfectly conducting material would not hold. These restrictions on the present analysis are then very similar to the ones holding for analyzing Casimir-like forces between plates or other similarly shaped structures. To move beyond this restriction, one would need to deal with individual sets of atoms and molecules, along the lines of Refs. 2–5, and examine the transition as one increased the number N of particles and their density.[26]

2. FIELD DESCRIPTION

We will investigate some of the statistical properties of the radiation in the cavity described in Sec. 1 that must hold to satisfy certain conditions of thermodynamic equilibrium. Only a single cavity will be considered, where all regions of the cavity are topologically connected. We will not consider the situation where the walls might be deformed such that two or more adjoining cavities may merge together, or one cavity may split into two or more cavities.

We will express the fields as a summation over normal modes. For the present article, attention will be restricted to the situation where the current density, $\mathbf{J}(\mathbf{x}, t)$, and charge density, $\rho(\mathbf{x}, t)$, equals zero within the free space of the cavity. Let us work in the Coulomb gauge, so that the vector potential $\mathbf{A}(\mathbf{x}, t)$ satisfies $\nabla \cdot \mathbf{A} = 0$. Within the empty cavity, $\mathbf{A}(\mathbf{x}, t)$ satisfies the wave equation. The transverse electric field $\mathbf{E}_{\perp}(\mathbf{x}, t) = -(1/c)(\partial/\partial t)\, \mathbf{A}(\mathbf{x}, t)$ and the magnetic field $\mathbf{B}(\mathbf{x}, t) = \nabla \times \mathbf{A}(\mathbf{x}, t)$ can be conveniently represented by expanding the vector potential in the following way

$$\mathbf{A}(\mathbf{x}, t) = \sum_{\alpha} [\bar{\mathbf{A}}_{\alpha}(\mathbf{x}, \omega_{\alpha})\, e^{-i\omega_{\alpha} t} + \bar{\mathbf{A}}_{\alpha}^{*}(\mathbf{x}, \omega_{\alpha})\, e^{i\omega_{\alpha} t}] \tag{2}$$

where

$$\nabla^2 \bar{\mathbf{A}}_{\alpha} + k_{\alpha}^2 \bar{\mathbf{A}}_{\alpha} = 0 \tag{3}$$

$$\nabla \cdot \bar{\mathbf{A}}_{\alpha} = 0 \tag{4}$$

and $c^2 k_{\alpha}^2 = \omega_{\alpha}^2$. Requiring that $\hat{\mathbf{n}} \times \bar{\mathbf{A}}_{\alpha}(\mathbf{x}, \omega_{\alpha}) = 0$ for all points $\mathbf{x}$ on the surface S of the cavity, ensures that the tangential components of the transverse electric field $\mathbf{E}_{\perp}$ and the normal component of the magnetic field equals zero on these surfaces, as must be satisfied for a perfect conductor. The Helmholtz equation satisfied by $\bar{\mathbf{A}}_{\alpha}$ and the boundary conditions jointly define a Hermitian eigenvalue problem. The modes corresponding to different eigenvalues are orthogonal. Reference 15, Sec. 3.1.2, summarizes these points, and Ref. 20, Chapter 4, explains them in much more detail. Following Ref. 15, we can work with a family of orthonormal functions $\mathbf{G}_{\alpha}(\mathbf{x}, \omega_{a})$,[5] where

$$\bar{\mathbf{A}}_{\alpha}(\mathbf{x}, \omega_{\alpha}) = b_{\alpha}\, \mathbf{G}_{\alpha}(\mathbf{x}, \omega_{a}) \tag{5}$$

$$\int_V d^3x\, \mathbf{G}_{\alpha}^{*} \cdot \mathbf{G}_{\beta} = \delta_{\alpha\beta} \tag{6}$$

and the integral is taken over the volume V of the cavity. In addition, any two functions $\mathbf{G}_{\alpha}$ and $\mathbf{G}_{\beta}$, or $\mathbf{G}_{\alpha}^{*}$ and $\mathbf{G}_{\beta}^{*}$, integrate to zero. We obtain that

[5] We can relate $\mathbf{G}_{\alpha}$ to the orthonormal functions $\mathbf{E}_{\alpha}$ and $\mathbf{H}_{\alpha}$ in Ref. 20 in the following way, namely, that $\mathbf{E}_{\alpha} = \mathbf{G}_{\alpha}(\mathbf{x}, \omega_{\alpha})$ and $\mathbf{H}_{\alpha} = (1/k_{\alpha})\, \nabla \times \mathbf{G}_{\alpha}(\mathbf{x}, \omega_{\alpha})$.

$$\mathbf{E}_{\perp}(\mathbf{x}, t) = i \sum_{\alpha} \frac{\omega_\alpha}{c} \left[\mathbf{G}_\alpha(\mathbf{x}, \omega_\alpha) \, b_a e^{-i\omega_a t} - \mathbf{G}_\alpha^*(\mathbf{x}, \omega_\alpha) \, b_\alpha^* e^{i\omega_a t} \right] \tag{7}$$

$$\mathbf{B}(\mathbf{x}, t) = \sum_{\alpha} \left[\nabla \times \mathbf{G}_\alpha(\mathbf{x}, \omega_\alpha) \, b_a e^{-i\omega_a t} + \nabla \times \mathbf{G}_\alpha^*(\mathbf{x}, \omega_\alpha) \, b_\alpha^* e^{i\omega_a t} \right] \tag{8}$$

The present analysis can be extended to include the situation where charges exist inside the cavity and where the conducting walls may be charged, via the representation discussed in Ref. 20, Chap. 4, involving a normal mode expansion of the irrotational electric field. However, here we will just note this point and restrict ourselves to the situation of uncharged conductors and no free charges, so that Eq. (7) represents the total electric field within the cavity.

The properties of the radiation that will be investigated here are those due to changes in thermodynamic equilibrium conditions. For a particular temperature T, we may imagine an ensemble of cavities, each cavity with an identical shape and size; hence, each cavity in the ensemble will have the same set of normal modes, and the same set of frequencies ω_α. However, each cavity will have a somewhat different set of electromagnetic mode amplitudes b_α, where the temperature T describes the distribution of this set of mode amplitudes across the ensemble. As the cavity shape is quasistatically changed, then the normal modes will change in the same way for each cavity in the ensemble. Moreover, for any one cavity in this hypothetical ensemble, the electromagnetic mode amplitudes b_α will change in a well defined way, which will enable us to determine the change in the distribution of the electromagnetic mode amplitudes b_α for the entire ensemble.

Any of the quasistatic deformation and displacement operations on the walls and inner objects will change the internal electromagnetic energy within the cavity. As the cavity boundaries are displaced, the rapidly fluctuating surface currents on the boundaries must also change to ensure zero field conditions within the perfectly conducting walls and interior objects. Changes in these currents will change the electromagnetic fields within the cavity interior.

The linear additive nature of the electrodynamic system considered here leads to the demand that each electromagnetic radiation mode should fluctuate independently of each other. Consequently, we will assume, as is usually done in SED,[15] that

$$\langle b_\alpha b_\beta \rangle = \langle b_\alpha^* b_\beta^* \rangle = 0 \tag{9}$$

$$\langle b_\alpha b_\beta^* \rangle = p(\omega_a, T) \, \delta_{\alpha\beta} \tag{10}$$

where the angle brackets represent an ensemble average. Equation (10) states that the mode amplitudes are uncorrelated for $\alpha \neq \beta$, and that

$\langle b_\alpha b_\alpha^* \rangle$ depends on temperature and frequency ω_α. This equation really incorporates a number of underlying assumptions. The dependence of p on ω_α, without any directional dependence in space, assumes that radiation of a single frequency is able to mix in the cavity for all spatial directions. As discussed in Ref. 31, and further in Ref. 1, for specular surfaces, this mixing condition naturally holds. For highly idealized polished surfaces, then one could construct a nonmixing condition that might violate Eq. (10), necessitating that a directional dependence also be included. The situation is analogous to an idealistic chamber with smooth walls and classical particles that interact via elastic collisions with the walls. If the initial set of particles are set in motion in the chamber in selected ways, they may always follow the same trajectories over and over within the chamber, and never fill the entire chamber. Even a slight degree of rough, specular walls, would change this condition enormously, as is more to be expected in realistic experimental conditions.

Moreover, as discussed in some detail in Ref. 31, and further in Ref. 1, one can certainly consider a situation where different radiation rays have different effective temperatures, rather than the condition in Eq. (10) where the same temperature holds for the entire radiation system. For a linear electrodynamic system, where radiation of different frequencies do not effectively mix, then different temperatures could be maintained indefinitely. However, a linear electrodynamic system is highly idealistic, and does not really occur in nature, so mixing is expected for realistic systems in nature. This condition was treated in Ref. 31 and followed in Ref. 1 via the concept of a hypothetical small "carbon particle" that effectively mixed the radiation sufficiently, to enable a single temperature to define the system of radiation.

These points are further commented on at the end of this article in Sec. 6. In particular, it is interesting to contemplate the experimentation of cavity structures where nonequilibrium conditions involving smooth planar surfaces and the imposition of forced oscillations, and their return to equilibrium, might be examined. Here we just note these interesting directions, and continue with the analysis involving the conditions set by Eqs. (9) and (10).

3. CHANGE IN INTERNAL ENERGY AND WORK DONE

The internal energy associated with our system, which just consists of a cavity of volume V filled with radiation, is expressed by

$$U \equiv \frac{1}{8\pi} \int_V d^3x(\mathbf{E}_\perp^2 + \mathbf{B}^2) = \sum_\alpha \frac{\omega_\alpha^2 |b_\alpha|^2}{2\pi c^2} \tag{11}$$

This quantity is a constant, independent of time, despite that the electromagnetic fields are rapidly fluctuating in time. The reason it is a constant is that we have made the idealistic assumption that the walls are perfect conductors, so that no energy flows through them (perfect adiabatic barriers).

We will be assuming that the ensemble of cavities has a distribution of b_α values that conform to thermodynamic equilibrium conditions. From Eq. (11), an infinitesimal change in the ensemble average of this internal electromagnetic energy can be expressed by

$$\delta\langle U\rangle = \frac{1}{2\pi c^2}\sum_\alpha [(\omega_\alpha\langle |b_\alpha|^2\rangle)\,\delta\omega_\alpha + \omega_\alpha\delta(\omega_\alpha\langle |b_\alpha|^2\rangle)] \tag{12}$$

Thus, we will need to deduce how the change in the boundaries of a cavity results in changing each of the normal mode frequencies. The following relationship will prove to be very helpful here:[6]

$$\delta(\omega_\alpha) = \frac{\omega_\alpha}{2}\int_{\delta V} d^3x(|\mathbf{H}_\alpha|^2 - |\mathbf{E}_\alpha|^2) \tag{13}$$

where $\mathbf{E}_\alpha = \mathbf{G}_\alpha(\mathbf{x}, \omega_\alpha)$ and $\mathbf{H}_\alpha = (1/k_\alpha)\,\nabla\times\mathbf{G}_\alpha(\mathbf{x}, \omega_\alpha)$. As stated by Casimir in Ref. 21, Eq. (13) "... is a very useful formula for calculating the influence of small errors in manufacture, accidental deformations or intentional displacements of pistons or membranes on the resonance frequencies." Here the volume integral is taken over the region δV in space that is defined by the boundaries of the old and new surfaces making up the cavity. If an infinitesimal portion of one of the walls of the cavity is pushed into the cavity, so an inward dent is made, or if one of the walls of the objects of the cavity is deformed so that the object protrudes more into the cavity (i.e., the cavity becomes smaller), then δV is simply the region in space composed of this displaced volume. If over this region, the original

[6] See Eq. (7.1) on p. 81 in Ref. 20, namely,

$$\delta(\omega_\alpha^2) = \omega_\alpha^2\int_{\delta V} d^3x(|\mathbf{H}_\alpha|^2 - |\mathbf{E}_\alpha|^2)$$

or Eq. (7.1) in Ref. 21, namely,

$$\frac{\delta k}{k} = \frac{\int_{\delta V}(|\mathbf{H}_0|^2 - |\mathbf{E}_0|^2)\,d^3x}{\int_V(|\mathbf{H}_0|^2 + |\mathbf{E}_0|^2)\,d^3x}$$

In Ref. 20, as in the present article, $\mathbf{H}_\alpha$ and $\mathbf{E}_\alpha$ are normalized. Hence, substituting $\int_V |\mathbf{H}_0|^2\,d^3x = \int_V |\mathbf{E}_0|^2\,d^3x = 1$ into the second equation above, and noting that $\delta k/k = (\delta\omega)/\omega = (1/2\omega^2)\,\delta(\omega^2)$, then one sees that the above two formulae agree.

magnetic field for the α mode, prior to displacement, is larger than the corresponding electric field, then ω_α will increase by the amount above. If instead a wall of the cavity or a surface of one of the objects is deformed so that the cavity is made larger, then the above volume integral must be interpreted as contributing a negative amount, with the fields being those after deformation. For a simple displacement of an object in the cavity, then the integral should be over the positive region of space that has been taken up by the displacement, minus an integral over the new region available in the cavity.

Now let us turn to the work done by external forces when this operation of deformation and/or displacement is carried out. The external forces in question here are the constraining forces that hold all the walls and interior objects in place. As deformations and displacements occur, these forces perform work on the electromagnetic cavity system. These constraining forces must just balance the force due to the radiation pressure acting on the walls, in order for the displacement/deformation operations to be reversible ones. The force due to the radiation pressure is readily calculated in the following way.

Let us consider a small Gaussian pillbox enclosing a small volume $\delta V'$ of a surface area $\delta S'$ of one of the metal walls. We can relate the Lorentz force due to the radiation to the Maxwell stress tensor T_{ij} in the following way:[32, 33]

$$\int_{\delta V'} d^3x \left[\rho \mathbf{E} + \frac{1}{c} (\mathbf{J} \times \mathbf{B}) \right]_i = -\frac{1}{c^2} \int_{\delta V'} d^3x \frac{\partial}{\partial t} S_i + \sum_{j=1}^{3} \int_{\delta V'} d^3x \frac{\partial}{\partial x_j} T_{ij} \tag{14}$$

We will reduce this expression in the following ways. For a radiation field fluctuating in time, but whose stochastic properties are stationary in time, the first term on the right will equal zero if we take either a time or ensemble average of this equation. Second, the term on the far right can be converted to a surface integral. Third, for a perfect conductor, the fields within the conductor equal zero. Consequently, for a small area dA on the surface, one can deduce that the average of the ith component of the Lorentz electromagnetic force on this patch can be expressed as

$$dA \sum_{j=1}^{3} (\hat{\mathbf{n}})_j \langle T_{ij} \rangle$$

where the angle brackets indicate an ensemble average and

$$T_{ij} = \frac{1}{4\pi} \left[(E_i E_j + B_i B_j) - \delta_{ij} \frac{1}{2} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) \right] \tag{15}$$

is the Maxwell stress tensor in the interior part of the cavity, right next to the surface. The external force must be equal and opposite to this quantity to enable the boundary to be constrained.

The work done by the constraining forces to displace this region by an infinitesimal amount $\delta\mathbf{z}$ is obtained by the dot product of these two quantities. By assuming that the displacements $\delta\mathbf{z}$ are made quasistatically, so that the rapidly fluctuating fields are essentially uncorrelated with the slow change in displacement, then

$$\begin{aligned}\langle W\rangle &= -\int_S d^2x \sum_{i,j=1}^{3} (\hat{\mathbf{n}})_j \langle T_{ij}\rangle\, \delta\mathbf{z}_i(\mathbf{x})\\ &= -\frac{1}{4\pi}\int_S d^2x \left\langle (\hat{\mathbf{n}}\cdot\mathbf{E})(\delta\mathbf{z}\cdot\mathbf{E}) + (\hat{\mathbf{n}}\cdot\mathbf{B})(\delta\mathbf{z}\cdot\mathbf{B}) - (\hat{\mathbf{n}}\cdot\delta\mathbf{z})\frac{1}{2}(E^2+B^2)\right\rangle\\ &= -\frac{1}{4\pi}\int_S d^2x(\hat{\mathbf{n}}\cdot\delta\mathbf{z})\frac{1}{2}\langle E^2-B^2\rangle \qquad (16)\end{aligned}$$

since $\mathbf{E}$ is parallel to $\hat{\mathbf{n}}$ and $\mathbf{B}$ is perpendicular to $\hat{\mathbf{n}}$ at the conductor surface. Now, $d^2x(\hat{\mathbf{n}}\cdot\delta\mathbf{z})$ is the infinitesimal volume carved out by displacing the patch of surface area by an infinitesimal amount $\delta\mathbf{z}$, where this volume is taken to be positive if $\delta\mathbf{z}$ has a positive component along $\hat{\mathbf{n}}$. Remembering that $\hat{\mathbf{n}}$ points inward to the cavity, then this change in volume is positive if a dent is made inward to the cavity, or the cavity becomes smaller, as was the convention taken in Eq. (13). Consequently,

$$\langle W\rangle = -\frac{1}{8\pi}\int_{\delta V} d^3x\langle E^2-B^2\rangle \qquad (17)$$

where δV is the same infinitesimal volume as in Eq. (13) that is defined by the region between the changes in the boundaries of the cavity and the boundaries of its interior objects.

Substituting in Eqs. (7) and (8) into 16 yields

$$\begin{aligned}\langle W\rangle &= -\frac{1}{8\pi}\int_{\delta V} d^3x \sum_\alpha 2\langle |b_\alpha|^2\rangle \left[\left(\frac{\omega_\alpha}{c}\right)^2 |\mathbf{G}_\alpha|^2 - |\nabla\times\mathbf{G}_\alpha(\mathbf{x},\omega_\alpha)|^2\right]\\ &= -\frac{1}{2\pi}\sum_\alpha \langle |b_\alpha|^2\rangle \frac{1}{2}\int_{\delta V} d^3x \left[\left(\frac{\omega_\alpha}{c}\right)^2 |\mathbf{E}_\alpha|^2 - |k_\alpha\mathbf{H}_\alpha|^2\right]\\ &= +\frac{1}{2\pi c^2}\sum_\alpha (\langle |b_\alpha|^2\rangle\, \omega_\alpha)\, \delta(\omega_\alpha) \qquad (18)\end{aligned}$$

4. ABSOLUTE ZERO TEMPERATURE SPECTRUM

We are now in position to examine a condition that must hold at $T=0$, namely, absolute zero temperature is the only temperature at which no heat will flow for all reversible isothermal processes. From Eqs. (1), (12), (18), and (10), the heat flow into the cavity due to displacing or deforming the walls or inner objects is given by

$$\langle Q \rangle = \frac{1}{2\pi c^2} \sum_{\alpha} \omega_\alpha \delta[\omega_\alpha p(\omega_\alpha, T)] \tag{19}$$

Since we are considering adiabatic conditions, as imposed by perfectly conducting walls preventing radiation from flowing through them, then we must require that $\langle Q \rangle = 0$. This adiabatic condition will be satisfied for all displacements and deformations if

$$0 = \delta[\omega p(\omega, T)] = \left[p + \omega \frac{\partial p}{\partial \omega} \right] \delta\omega + \omega \frac{\partial p}{\partial T} \delta T \tag{20}$$

Equation (20) relates how the temperature and $p(\omega, T)$ must change as the resonant frequencies in the cavity change.

Although Eq. (20) must hold at all initial temperatures for the adiabatic cavity, there is only one situation where no temperature changes will occur, namely, at absolute zero temperature.[2] Setting $\delta T = 0$ in Eq. (20), then yields the absolute zero temperature spectral condition, namely, that

$$p(\omega, T=0) = \frac{K}{\omega} \tag{21}$$

where K is a constant. The more familiar outcome of this result is

$$\langle U \rangle_{T=0} = \sum_{\alpha} \frac{\omega_\alpha^2 \langle |b_\alpha|^2 \rangle_{T=0}}{2\pi c^2} = \sum_{\alpha} \frac{K\omega_\alpha}{2\pi c^2} \tag{22}$$

Upon calibrating K to experiment,[1, 3] such as by making Casimir force-like measurements,[34–36] then the constant K can be determined, leading to the identification that $K = \pi c^2 \hbar$.

5. GENERALIZED WIEN'S DISPLACEMENT LAW

Following the method discussed in Refs. 2 and 1, we can deduce the generalized Wien's displacement law involving frequency and temperature, but now for radiation in an arbitrarily shaped cavity with perfectly conducting walls and interior objects. We need to assume, however, that reversible thermodynamic processes can be performed that change the temperature of the radiation. Section III.B in Ref. 1 discussed many of the physical constructs needed here, such as the hypothetical and idealistic use of pinholes, stopcocks, and infinite collection of heat reservoirs at different temperatures. These ideas will be assumed to hold here as well.

From Eq. (11),

$$\delta\langle U\rangle = \frac{1}{2\pi c^2}\sum_\alpha\left[\omega_\alpha^2\frac{\partial p}{\partial T}\delta T + \left(2\omega_\alpha p + \omega_\alpha^2\frac{\partial p}{\partial\omega_\alpha}\right)\delta\omega_\alpha\right] \tag{23}$$

Using this with Eqs. (18) and (1), then the change in entropy is

$$\delta S = \frac{1}{T}\langle Q\rangle = \frac{1}{T}\frac{1}{2\pi c^2}\sum_\alpha\left[\omega_\alpha^2\frac{\partial p}{\partial T}\delta T + \left(\omega_\alpha p + \omega_\alpha^2\frac{\partial p}{\partial\omega_\alpha}\right)\delta\omega_\alpha\right] \tag{24}$$

Demanding that δS be an exact differential in accordance with the second law of thermodynamics, then

$$\frac{\partial^2 S}{\partial T\,\partial\omega_\alpha} = \frac{\partial}{\partial\omega_\alpha}\left(\frac{\omega_\alpha^2}{T}\frac{\partial p}{\partial T}\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\omega_\alpha p + \omega_\alpha^2\frac{\partial p}{\partial\omega_\alpha}\right)\right] \tag{25}$$

which leads to the condition

$$\frac{\omega}{T}\frac{\partial p}{\partial T} + \frac{\omega}{T^2}p + \frac{\omega^2}{T^2}\frac{\partial p}{\partial\omega} = 0 \tag{26}$$

As can be readily verified, this condition is satisfied if p satisfies the following functional form

$$p(\omega, T) = \frac{1}{\omega}f\left(\frac{\omega}{T}\right) \tag{27}$$

or

$$\langle U\rangle_T = \sum_\alpha\frac{\omega_\alpha f(\omega_\alpha/T)}{2\pi c^2} \tag{28}$$

These functional forms describe the generalized Wien's displacement theorem, with the word "generalized" meaning that their derivation is valid even when radiation does not vanish at $T=0$.[2, 1] Thus, we have that the radiation spectrum in thermal equilibrium within an arbitrarily shaped cavity with perfectly conducting walls, or with an arbitrary number of electric dipole harmonic oscillators,[2] must have second moments of the fields possessing a functional property that yield Eqs. (27) and (28) above, or Eq. (27) in Ref. 2, namely, $\rho_{\mathrm{in}}(\omega, T) = \omega^3 f_{\mathrm{in}}(\omega/T)$.

6. CONCLUDING REMARKS

A thermodynamical analysis was carried out here for arbitrarily shaped cavities in perfectly conducting medium. The thermodynamic operations examined involved quasistatic deformations of the walls, and quasistatic deformations and/or displacements of perfectly conducting objects within the cavity, and quasistatic changes in temperature of the cavity radiation. The result was found that only one spectral distribution would enable no heat to flow during isothermal deformation operations, namely, the classical electromagnetic ZP spectrum. This result agrees exactly with what one should expect to occur at $T = 0$, namely, that adiabatic and isothermal reversible operations coincide. Under this condition, each normal mode of the radiation spectrum in the cavity was shown to have an energy proportional to the angular frequency ω associated with the normal mode in question. Moreover, at any temperature, each normal mode of the radiation spectrum in the cavity was shown to have an energy proportional to $\omega f(\omega/T)$. Thus, $\lim_{T \to 0} \omega f(\omega/T)$ converges to a constant times ω, in agreement with the ZP spectral finding.

The thermodynamic analysis here yielding a ZP spectrum is in sharp contrast to the usual quantization approach of arriving at the same spectrum in QED. Agreement between the results is satisfying, but the underlying physical approaches differ considerably, as discussed in the end of Sec. VIII.D in Ref. 2 (i.e., see footnote 51). Much earlier analysis near 1900 carried out a similar analysis, but restricted attention to larger cavity structures, and imposed assumptions that prevented the analysis from being sufficiently general to hold for the case where nonzero radiation exists at $T = 0$.[1] A more general analysis involves accounting for the thermodynamics of Casimir-like forces acting between the walls of the cavity in Wien's analysis. Although such forces are generally quite weak in most experimental situations carried out to date, in terms of calculations, they originate from changes in infinite, or extremely large quantities. Consequently, calculations of Casimir forces are notoriously difficult, except for relatively simple geometrical configurations.

One outcome of the calculations carried out here is the clear recognition that one may calculate Casimir forces, at $T = 0$, on perfectly conducting medium, via either of two equivalent ways. The net change in an internal energy calculation could be carried out, where for example a sphere or cube is made to grow or shrink slightly [Eq. (12)], and where one makes sure to include regions both outside and inside the object in question.[16] Equivalently, one could use a virtual work-like calculation via finding the average of the Maxwell stress tensor integrated over a surface enclosing the structure, as in Eq. (16). The two methods must agree at $T=0$. In the language of SED, they agree because no heat can flow at $T=0$ during reversible thermodynamic processes.

Here it should be pointed out that the present analysis did not directly evaluate the experimentally measurable Casimir-like forces involved in the cavity structures. The calculation of these quantities requires evaluating the ensemble average of Eq. (14) over an entire object within the cavity, or over an entire wall of a cavity, including both the inside and outside wall sections. This point is explained in more detail in Ref. 1 (see the discussion involving Figs. 1 and 2). However, the present analysis is valid for heat flow calculations, as was the focus here. To accomplish this task, despite the presence of singular quantities, the following quantities were calculated, namely, perturbations in internal energy, work done, average changes in electromagnetic mode amplitudes, and the perturbation of normal mode frequencies [Eq. (13)].

Much of this work should be extendable beyond perfectly conducting materials to more general dielectric conditions. This statement can be made in some confidence, since the derivation of the classical electromagnetic ZP spectrum and the generalized Wien displacement law was shown to hold for displacement operations of N electric dipole harmonic oscillators.[2–5] Since it is well known that a wide range of conditions for dielectric medium can be modelled as being composed of "atoms" of these oscillators,[25] then the means should exist to extend much of the results considered in the present article to yet more general conditions.

A number of reasons exist to motivate extending such calculations. Interesting experiments and calculations have now been ongoing for a number of years in cavity QED.[10–13] An area that could be considered a subset of this field, might be termed "cavity thermodynamics," and would involve reversible thermodynamic operations like those described here, but also might be used to analyze irreversible thermodynamic operations, and steady-state behavior. Some of this work was begun by Kirchoff, Wien, Planck, and others. Planck's discussion on the effective temperature of a pencil of rays of radiation, and its incorporation into a cavity structure,[31] provides ample directions for future research, given present experimentally available techniques such as in MEMS, microelectronics, and photonics. Modes of radiation that are prevented from interacting, at least within typical experimental time constraints, can provide interesting means for exploring thermodynamic changes. Generalizing the analysis here to include charged interior walls and objects within, general dielectric structures, and modifications of these conditions, such as by doping semiconductor materials and applying potentials, all provide the basis for interesting device oriented physical investigations.[(37), 7] Indeed, the consideration of piezoelectric crystalline structures, with cavities, allows the means for deforming cavity structures via applying potentials. Even novel measurement devices, such as involved in atomic force microscopes, should be analyzable in some detail via extending the calculations contained here.[(38)]

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[7] See, for example, the novel cavity structure reported that consists of an extremely small vacuum tube created out of semiconductor medium in Ref. 37.

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