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Entropy and other thermodynamic properties of classical electromagnetic thermal radiation

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Building upon previous work, several new thermodynamic properties are found for classical electromagnetic random radiation in thermal equilibrium with classical electric dipole harmonic oscillators. Entropy is calculated as a function of temperature and as a function of the positions of the dipole oscillators. In the process, a new derivation is obtained for what is often called Wien's displacement law. The original derivation of this law makes a number of implicit assumptions not found in the present derivation, which prevents the original analysis from being sufficiently general to address an important class of thermal radiation spectrum candidates: namely, those that are nonzero at $T=0$. While leading up to the entropy calculation, a number of other thermodynamic properties are deduced. For example, a natural development is presented for reformulating the Stéfan-Boltzmann law to correspond to experimental observations about changes in thermal radiation energy. Also, the Rayleigh-Jeans spectrum is shown to conflict with basic concepts of thermodynamic processes, and asymptotic limits are found for the spectrum of classical electromagnetic thermal radiation. One asymptotic restriction arises from the demand of finite specific heat for thermal radiation. This restriction is sufficient to ensure that the classical electrodynamic system of dipole oscillators and thermal radiation must obey the third law of thermodynamics. The calculations described here include full nonperturbative evaluations of retarded van der Waals thermodynamic functions.

I. INTRODUCTION

Analysis is continued here from previous work on the thermodynamic properties of a particular classical electrodynamic system: namely, classical electromagnetic random radiation in thermal equilibrium with classical electric dipole simple harmonic oscillators. The initial work was carried out in Ref. 1. There an isothermal reversible process was investigated that consisted of quasistatic displacements of N such dipole oscillators. The following result was found: in order for no heat to be radiated out of a large volume enclosing these particles during this isothermal reversible process, the spectrum of the classical electromagnetic radiation in thermal equilibrium with the oscillators must be proportional to ω^3. Aside from the proportionality constant, this spectrum is precisely the spectrum of classical electromagnetic zero-point (ZP) radiation (see Refs. 2–6 for reviews and research papers that serve as good introductions). Since the flow of no heat during a reversible isothermal process is, by definition,[7] the condition for a system to be at the temperature of absolute zero, the conclusion follows that aside from the proportionality constant, classical electromagnetic ZP radiation possesses the unique thermal radiation spectrum that can form an equilibrium state with the oscillators at $T=0$.

In the present article, the thermodynamic analysis carried out in Ref. 1 will be extended by considering more general thermodynamic processes for the system of dipole oscillators. Instead of only isothermal quasistatic displacement operations on the set of oscillators, we will now also consider thermodynamic processes involving changes in temperature. The change in entropy between these different states will be calculated in Sec. VII. During the analysis leading up to this calculation, a number of new results will be obtained that involve the thermodynamic properties of this electrodynamic system.

In particular, as a consequence of the demand imposed in Secs. II and III that the second law of thermodynamics must hold for this system of classical dipole oscillators and classical thermal radiation, we will obtain a new derivation in Sec. IV for what is often referred to as Wien's displacement law. However, as will be noted in Sec. IV, a number of assumptions and steps were made in the original derivation that are not in general valid. These additional assumptions prevent the original derivation from being sufficiently general to address the possible existence of nonzero radiation being present at $T=0$ (i.e., zero-point radiation). Since this property for classical electromagnetic thermal radiation may be a fundamentally important concept, and even a necessary one for the appropriate thermodynamic analysis of certain classical electrodynamic systems,[1,8–10] then overcoming the limitations imposed in the original derivation is clearly desirable. These limitations do not appear in the present work, thereby making a contribution to the study of the thermodynamics of classical electrodynamic systems.

From the "displacement law" found in Sec. IV, a "generalized Stéfan-Boltzmann law" is obtained in Sec. V that allows for ZP radiation and describes what is measured experimentally: namely differences in thermal radiation energy. In order for these differences in thermal energy to be finite for a change in temperature, so that the specific heat is not infinite, an asymptotic restriction must be imposed on the thermal radiation spectrum. In Sec. VI, Rayleigh-Jeans (RJ) radiation is shown to fail this restriction, thereby resulting in singular behavior for typical thermodynamic processes. Section VI describes some of the problems associated with RJ radiation and shows that classical electromagnetic zero-point plus Planckian (ZPP) radiation does not experience such problems.

In Sec. VII, the change in entropy is calculated for arbitrary changes in temperature and changes in dipole oscillator positions. Some of the required calculations in Sec. VII are placed in the Appendix. Here additional asymptotic restrictions on the thermal spectrum are deduced, and two earlier assumptions in our work are proven to be true: namely, that Eq. (66) in Ref. 1 must hold for thermal radiation obeying certain physically imposed restrictions, and likewise for the statement following Eq. (54) in Sec. VII of the present article.

Having worked with the first and second laws of thermodynamics in obtaining the results up through the entropy calculation in Sec. VII, the system of dipole oscillators and thermal radiation is then analyzed in Sec. VIII from the standpoint of the third law of thermodynamics. The surprising result is shown there that the demand of a finite specific heat for classical electromagnetic thermal radiation is sufficient to prove that the Nernst-Simon form of the third law of thermodynamics holds for this system. Section VIII D makes the following observation concerning the third law: at temperatures near $T=0$, the third law acts as an effective barrier against energy reduction via heat extraction, which gives a new perspective on the physical significance of the ZP energy for classical systems.

Finally, Sec. IX makes some points about irreversible versus reversible processes for our system of dipole oscillators. Section X then contains some concluding remarks.

II. SETTING UP THE ANALYSIS FOR FINDING dS_{cal}

Undoubtedly, the use of traditional thermodynamic ideas and principles may be first seem irreconcilable with the concept of a classical system that possesses fluctuating motion at $T=0$ (i.e., ZP energy). Nevertheless, as will be seen here, these principles do apply quite naturally. After all, at $T=0$ the *flow* of heat (i.e., the transfer of average energy) from one point to another in space should vanish during reversible processes; however, fluctuating energy can still be present at any point in space. To emphasize the compatibility of ZP energy with classical thermodynamics, much of the present section will closely follow the general discussion in traditional thermodynamic textbooks[11] as we set up the base for calculating the change in entropy of a particular thermodynamic system.

The specific classical thermodynamic system we will analyze consists of N classical, electric dipole harmonic oscillators in thermal equilibrium with classical electromagnetic random radiation. All energies of our system, including electromagnetic and mechanical energies, will be calculated within some large volume $\mathcal{V}$ enclosing the dipole oscillators. Heat, in the form of electromagnetic radiated energy, can flow either into or out of $\mathcal{V}$ due to changes in the total energy within $\mathcal{V}$ and due to any work done by external forces in displacing the dipole oscillators.

In Ref. 1, the effect of the rest of the universe interacting with the system of dipole particles was treated via the incident electromagnetic field expressions in Eqs. (22) and (23) in Ref. 1. The thermal radiation was assumed to be held at a fixed temperature T, regardless of how the dipole particles were quasistatically displaced. Hence, in Ref. 1, the radiation was treated as though it acted like a heat reservoir at a fixed temperature T.

To accomplish the task of finding how the entropy associated with this thermodynamic system must change with temperature, let us follow the prescription usually given in thermodynamics for calculating changes in entropy: namely, the temperature of a thermodynamic system is changed quasistatically by imagining the system to be placed in contact with an infinite series of heat reservoirs ranging in temperature from T_{I} to T_{II}.[12] Thus, to quasistatically change the temperature of the system of dipole particles, we should treat the temperature of our effective heat reservoir, namely, the thermal radiation, as though it changes at an infinitesimally slow rate. Indeed, let us assume that this rate is sufficiently slow that at any given moment the radiation field within the volume $\mathcal{V}$ may be approximated by Eqs. (22) and (23) in Ref. 1, with spectra like Eqs. (27) and (28) in Ref. 1 that are specified by a single temperature. Likewise, let the change occur slowly enough that at any instant of time, a good approximation to the internal motion of the dipole particles is given by the steady-state motion of Eqs. (42) and (44) in Ref. 1.

Next, let us assume that the first and second laws of thermodynamics are, indeed, obeyed by our particular classical electrodynamic system. From the second law of thermodynamics, an integrating factor must exist for the heat flow dQ into the system during any reversible process.[13] Thus

$$\frac{dQ_R}{\lambda}=d\sigma \;, \tag{1}$$

where the subscript R means a reversible process, $1/\lambda$ is the integrating factor of dQ_R, and σ labels the reversible adiabatic surfaces for the system.

Also, the second law of thermodynamics yields the result

$$\lambda=\phi(T)f(\sigma) \;, \tag{2}$$

so that λ can be written as a product of two functions: one that depends entirely on the temperature T, and one that depends entirely on σ.[14] From Eqs. (1) and (2) follows the first equality below, where the quantity $\int_{\sigma_{\text{I}}}^{\sigma_{\text{II}}} f(\sigma)d\sigma$ canceled out between the numerator and denominator; the arrow below then indicates how the ratio of two Kelvin temperatures is defined:

$$\frac{Q_R(\text{between } \sigma_{\text{I}} \text{ and } \sigma_{\text{II}} \text{ at } T_a)}{Q_R(\text{between } \sigma_{\text{I}} \text{ and } \sigma_{\text{II}} \text{ at } T_b)}=\frac{\phi(T_a)}{\phi(T_b)}$$

$$\Longrightarrow \frac{T_a}{T_b} \quad \text{on a Kelvin scale .} \tag{3}$$

Due to the Kelvin scale definition, at $T=0$ no heat transfer can occur during any reversible isothermal process performed on the system (i.e., $Q_R=0$ at $T=0$). This condition was used in Ref. 1 to show that aside from a proportionality constant, classical electromagnetic ZP radiation is the only radiation spectrum that can be in thermal equilibrium with the N electric dipole oscillators at $T=0$.

From Eq. (3), we must have $T=k\phi(T)$, where k is an arbitrary constant. Hence, from above,

$$\frac{dQ_R}{T}=\frac{1}{k}f(\sigma)d\sigma \; . \tag{4}$$

The right-hand side (rhs) is an exact differential. The change in entropy dS_{cal} of the system is then defined via

$$dS_{\text{cal}}\equiv\frac{dQ_R}{T} \; . \tag{5}$$

For a finite change in state,

$$S_{\text{cal}f}-S_{\text{cal}i}=\int_{R\,i}^{f}\frac{dQ}{T} \; , \tag{6}$$

where the integration is over any reversible path connecting the two states.

Using the results from Ref. 1, we can immediately evaluate Eq. (6) for an isothermal process, since the $1/T$ factor can be pulled out of the integral, and then Eq. (65) or (67) from Ref. 1 can be used. Here, however, we will evaluate Eq. (6) under the more general condition where the temperature can change.

We can view the system of N fluctuating electric dipole particles as possessing $1+6N$ thermodynamic coordinates (the coordinates are not all independent of each other, as will be discussed shortly): (i) the temperature T; (ii) the $3N$ displacement coordinates $Z_{A,i}$ that define the locations of the N dipoles, where $A=1,\ldots,N$ and $i=1,2,3$; and (iii) the $3N$ generalized forces $Y_{A,i}$, where $Y_{A,i}$ represents the ith component of the expectation value of the external force $\mathbf{F}_{\text{ext},A}$ required to hold the Ath dipole particle stationary.

From the first law of thermodynamics,

$$dQ=dU_{\text{int}}-\sum_{A=1}^{N}\sum_{i=1}^{3}Y_{Ai}dZ_{Ai} \; , \tag{7}$$

where U_{int} represents the total mechanical and electromagnetic energy within the volume $\mathcal{V}$.

However, $\mathbf{Y}_A=\langle\mathbf{F}_{\text{ext},A}\rangle$, and from Eqs. (61)–(63) in Ref. 1, $\langle\mathbf{F}_{\text{ext},A}\rangle=\nabla_{\mathbf{Z}_A}U_0$ can be expressed in terms of T and $\mathbf{Z}_{A'}$, $A'=1,\ldots,N$. Thus we really only have $1+3N$ independent thermodynamic coordinates. Hence Eqs. (61)–(63) in Ref. 1 may be viewed as constituting $3N$ equations of state that relate $\mathbf{Y}_A$ to $\mathbf{Z}_{A'}$ and T, for A and $A'=1,\ldots,N$.

Consequently, we can view T and $\mathbf{Z}_A$, $A=1,\ldots,N$, as being the $1+3N$ independent thermodynamic coordinates that define the state of our N dipole particle system. Hence

$$dS_{\text{cal}}=\frac{1}{T}\left.\frac{\partial U_{\text{int}}}{\partial T}\right|_{\mathbf{Z}}dT+\sum_{A=1}^{N}\sum_{i=1}^{3}\frac{1}{T}\left[\left.\frac{\partial U_{\text{int}}}{\partial Z_{Ai}}\right|_{(T,\mathbf{Z}_{|Ai})}-Y_{Ai}\right]dZ_{Ai} \; , \tag{8}$$

where $|_{\mathbf{Z}}$ is meant to indicate that all coordinates Z_{Ai} are held fixed for all A and i, while $|_{(T,\mathbf{Z}_{|Ai})}$ is meant to indicate that T and all coordinates Z_{Bj}, except Z_{Ai}, are held fixed.

III. THE CONDITION THAT dS_{cal} IS AN EXACT DIFFERENTIAL

From Eq. (4), which follows from the second law of thermodynamics, and from Eq. (5), dS_{cal} in Eq. (8) must be an exact differential. Hence

$$\left.\frac{\partial S_{\text{cal}}}{\partial T}\right|_{\mathbf{Z}}=\frac{1}{T}\left.\frac{\partial U_{\text{int}}}{\partial T}\right|_{\mathbf{Z}} , \tag{9}$$

$$\left.\frac{\partial S_{\text{cal}}}{\partial Z_{Ai}}\right|_{(T,\mathbf{Z}_{|Ai})}=\frac{1}{T}\left[\left.\frac{\partial U_{\text{int}}}{\partial Z_{Ai}}\right|_{(T,\mathbf{Z}_{|Ai})}-Y_{Ai}\right] . \tag{10}$$

To guarantee that dS_{cal} in Eq. (8) is an exact differential, we must have[15]

$$\begin{aligned}\frac{\partial^2 S_{\text{cal}}}{\partial Z_{Ai}\partial T}&=\frac{1}{T}\frac{\partial^2 U_{\text{int}}}{\partial Z_{Ai}\partial T}\\&=\frac{1}{T}\left[\frac{\partial^2 U_{\text{int}}}{\partial T\partial Z_{Ai}}-\left.\frac{\partial Y_{Ai}}{\partial T}\right|_{\mathbf{Z}}\right]\\&\quad-\frac{1}{T^2}\left[\left.\frac{\partial U_{\text{int}}}{\partial Z_{Ai}}\right|_{(T,\mathbf{Z}_{|Ai})}-Y_{Ai}\right]\end{aligned} \tag{11}$$

or

$$0=-\frac{1}{T}\left.\frac{\partial Y_{Ai}}{\partial T}\right|_{\mathbf{Z}}-\frac{1}{T^2}\left.\frac{\partial U_{\text{int}}}{\partial Z_{Ai}}\right|_{(T,\mathbf{Z}_{|Ai})}+\frac{1}{T^2}Y_{Ai} \; . \tag{12}$$

From Eqs. (61)–(63) in Ref. 1,

$$Y_{Ai}=\left.\frac{\partial U_0}{\partial Z_{Ai}}\right|_{(T,\mathbf{Z}_{|Ai})} , \tag{13}$$

$$U_0=\pi\int_0^\infty d\omega\frac{[h_{\text{in}}(\omega,T)]^2}{\omega}\{\operatorname{Im}\ln\det[\underline{M}(\omega,\mathbf{Z})]\} \; . \tag{14}$$

Here the arguments for $\underline{M}$ and h_{in} in Eq. (14) have been changed from Eq. (62) in Ref. 1, to explicitly indicate the part of U_0 that will depend upon the positions of the dipole oscillators, and the part that will depend upon temperature. From Eq. (46) in Ref. 1, $M_{Ai;Bj}$ is a function of frequency and of $(\mathbf{Z}_A-\mathbf{Z}_B)$, so the notation $\underline{M}(\omega,\mathbf{Z})$ in Eq. (14) is meant to indicate that $\underline{M}$ depends on ω and $\mathbf{Z}_A$, for $A=1,2,\ldots,N$. Also, in Ref. 1 we did not explicitly indicate the temperature dependence of $(h_{\text{in}})^2$ since the temperature was held fixed. However, since the radiation's spectral electromagnetic energy density ρ_{in} will depend upon the temperature characterizing the thermal radiation, then $(h_{\text{in}})^2$ must also. More specifically, from Eqs. (22) and (23) in Ref. 1, one can show that

$$\frac{1}{8\pi}\langle(\mathbf{E}_{\text{in}})^2+(\mathbf{B}_{\text{in}})^2\rangle=\int_0^\infty d\omega\,\rho_{\text{in}}(\omega,T)\;, \tag{15}$$

where

$$\rho_{\text{in}}(\omega,T)=\frac{\omega^2}{c^3}[h_{\text{in}}(\omega,T)]^2\;. \tag{16}$$

As for U_{int} in Eq. (12), from Eqs. (11) and (58) in Ref. 1, plus Eqs. (15) and (16) above, any change in U_{int} can be calculated by finding the change in the sum of the following terms:

$$\begin{aligned}U_{\text{KE}}+U_{\text{PE}}+U_{\text{EM}|\text{in}}\;U_{\text{EM,in}}&\\=-\pi\int_0^\infty d\omega[h_{\text{in}}(\omega,T)]^2&\left\{\frac{\partial}{\partial\omega}\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z})]\right.\\&\left.+3N\frac{\partial}{\partial\omega}\text{Im}\ln C(\omega)\right\}\\+\mathcal{V}\int_0^\infty d\omega\frac{\omega^2}{c^3}[h_{\text{in}}(\omega,T)]^2&\end{aligned} \tag{17}$$

(where U_{KE} is the kinetic energy, U_{PE} is the potential energy, and $U_{\text{EM}|\text{in}}+U_{\text{EM,in}}$ is the remaining electromagnetic energy in the volume $\mathcal{V}$).

Using Eq. (66) in Ref. 1,[16] we can integrate, by parts, the term above involving $\det(\underline{M})$, and replace it by

$$+\pi\int_0^\infty d\omega\frac{\partial\{[h_{\text{in}}(\omega,T)]^2\}}{\partial\omega}\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z})]\;.$$

Consequently, from Eqs. (13)–(17) we obtain the following partial derivatives that will be needed in Eq. (12):

$$\left.\frac{\partial Y_{Ai}}{\partial T}\right|_{\mathbf{Z}}=\pi\int_0^\infty d\omega\frac{c^3}{\omega^3}\frac{\partial[\rho_{\text{in}}(\omega,T)]}{\partial T}\frac{\partial}{\partial Z_{Ai}}\times\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z})]\;, \tag{18}$$

$$\left.\frac{\partial U_{\text{int}}}{\partial Z_{Ai}}\right|_{(T,\mathbf{Z}_{|Ai})}=\pi\int_0^\infty d\omega\,c^3\frac{\partial}{\partial\omega}\left[\frac{\rho_{\text{in}}(\omega,T)}{\omega^2}\right]\frac{\partial}{\partial Z_{Ai}}\times\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z})]\;. \tag{19}$$

Substituting into Eq. (12) yields

$$\begin{aligned}0=\frac{\pi c^3}{T^2}\int_0^\infty d\omega\frac{\partial}{\partial Z_{Ai}}&[\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z})]\\&\times\left[-\frac{T}{\omega^3}\frac{\partial\rho_{\text{in}}(\omega,T)}{\partial T}-\frac{\partial}{\partial\omega}\left[\frac{\rho_{\text{in}}(\omega,T)}{\omega^2}\right]\right.\\&\left.+\frac{\rho_{\text{in}}(\omega,T)}{\omega^3}\right]\;.\end{aligned} \tag{20}$$

The above equation must be satisfied for any number N of the electric dipole oscillators, and for any positions $\mathbf{Z}_A$, $A=1,\ldots,N$. Only $\underline{M}$ in Eq. (20) depends on these quantities. The following condition is then sufficient to guarantee that Eq. (20) is satisfied under all these conditions:

$$\begin{aligned}0&=-\frac{T}{\omega^3}\left.\frac{\partial\rho_{\text{in}}(\omega,T)}{\partial T}\right|_{\omega}-\frac{\partial}{\partial\omega}\left[\frac{\rho_{\text{in}}(\omega,T)}{\omega^2}\right]+\frac{\rho_{\text{in}}(\omega,T)}{\omega^3}\\&=\frac{1}{\omega^3}\left[-T\left.\frac{\partial\rho_{\text{in}}(\omega,T)}{\partial T}\right|_{\omega}-\omega\left.\frac{\partial\rho_{\text{in}}(\omega,T)}{\partial\omega}\right|_{T}+3\rho_{\text{in}}(\omega,T)\right]\;.\end{aligned} \tag{21}$$

Moreover, we can follow the analysis of Sec. VI C in Ref. 1, to argue that Eq. (21) *must* be satisfied.

Thus we arrive at the conclusion that for the thermodynamic system we are investigating to obey the second law of thermodynamics, the thermal radiation spectrum must satisfy Eq. (21). We will make use of the above result in the following section.

IV. SAME RESULT AS USUALLY OBTAINED FROM WIEN'S DISPLACEMENT LAW AND THE STÉFAN-BOLTZMANN LAW

A. Overview

From Eq. (21), we can deduce an important property for $\rho_{\text{in}}(\omega,T)$: namely, Eq. (27) below, which describes the way in which ω and T must combine together in the functional form of $\rho_{\text{in}}(\omega,T)$ for the second law of thermodynamics to hold. Indeed Eq. (27) is usually described in the physics literature[17] as resulting from a combination of Wien's displacement law and the Stéfan-Boltzmann law, although in many cases it is simply referred to as being Wien's displacement law.[18] However, the usual derivations[19] of these two laws make some assumptions that do not hold in the case of ZP radiation.

In particular, the usual derivations of these laws treat the internal electromagnetic thermal energy of a cavity at temperature T as being an extensive quantity that is proportional to the volume of the cavity. This assumption is not generally valid, as we know from the study of Casimir forces.[20] The electromagnetic energy within a cavity due to the presence of electromagnetic ZP radiation is infinite. Likewise, the same energy outside the cavity is infinite. However, the change in total electromagnetic energy due to a charge in volume of a cavity is finite. Calculating this finite change in energy cannot be done by treating the total electromagnetic energy within the cavity as being equal to the volume of the cavity times an electromagnetic energy density that is independent of the shape and size of the cavity. The traditional analysis, as presented in Ref. 17, makes this assumption.

Several other quick ways exist for convincing oneself that the usual derivation of Eq. (27) below is not sufficiently general to account for the possible existence of classical electromagnetic ZP radiation. For example, the usual expression for the radiation pressure on the wall of a cavity is $p=\frac{1}{3}\int_0^\infty\rho_{\text{in}}(\omega,T)d\omega$, which, as we will see, is infinite if nonzero radiation is present at $T=0$ or, more precisely, if $\lim_{T\to 0}\rho_{\text{in}}(\omega,T)\neq 0$. This infinity is not addressed in the usual derivation of the Stéfan-Boltzmann law, thereby again illustrating that the implicit assumption is made that $\lim_{T\to 0}\rho_{\text{in}}(\omega,T)=0$. Indeed, two lines after Eq. (96) in Ref. 17, and in the subsequent paragraph, the explicit assumption is made that the thermal spectrum vanishes at large frequencies, which is not the case if ZP radiation is present.[21]

Since we saw in Ref. 1 that the possibility should not be excluded *a priori* that the correct classical thermal equilibrium radiation spectrum may be nonzero at $T=0$, then clearly a more general analysis of these two thermodynamic laws is highly desirable. Such an analysis can indeed be carried out, but it involves accounting for the thermodynamics of Casimir-like forces acting between the walls of the cavity in Wien's analysis. Calculations of Casimir forces typically deal with macroscopic boundary conditions (i.e., the walls of the cavity are treated as macroscopic quantities rather than as being composed of microscopic atomic systems). In contrast, the present article derives the result of Eq. (27) below by analyzing the microscopic physical behavior of electric dipole oscillators.

B. Functional dependence of spectrum on T and w

In Eq. (21), let us make the substitution of variables that $T=\omega/\Theta$. Clearly,

$$\left.\frac{\partial\rho_{\rm in}\left[\omega,\frac{\omega}{\Theta}\right]}{\partial\Theta}\right|_{\omega}=\left.\frac{\partial\rho_{\rm in}(\omega,T)}{\partial T}\right|_{\omega}\left.\frac{\partial T}{\partial\Theta}\right|_{\omega} . \tag{22}$$

Hence, from Eq. (22) we obtain for the first term in Eq. (21)

$$\left.\frac{\partial\rho_{\rm in}(\omega,T)}{\partial T}\right|_{\omega}=-\left[\frac{\Theta^2}{\omega}\right]\left.\frac{\partial\rho_{\rm in}\left[\omega,\frac{\omega}{\Theta}\right]}{\partial\Theta}\right|_{\omega} . \tag{23}$$

As for the second term in Eq. (21), we can obtain the desired relationship via considering

$$\left.\frac{\partial\rho_{\rm in}\left[\omega,\frac{\omega}{\Theta}\right]}{\partial\omega}\right|_{\Theta}=\left.\frac{\partial\rho_{\rm in}(\omega,T)}{\partial\omega}\right|_{T}+\left.\frac{\partial\rho_{\rm in}(\omega,T)}{\partial T}\right|_{\omega}\left.\frac{\partial\left[\frac{\omega}{\Theta}\right]}{\partial\omega}\right|_{\Theta} . \tag{24}$$

Solving for the first term on the rhs and substituting Eq. (23) in the second term on the rhs yields

$$\left.\frac{\partial\rho_{\rm in}(\omega,T)}{\partial\omega}\right|_{T}=\left.\frac{\partial\rho_{\rm in}\left[\omega,\frac{\omega}{\Theta}\right]}{\partial\omega}\right|_{\Theta}+\frac{\Theta}{\omega}\left.\frac{\partial\rho_{\rm in}\left[\omega,\frac{\omega}{\Theta}\right]}{\partial\theta}\right|_{\omega} . \tag{25}$$

Using Eqs. (23) and (25) in Eq. (21), then results in

$$\begin{aligned}0&=\left[\frac{-\omega}{\Theta}\right]\left[\frac{-\Theta^2}{\omega}\right]\left.\frac{\partial\rho_{\rm in}}{\partial\Theta}\right|_{\omega}\\&\quad-\omega\left[\left.\frac{\partial\rho_{\rm in}}{\partial\omega}\right|_{\Theta}+\frac{\Theta}{\omega}\left.\frac{\partial\rho_{\rm in}}{\partial\Theta}\right|_{\omega}\right]+3\rho_{\rm in}\\&=-\omega\left.\frac{\partial\rho_{\rm in}}{\partial\omega}\right|_{\Theta}+3\rho_{\rm in} .\end{aligned} \tag{26}$$

From Eq. (26), we deduce that for a fixed ratio of $\Theta=\omega/T$, then $\rho_{\rm in}(\omega,T)$ will depend upon ω by being proportional to ω^3. Hence

$$\rho_{\rm in}(\omega,T)=\omega^3 f_{\rm in}\left[\frac{\omega}{T}\right] . \tag{27}$$

This result is the same one as given at the bottom of p. 83 in Ref. 17. There the above result was deduced via the traditional arguments of Wien's displacement law and entropy as obtained from the Stéfan-Boltzmann's law [see Eqs. (99) and (100) in Ref. 17)]. However, our analysis accounts for the case when nonzero radiation is present at $T=0$. We derived Eq. (27) by analyzing quasistatic displacements of the dipole oscillators in thermal radiation and by demanding that the second law of thermodynamics must hold.

In comparison, Ref. 17 deduced Eq. (27) by analyzing quasistatic displacements of the wall of a cylinder, where the cylinder contained thermal radiation and by also demanding that the second law of thermodynamics must hold. The implicit assumption was made that $\lim_{\omega\to\infty}\rho_{\rm in}(\omega,T)=0$. From Eq. (27), this assumption also implies the assumption $\lim_{T\to 0}\rho_{\rm in}(\omega,T)=0$.

C. Specific cases of RJ and ZPP radiation

At this point it is interesting to see if RJ and ZPP radiation fit the required property for thermal radiation that we just obtained. From Eq. (16) here and Eqs. (27) and (28) in Ref. 1,

$$\rho_{\rm RJ}(\omega,T)=\frac{\omega^2}{c^3}\left[\frac{k_B T}{\pi^2}\right]=\omega^3\left[\frac{k_B}{c^3\pi^2}\frac{1}{\omega/T}\right] , \tag{28}$$

$$\begin{aligned}\rho_{\rm ZPP}(\omega,T)&=\frac{\omega^2}{c^3}\left[\frac{\hbar\omega}{2\pi^2}\coth\left[\frac{\hbar\omega}{2k_B T}\right]\right]\\&=\omega^3\left[\frac{\hbar}{c^3 2\pi^2}\coth\left[\frac{\hbar}{2k_B}\frac{\omega}{T}\right]\right] .\end{aligned} \tag{29}$$

Thus the spectrums of both RJ and ZPP radiation do satisfy our thermodynamically imposed restriction of Eq. (27). Below $f_{\rm RJ}$ and $f_{\rm ZPP}$ are listed, as well as their limiting values, when $T\to 0$, since we will make use of these properties later:

$$f_{\rm RJ}\left[\frac{\omega}{T}\right]=\frac{k_B}{c^3\pi^2}\frac{1}{\omega/T}\underset{T\to 0}{\Longrightarrow}0 , \tag{30}$$

$$f_{\rm ZPP}\left[\frac{\omega}{T}\right]=\frac{\hbar}{c^3 2\pi^2}\coth\left[\frac{\hbar}{2k_B}\frac{\omega}{T}\right]\underset{T\to 0}{\Longrightarrow}\frac{1}{c^3}\frac{\hbar}{2\pi^2} . \tag{31}$$

V. A GENERALIZATION OF THE STÉFAN-BOLTZMANN LAW

A. Usual result

The Stéfan-Boltzmann law deals with the temperature dependence of the electromagnetic energy of thermal radiation within a volume of space $\mathcal{V}$. In this section, we will easily obtain the way that this law is usually expressed by using our result of Eq. (27).[22] In Sec. V B we will then show how the usual expression of this law needs to be generalized to allow for the possibility of nonzero radiation being present at $T=0$.[23]

Within a volume $\mathcal{V}$ of free space, the electromagnetic energy due to incident thermal radiation is given by the integral of Eq. (15) over $\mathcal{V}$:

$$\begin{aligned} U_{\mathrm{EM,in}} &= \mathcal{V}\int_0^\infty d\omega\, \rho_{\mathrm{in}}(\omega,T) \\ &= \mathcal{V}\int_0^\infty d\omega\, \omega^3 f_{\mathrm{in}}\left[\frac{\omega}{T}\right] \\ &= \sigma' T^4 \mathcal{V}\ , \end{aligned} \tag{32}$$

where

$$\sigma' = \int_0^\infty d\Theta\, \Theta^3 f_{\mathrm{in}}(\Theta)\ , \tag{33}$$

and the substitution was made that $\Theta=\omega/T$. This result represents the usual form of the Stéfan-Boltzmann law.[24]

B. Restriction on $f_{\mathrm{in}}(\omega/T)$ from earlier analysis

As shown in Ref. 1, the electromagnetic radiation spectrum at $T=0$ must be given by

$$\rho_{\mathrm{in}}(\omega, T=0) = \omega^3 \frac{\kappa}{c^3}\ , \tag{34}$$

where κ is a constant. The analysis of Ref. 1 suggests that $\kappa \neq 0$; indeed, experimental agreement with Casimir forces is obtained if $\kappa=\hbar/2\pi^2$.[25]

Combining the two thermodynamic restrictions of Eqs. (34) and (27) yields

$$\lim_{\Theta\to\infty} f_{\mathrm{in}}(\Theta) = \frac{\kappa}{c^3}\ . \tag{35}$$

In the case of RJ and ZPP radiation, we can see from Eqs. (30) and (31) that they obey Eq. (35), with $\kappa_{\mathrm{RJ}}=0$ and $\kappa_{\mathrm{ZPP}}=\hbar/2\pi^2$.

If we examine the integral in Eq. (33) in light of our result of Eq. (35), we see that the integrand will behave as

$$\Theta^3 f_{\mathrm{in}}(\Theta) \approx \Theta^3 \frac{\kappa}{c^3} \tag{36}$$

for large Θ. Hence Eq. (33) is divergent if $\kappa\neq 0$. Indeed, Eq. (33) can even be divergent if $\kappa=0$, as in the case of RJ radiation. Here, even though $f_{\mathrm{RJ}}(\Theta)$ goes to zero for large Θ, it does not go to zero fast enough to prevent the integral in Eq. (33) from being divergent. Specifically, if we insert f_{RJ} into Eq. (33), then the integrand will vary as Θ^2. Consequently, we need to reexamine the analysis leading to the Stéfan-Boltzmann law.

C. Generalized result

Thermal measurements do not deal directly with $U_{\mathrm{EM,in}}$. Instead they always involve *changes* in $U_{\mathrm{EM,in}}$. Consequently, what we really need to determine is how the internal electromagnetic energy within a volume $\mathcal{V}$ of space will change if we make a change in the temperature of the thermal radiation. Indeed, our expectation should be that we may not be able to extract all of the internal electromagnetic energy out of space; instead, when we have lowered the temperature of a system to $T=0$, then no more heat energy can be extracted, even though the system may still contain a zero-point energy. Reference 1 gave a particular detailed example where precisely this behavior took place; Sec. VIII D of the present article discusses this point in more generality.

Consequently, the thermodynamic quantity of importance upon changing the temperature of the radiation from T to $T+\Delta T$ is the change in internal energy arising from the energy density spectrum changing from $\rho_{\mathrm{in}}(\omega,T)$ to $\rho_{\mathrm{in}}(\omega,T+\Delta T)$:

$$\Delta U_{\mathrm{EM,in}} \equiv \mathcal{V}\int_0^\infty d\omega [\rho_{\mathrm{in}}(\omega,T+\Delta T)-\rho_{\mathrm{in}}(\omega,T)]\ . \tag{37}$$

If we slowly change the temperature of the radiation in small increments ΔT, from $0\to\Delta T\to 2\Delta T\to\cdots\to T$, and we keep adding the above $\Delta U_{\mathrm{EM,in}}$ energies, then we will obtain

$$\begin{aligned} U_{\mathrm{EM,in}}(T) &- U_{\mathrm{EM,in}}(T=0) \\ &= \mathcal{V}\int_0^\infty d\omega [\rho_{\mathrm{in}}(\omega,T)-\rho_{\mathrm{in}}(\omega,T=0)] \\ &= \mathcal{V}\int_0^\infty d\omega\, \omega^3 \left[f_{\mathrm{in}}\left[\frac{\omega}{T}\right] - \frac{\kappa}{c^3}\right] \\ &= \sigma' T^4 \mathcal{V}\ , \end{aligned} \tag{38}$$

where

$$\sigma' = \int_0^\infty d\Theta\, \Theta^3 \left[f_{\mathrm{in}}(\Theta) - \frac{\kappa}{c^3}\right]\ . \tag{39}$$

Equation (38) gives the energy that must be added to a volume $\mathcal{V}$ in free space to change the temperature of thermal radiation from 0 to T. The above result is a generalized Stéfan-Boltzmann law for the dependence of the thermal radiation's internal energy upon temperature and volume, for a region in space without matter nearby.

Here we should note that another way to express the change in energy from T_i to T_f is

$$
\begin{aligned}
U_{\mathrm{EM,in}}(T_f)-U_{\mathrm{EM,in}}(T_i)&=\mathcal{V}\int_{T_i}^{T_f}dT\int_0^{\infty}d\omega\frac{\partial\rho_{\mathrm{in}}(\omega,T)}{\partial T}\\
&=\mathcal{V}\int_{T_i}^{T_f}dT\int_0^{\infty}d\omega\,\omega^3\frac{\partial f_{\mathrm{in}}(\omega/T)}{\partial T}=\mathcal{V}\int_{T_i}^{T_f}dT\,T^3\left[-\int_0^{\infty}d\Theta\,\Theta^4\frac{\partial f_{\mathrm{in}}}{\partial\Theta}\right]\\
&=\sigma'(T_f^4-T_i^4)\mathcal{V}\ ,
\end{aligned}
\tag{40}
$$

where we obtain another convenient form for σ',[26]

$$
\sigma'=-\tfrac{1}{4}\int_0^{\infty}d\Theta\,\Theta^4\frac{\partial f_{\mathrm{in}}}{\partial\Theta}\ . \tag{41}
$$

In the case of ZPP radiation,[27]

$$
\begin{aligned}
\sigma'_{\mathrm{ZPP}}&=\frac{\hbar}{c^3 2\pi^2}\int_0^{\infty}d\Theta\,\Theta^3\left[\coth\left[\frac{\hbar}{2k_B}\Theta\right]-1\right]\\
&=\frac{\hbar}{c^3 2\pi^2}\int_0^{\infty}d\Theta\,\Theta^3\frac{2}{\left[\exp\left[\frac{\hbar\Theta}{k_B}\right]-1\right]}=\frac{\pi^2 k_B^4}{c^3\hbar^3 15}\ ,
\end{aligned}
\tag{42}
$$

which agrees with physical observation.[24] However, in the case of RJ radiation, $\kappa=0$ in Eq. (39). Consequently, we still obtain a divergent result for Eqs. (38) and (39). This divergent result for RJ radiation will serve as the focal point for our discussion in the following section.

VI. UNACCEPTABILITY OF RJ RADIATION FOR REALIZING USUAL TYPES OF THERMODYNAMIC PROCESSES

A. General discussion on thermal radiation spectrum candidates

Up until now, we have seen a number of thermodynamic restrictions that are satisfied by both ZPP and RJ radiation. Specifically, ZPP and RJ radiation fulfill the condition that at $T=0$, no heat flow can take place during the reversible isothermal process examined in Ref. 1. Also, both spectra satisfy the condition of Eq. (21) in Sec. III, which is required for dS_{cal} to be an exact differential. Equation (21) enabled us to derive the displacement law found here of Eq. (27), which ZPP and RJ radiation follow via Eqs. (28) and (29).

However, ZPP radiation yields several other thermodynamic related physical properties that we observe in nature, but that are not obtained with RJ radiation. Here we mention three such examples. First, as shown in Sec. VII of Ref. 1, the Nernst-Simon form of the third law of thermodynamics is satisfied if the system of electric dipoles is in equilibrium with ZPP radiation rather than with RJ radiation. Second, as discussed in Ref. 1, ZPP radiation yields a thermal equilibrium state with classical electric dipole oscillators such that the oscillators exist in a fluctuating state at $T=0$. This property agrees with the zero-point fluctuating motion we observe in nature for physical systems, as opposed to the nonfluctuating state predicted with RJ radiation. Third, ZPP radiation agrees with quantum theory predictions for the behavior of the Casimir force between parallel conducting plates at all temperatures, as well as with existing experimental measurements of this force, whereas RJ radiation only yields agreement with quantum theory predictions for very high temperatures.[28,29]

Thus the assumption of RJ radiation as classical electromagnetic thermal radiation yields a number of results that conflict with what we observe in nature. However, since classical physics is generally expected by most physicists to provide an inadequate description of quantum phenomena, this disagreement with physical observation undoubtedly comes as no surprise to most researchers. After all, (i) the third law of thermodynamics, (ii) the existence of fluctuating motion at $T=0$ (ZP motion), and (iii) the existence of Casimir and van der Waals forces are all usually thought to arise from the discrete quantum-mechanical behavior of physical systems. Thus, for example, the failure of the third law for RJ radiation might only be reflection of the fact that classical physics (i.e., Maxwell's equations plus the relativistic generalization of Newton's second law) is not entirely applicable for physical systems. Indeed, the third law of thermodynamics is generally considered as being fundamentally different in origin than the first and second laws of thermodynamics: these last two laws are expected to hold for systems obeying either the laws of classical physics or of quantum mechanics, while the third law is expected to hold only for quantum-mechanical systems.[30,31]

Of course, certainly here we must admit that it is interesting and significant that classical electromagnetic ZPP radiation yields some properties that were only expected to hold for quantum-mechanical systems. Undoubtedly, there has been some misunderstanding in the past by physicists on what was fundamental about the origin of these properties that are usually associated only with quantum mechanics. For example, in Ref. 1 we saw no fundamental thermodynamic reasons why nonzero fluctuating motion cannot occur for classical systems at $T=0$.

At this point, we should probably distinguish between two sets of questions that interest us and that are related to each other, but are, nevertheless, quite different from one another. The first set of questions deals exclusively with the deduction of the thermodynamic behavior of physical systems, given the hypothetical assumption that these systems obey purely classical laws of physics. In particular, can classical electromagnetic radiation exist in thermodynamic equilibrium with classical electrodynamic systems, such as classical charged particles? If not, why not? Are there restrictions on the types of classical electrodynamic systems that can exist in thermal equilibrium with classical electromagnetic radiation? If equilibrium can exist, what is the statistical behavior of the radiation and the particles? Finally, how do these properties change due to typical reversible thermodynamic processes, or, more generally, what is the thermodynamic behavior of the combined system of particles and radiation?

As for the second set of related, but distinctly different questions, here we are interested in the following: if thermal equilibrium can exist between classical electromagnetic radiation and classical electrodynamic systems, what is the relationship of the predicted thermal equilibrium behavior with physical observation? If the predicted behavior does not agree with what we measure experimentally, is the lack of agreement simply a result of the fact that classical physics does not adequately describe the behavior of physical systems?

B. Fundamental problem for RJ radiation: Infinite specific heat

Thus, for the properties mentioned up until now, we cannot yet definitively state that RJ radiation must be ruled out as constituting classical electromagnetic thermal radiation. Indeed, given what we have investigated so far, RJ radiation may still be the appropriate classical thermal radiation spectrum, while the disagreement with the third law of thermodynamics, etc., may be due to classical physics being an inadequate description for physical systems.

Here we should also note that other work exists in the physics literature that provides some support to the idea that RJ radiation may constitute classical thermal radiation. In particular, Refs. 32–36 show that RJ radiation forms an equilibrium state with a classical charged particle oscillating in certain classes of nonlinear binding potentials.

Nevertheless, the situation now changes. The generalized Stéfan-Boltzmann law gives us a strong reason for stating that RJ radiation fails, and fails quite badly, for constituting the appropriate thermal radiation spectrum in equilibrium with our system of electric dipole harmonic oscillators, and that also possesses properties that enable basic, fundamental thermodynamic processes to occur.

Specifically, we cannot make even an infinitesimal change ΔT in temperature for RJ radiation in a finite volume $\mathcal{V}$ of space without obtaining an infinite change in the internal energy of the radiation. Thus, from Eq. (28),

$$\begin{aligned}\Delta U_{\mathrm{EM,RJ}} &= \mathcal{V}\int_0^\infty d\omega[\rho_{\mathrm{RJ}}(\omega,T+\Delta T)-\rho_{\mathrm{RJ}}(\omega,T)]\\ &= \frac{k_B}{c^3\pi^2}\mathcal{V}\int_0^\infty d\omega[\omega^2(T+\Delta T)-\omega^2 T]\\ &= \left[\frac{k_B}{4c^3\pi^2}\int_0^\infty d\Theta\,\Theta^2\right]4T^3\Delta T \;. \end{aligned} \tag{43}$$

[Equation (43) also follows from Eqs. (40) and (41).] From the second line above, we can immediately see that the divergence of $U_{\mathrm{EM,RJ}}$ does not drop out upon calculating a change in $U_{\mathrm{EM,RJ}}$. Dividing by ΔT on both sides of Eq. (43) shows that the specific heat associated with RJ radiation is infinite for any value of T. For the special case of $T=0$, the second line of Eq. (43) shows that an infinite specific heat is obtained here also.[37]

The situation is much different for ZPP radiation. Of course, as noted earlier, both $U_{\mathrm{EM,ZPP}}$ and $U_{\mathrm{EM,RJ}}$ are divergent quantities, but changes in $U_{\mathrm{EM,ZPP}}$ due to changes in temperature result in finite changes in electromagnetic energy, unlike the case for RJ radiation. To clearly see how this result arises, we obtain from Eq. (27) that for an infinitesimal change in temperature, then

$$\Delta U_{\mathrm{EM,in}} = \mathcal{V}\int_0^\infty d\omega\,\omega^3\left[f_{\mathrm{in}}\left[\frac{\omega}{T+\Delta T}\right]-f_{\mathrm{in}}\left[\frac{\omega}{T}\right]\right] . \tag{44}$$

The ω^3 factor in the integrand diverges as $\omega\rightarrow\infty$, while the other factor in the integrand behaves like

$$\lim_{\omega\rightarrow\infty}\left[f_{\mathrm{in}}\left[\frac{\omega}{T+\Delta T}\right]-f_{\mathrm{in}}\left[\frac{\omega}{T}\right]\right]=0 \;, \tag{45}$$

due to Eq. (35). The overall product of the two factors in the integrand in Eq. (44) is divergent for RJ radiation, as can be clearly seen in the second line of Eq. (43). In contrast, for ZPP radiation the overall product goes to zero as $\omega\rightarrow\infty$, since for large Θ,

$$\begin{aligned} f_{\mathrm{ZPP}}(\Theta) &= \frac{\hbar}{c^3 2\pi^2}\left[\frac{e^{\Theta}+e^{-\Theta}}{e^{\Theta}-e^{-\Theta}}\right]\\ &\approx \frac{\hbar}{c^3 2\pi^2}[1+2e^{-2\Theta}] \;. \end{aligned} \tag{46}$$

Hence f_{ZPP} decreases exponentially toward its limiting value of $\hbar/c^3 2\pi^2$, as $\omega\rightarrow\infty$ and T is held fixed.

We then arrive at the conclusion that to raise the temperature of RJ radiation by just an infinitesimal amount in a region in free space of volume $\mathcal{V}$ requires that an infinite amount of energy be suppled to the region. Our usual notions of thermodynamic processes involve finite amounts of work being done, which would then not effect the temperature of RJ radiation at all. Instead, only the physically unacceptable concept of an infinite amount of work being done will result in a change in temperature.

Also, situations involving, for example, two cavities of radiation at infinitesimally different temperatures, separated by an insulating wall, will result in the following rather bizarre situation: when a pinhole is made in the wall to allow the two cavities to come to one equilibrium temperature, a flow of infinite energy will occur between the two cavities.

Clearly, RJ radiation is in complete opposition to our usual ideas on such thermodynamic operations. Rayleigh-Jeans radiation may serve to form an equilibrium state with certain electrodynamic systems, such as charged particles oscillating within certain classes of nonlinear binding forces that are not electromagnetic in origin, as Refs. 38 and 39 imply. However, our usual concepts of thermodynamics involve operations that can change the temperature of the equilibrium system; such changes result in physically impermissible consequences if RJ radiation is present.

In summary of our study of RJ radiation and its relationship to thermodynamic processes, we can make the following conclusions: (i) RJ radiation yields results that do not agree with physical observation. (ii) RJ radiation may serve to form an equilibrium state with certain classes of classical systems at some temperature T, as in Refs. 32–36, although these classes have little to do with electrodynamic systems appropriate for atomic and molecular physics.[38,39] (iii) The only reasonable thermodynamic processes that we can perform on the electrodynamic systems just mentioned in RJ radiation are isothermal processes, such as the operation analyzed in Ref. 1. Other thermodynamic processes result in absurd consequences of *changes* in energy of infinite magnitude, as well as flows of infinite energy. Also, infinite work is required to be performed for adiabatic processes involving changes in temperature.

Hence RJ radiation provides us with an interesting example of equilibrium for certain types of classical systems. However, simple changes to these equilibrium conditions can result in singular behavior for these systems.

C. Ultraviolet catastrophe

The infinite specific heat of RJ radiation is related, but not quite equivalent, to what is usually referred to as the ultraviolet catastrophe for the RJ distribution.[40] More specifically, the ultraviolet catastrophy of the Rayleigh-Jeans law is typically described as the prediction of an "... infinite energy density whereas experiment shows that the energy density goes to zero at very high frequencies."[41]

However, we know from working with the ZPP distribution that an infinite electromagnetic energy density is not what causes thermodynamic problems with the behavior of classical systems; rather, the important physical quantity is the change in electromagnetic energy due to a change in temperature, or due to work being performed on the system. The ZPP spectral electromagnetic energy density of Eq. (29) goes to infinity as $\omega\rightarrow\infty$, just as occurs for the RJ case of Eq. (28). Indeed, the ZPP spectrum goes to infinity as ω^3, which increases more rapidly with ω than the RJ spectrum, which has an ω^2 dependence. However, in the ZPP case, changes in temperature result in a finite change in energy due to a cancellation of singularities; this cancellation does not occur in the RJ case.

At this point, perhaps it is worthwhile to comment on what has been measured experimentally to lead people to conclude that measurements show that "... the energy density [of thermal radiation] goes to zero at very high frequencies."[41] Clearly if this statement was indeed correct, then we would also have to conclude that ZPP radiation is in conflict with physical observation. However, as we will see, this statement is not quite accurate.

The spectral energy density of blackbody electromagnetic radiation is typically inferred experimentally by measuring the energy per unit time, per unit frequency interval, and per unit area, that is emitted through a pinhole in the wall of a blackbody cavity. Let us call this spectral energy flux $K(\omega,T)$. The assumption is then generally made that[42]

$$\rho_{\text{in}}(\omega,T)=\frac{4\pi}{c}K(\omega,T)\ . \tag{47}$$

Since $K(\omega,T)$ has been measured experimentally as going to zero as $\omega\rightarrow\infty$, the conclusion is then usually deduced that $\rho_{\text{in}}(\omega,T)$ must also go to zero.

However, any measurement of the average energy flux radiated through a pinhole of a blackbody cavity must actually be a measurement of the difference in the energy radiated out of the cavity, versus the energy radiated into the cavity. This point is generally recognized, but the additional assumption is also usually made that if the temperature outside of the cavity is small, then we can ignore the energy flux into the cavity, since it reduces to zero as $T\rightarrow 0$. This assumption is not valid if ZP radiation is present.

Indeed, the energy flux out of the cavity can be approximated as being due to the superposition of electromagnetic plane waves traveling in the direction out of the cavity. This flux is then related to the electromagnetic energy density inside the cavity. Likewise, the energy flux into the cavity must be due to the superposition of electromagnetic plane waves traveling toward the cavity wall that originate from outside of the cavity, and so is related to the energy density on the outside of the cavity. The net flux is then due to the difference in the energy densities inside and outside the cavity. The energy density of ZP radiation will then enter into this difference if the temperature outside the cavity is near $T=0$.

D. Restriction imposed by the demand of finite specific heat

In connection with the above analysis, let us now find the precise restriction placed upon the thermal spectrum by the demand of a finite specific heat for classical electromagnetic thermal radiation. As will be seen, this result will be needed in Sec. VII when we calculate changes in entropy associated with our system of electric dipole oscillators.

From Eq. (40), the specific heat of thermal radiation in a fixed volume $\mathcal{V}$ in free space is given by

$$C_{\mathcal{V}}=4\sigma' T^3\mathcal{V}\ . \tag{48}$$

For $C_{\mathcal{V}}$ to be finite, σ' in Eq. (39) or (41) must be finite. If σ' is finite, we then see that $C_{\mathcal{V}}\rightarrow 0$ as $T\rightarrow 0$, which follows the behavior of quantum-mechanical systems.

Now let us make the natural assumption that $f_{\text{in}}(\Theta)$ monotonically approaches its limiting value of κ/c^3 for large Θ rather than, for example, approaching κ/c^3 via oscillating about this value with decreasing amplitude as $\Theta\rightarrow\infty$. We then have from Eq. (39) that for large Θ, $f(\Theta)$ will behave like

$$f_{\text{in}}(\Theta)\approx\frac{\kappa}{c^3}+g(\Theta)\ , \tag{49}$$

where $g(\Theta)$ goes to zero faster than $1/\Theta^x$, $x>4$, as

$\Theta \to \infty$.

In agreement with our previous discussion, we see from Eq. (30) that RJ radiation does not satisfy the above condition of a finite specific heat, while from Eq. (46), ZPP radiation does satisfy this condition.

VII. DETERMINATION OF THE ENTROPY FUNCTION

Our work up until now has been strongly based on Eq. (27), which in turn was based on the demand that the infinitesimal change in entropy in Eq. (8) should be an exact differential. We will now integrate Eq. (8) to obtain the general expression for the change in entropy upon performing a reversible thermodynamic process from the state T_{I} and $\mathbf{Z}_{A,\text{I}}$ to any other state T_{II} and $\mathbf{Z}_{A,\text{II}}$, for $A=1,\ldots,N$. Let us indicate these states by $(T_{\text{I}},\mathbf{Z}_{\text{I}})$ and $(T_{\text{II}},\mathbf{Z}_{\text{II}})$. The work of Sec. III guarantees us that S_{cal} will be a function of state, so that we are free to choose any reversible process that proceeds from $(T_{\text{I}},\mathbf{Z}_{\text{I}})$ to $(T_{\text{II}},\mathbf{Z}_{\text{II}})$. Consequently, let us calculate the change in entropy by (i) changing the system from $\mathbf{Z}_{\text{I}}$ to $\mathbf{Z}_{\text{II}}$ via the isothermal operation we have already investigated in Ref. 1, and then (ii) slowly change the temperature from T_{I} to T_{II} while holding the coordinates $\mathbf{Z}_A$ fixed. This second operation corresponds most closely to what is usually called an isochoric process. For this process, $dW=0$, and only U_{int} will vary.

From Eqs. (16) and (27),

$$h_{\text{in}}^2(\omega,T)=c^3\omega f_{\text{in}}\left[\frac{\omega}{T}\right]. \tag{50}$$

Hence

$$\begin{aligned}\left[-\frac{\partial h_{\text{in}}^2}{\partial\omega}+\frac{h_{\text{in}}^2}{\omega}\right]&=-c^3\omega\frac{\partial}{\partial\omega}f_{\text{in}}\left[\frac{\omega}{T}\right]\\&=c^3T\frac{\partial}{\partial T}f_{\text{in}}\left[\frac{\omega}{T}\right].\end{aligned} \tag{51}$$

For the change in entropy in the isothermal operation of $(T_{\text{I}},\mathbf{Z}_{\text{I}})$ to $(T_{\text{I}},\mathbf{Z}_{\text{II}})$, we obtain from Eq. (6) in Sec. II, Eq. (67) in Ref. 1, and Eq. (51) above,

$$\begin{aligned}&S_{\text{cal}}(T_{\text{I}},\mathbf{Z}_{\text{II}})-S_{\text{cal}}(T_{\text{I}},\mathbf{Z}_{\text{I}})\\&\quad=\pi c^3\int_0^\infty d\omega\frac{\omega}{T_{\text{I}}}\frac{\partial f_{\text{in}}\left[\dfrac{\omega}{T_{\text{I}}}\right]}{\partial\omega}\\&\qquad\times\{\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z}_{\text{II}})]\\&\qquad\quad-\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z}_{\text{I}})]\}.\end{aligned} \tag{52}$$

For the second part of our operation from $(T_{\text{I}},\mathbf{Z}_{\text{II}})$ to $(T_{\text{II}},\mathbf{Z}_{\text{II}})$, we have, from Eqs. (8) and (17),

$$S_{\text{cal}}(T_{\text{II}},\mathbf{Z}_{\text{II}})-S_{\text{cal}}(T_{\text{I}},\mathbf{Z}_{\text{II}})=\int_{T_{\text{I}}}^{T_{\text{II}}}\frac{dT}{T}\left.\frac{\partial U_{\text{int}}}{\partial T}\right|_{\mathbf{Z}_{\text{II}}}, \tag{53}$$

where

$$\begin{aligned}\left.\frac{\partial U_{\text{int}}}{\partial T}\right|_{\mathbf{Z}_{\text{II}}}&=\int_0^\infty d\omega\frac{\partial h_{\text{in}}^2(\omega,T)}{\partial T}\frac{\partial}{\partial\omega}\\&\quad\times\left[-\pi\,\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z}_{\text{II}})]\right.\\&\qquad\left.-\pi 3N\,\text{Im}\ln C(\omega)+\frac{\mathcal{V}\omega^3}{3c^3}\right].\end{aligned} \tag{54}$$

Let us first put Eq. (54) into a different form by integrating this expression by parts. As proven in the Appendix, if the thermal radiation is to obey natural physical requirements, such as a finite specific heat, we must have that

$$\left[\frac{\partial h_{\text{in}}^2(\omega,T)}{\partial T}\left[-\pi\,\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z}_{\text{II}})]-\pi 3N\,\text{Im}\ln C(\omega)+\frac{\mathcal{V}\omega^3}{3c^3}\right]\right]$$

goes to zero as $\omega\to 0$ and ∞. Consequently,

$$\begin{aligned}\left.\frac{\partial U_{\text{int}}}{\partial T}\right|_{\mathbf{Z}_{\text{II}}}&=\int_0^\infty d\omega\frac{\partial^2 h_{\text{in}}^2(\omega,T)}{\partial\omega\partial T}\\&\quad\times\left[\pi\,\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z}_{\text{II}})]\right.\\&\qquad\left.+\pi 3N\,\text{Im}\ln C(\omega)-\frac{\mathcal{V}\omega^3}{3c^3}\right].\end{aligned} \tag{55}$$

The following identity can be verified:

$$\frac{1}{T}\frac{\partial^2}{\partial\omega\partial T}\left[\omega f_{\text{in}}\left[\frac{\omega}{T}\right]\right]=\frac{\partial}{\partial T}\left[\frac{\omega}{T}\frac{\partial}{\partial\omega}f_{\text{in}}\left[\frac{\omega}{T}\right]\right]. \tag{56}$$

Consequently, from Eqs. (50), (53), (55), and (56),

$$\begin{aligned}&S_{\text{cal}}(T_{\text{II}},\mathbf{Z}_{\text{II}})-S_{\text{cal}}(T_{\text{I}},\mathbf{Z}_{\text{II}})\\&\quad=\int_{T_{\text{I}}}^{T_{\text{II}}}dT\frac{\partial}{\partial T}\left\{\int_0^\infty d\omega\left[c^3\frac{\omega}{T}\frac{\partial}{\partial\omega}f_{\text{in}}\left[\frac{\omega}{T}\right]\right]\left[\pi\,\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z}_{\text{II}})]+\pi 3N\,\text{Im}\ln C(\omega)-\frac{\mathcal{V}\omega^3}{3c^3}\right]\right\}\\&\quad=\pi c^3\int_0^\infty d\omega\left[\frac{\omega}{T_{\text{II}}}\frac{\partial}{\partial\omega}f_{\text{in}}\left[\frac{\omega}{T_{\text{II}}}\right]-\frac{\omega}{T_{\text{I}}}\frac{\partial}{\partial\omega}f_{\text{in}}\left[\frac{\omega}{T_{\text{I}}}\right]\right]\left[\text{Im}\ln\det[\underline{M}(\omega,\mathbf{Z}_{\text{II}})]+3N\ln C(\omega)-\frac{\mathcal{V}\omega^3}{3\pi c^3}\right].\end{aligned} \tag{57}$$

Adding Eqs. (52) and (57) to find the total entropy change from states $(T_{\rm I},\mathbf{Z}_{\rm I})$ to $(T_{\rm II},\mathbf{Z}_{\rm II})$, we see that the cross terms involving coordinates $(T_{\rm I},\mathbf{Z}_{\rm II})$ cancel out, leaving the following difference between states of

$$S_{\rm cal}(T_{\rm II},\mathbf{Z}_{\rm II})-S_{\rm cal}(T_{\rm I},\mathbf{Z}_{\rm I}) =\pi\int_0^\infty d\omega\left[-\frac{c^3\omega}{T}\frac{\partial}{\partial\omega}f_{\rm in}\left[\frac{\omega}{T}\right]\right]\left[-{\rm Im}\ln\det[\underline{M}(\omega,\mathbf{Z})]-3N\,{\rm Im}\ln C(\omega)+\frac{\mathcal{V}\omega^3}{3\pi c^3}\right]\Bigg|_{T_{\rm I},\mathbf{Z}_{\rm I}}^{T_{\rm II},\mathbf{Z}_{\rm II}} . \tag{58}$$

Here, the first factor in brackets above can be conveniently converted via Eq. (50) to other useful forms for calculating other thermodynamic functions. The above term involving $\underline{M}(\omega,\mathbf{Z})$ represents the contribution to the entropy due to the interaction between the fluctuating electric dipoles; this term depends on both temperature and the positions of the oscillators. The terms involving $C(\omega)$ and $\mathcal{V}$ depend only upon temperature, and represent the contribution to the entropy due to, respectively, $3N$ independent fluctuating electric dipoles, and thermal radiation in a volume $\mathcal{V}$ of free space.

Thus the entropy at a state $(T,\mathbf{Z})$ is given by

$$S_{\rm cal}(T,\mathbf{Z})=\pi\int_0^\infty d\omega\left[-\frac{c^3\omega}{T}\frac{\partial}{\partial\omega}f_{\rm in}\left[\frac{\omega}{T}\right]\right]\times\left[-{\rm Im}\ln\det[\underline{M}(\omega,\mathbf{Z})]-3N\,{\rm Im}\ln C(\omega)+\frac{\mathcal{V}\omega^3}{3\pi c^3}\right]+S_0 , \tag{59}$$

where S_0 is an arbitrary constant. As was the case in our discussions involving internal energy, the precise value of Eq. (59) is not the important thermodynamic quantity, but rather the difference in Eq. (59) from one state to another.

As a point of interest to connect with work by Boltzmann, Planck, and others, on the entropy of thermal radiation in a volume $\mathcal{V}$ of free space, let us examine the third term in Eq. (59),

$$S_{\rm cal,free}(T)\equiv-\frac{\mathcal{V}}{3T}\int_0^\infty d\omega\,\omega^4\frac{\partial}{\partial\omega}f_{\rm in}\left[\frac{\omega}{T}\right]+S_{0,\rm free} , \tag{60}$$

where $S_{0,\rm free}$ is an arbitrary part of S_0 in Eq. (59). Again letting $\Theta=\omega/T$, we obtain from Eq. (41)

$$S_{\rm cal,free}(T)=\tfrac{4}{3}\sigma'T^3\mathcal{V}+S_{0,\rm free} . \tag{61}$$

This result agrees with the usual one [see, for example, Eq. (81) in Ref. 17] obtained via the conventional arguments leading to the Stéfan-Boltzmann law; again, however, these arguments do not account for the possibility of ZP radiation.

VIII. DERIVATION OF THE THIRD LAW OF THERMODYNAMICS FROM THE DEMAND OF FINITE SPECIFIC HEAT

A. Restriction imposed on $f_{\rm in}(\Theta)$ by the third law

Our analysis to this point has involved the first and second laws of thermodynamics. Now let us turn to see what bearing the third law of thermodynamics has upon our electrodynamic system.

From Eq. (77) of Ref. 1,

$$\lim_{T\to 0}\left[\frac{-\dfrac{\partial h_{\rm in}^2(\omega,T)}{\partial\omega}+\dfrac{h_{\rm in}^2(\omega,T)}{\omega}}{T}\right]=0 , \tag{62}$$

in order for the Nernst-Simon form of the third law of thermodynamics to be satisfied for our system of electric dipoles in equilibrium with thermal radiation. From Eq. (51), Eq. (62) then becomes

$$\lim_{T\to 0}\frac{\partial f_{\rm in}\left[\dfrac{\omega}{T}\right]}{\partial T}=0 . \tag{63}$$

Hence, in order to satisfy Eq. (63), then as $T\to 0$, f_{in} must approach a constant value faster than T^x, with $x>1$. Therefore, from Eq. (35), for large Θ, $f_{\rm in}(\Theta)$ must behave as in Eq. (49), but with $g(\Theta)$ going to zero faster than $1/\Theta^x$, $x>1$, as $\Theta\to\infty$.

From Eq. (46), ZPP radiation satisfies this condition. In contrast, from Eq. (30), RJ radiation barely misses this criteria, since it follows the form of Eq. (49) with $\kappa=0$ and $x=1$, rather than $x>1$.

B. Restriction imposed on $f_{\rm in}(\Theta)$ by finite changes in energy

Thus, in terms of our thermodynamic system, the Nernst-Simon form of the third law deals with the rate at which $f_{\rm in}(\Theta)$ approaches its constant value of κ/c^3 as $\Theta\to\infty$. However, from our work in Sec. VI D, we have the interesting situation that for the specific heat of thermal radiation to be finite, we actually obtain a stronger condition on the asymptotic behavior of $f_{\rm in}(\Theta)$ than what the third law of thermodynamics demands. For $C_{\mathcal{V}}$ to be finite, then $g(\Theta)$ in Eq. (49) must go to zero faster than $1/\Theta^x$, $x>4$, as $\Theta\to\infty$, while for the Nernst-Simon form of the third law to be satisfied for our system, the requirement is $x>1$.

What makes this observation particularly interesting is that, as remarked earlier, the third law of thermodynamics has long been regarded as arising from a much different basis than the first and second laws of thermodynamics. Specifically, the third law is usually attributed to the existence of a zero-point energy state for quantum-mechanical systems[43] and the density-of-energy states near the zero-point energy of quantum-mechanical systems.[44]

For classical electromagnetic thermal radiation, we see a situation that is somewhat analogous to the quantum-mechanical case, but one that is also quite different. For the specific heat of electromagnetic thermal energy to be finite, we obtain a restriction on the behavior of $f_{\text{in}}(\omega/T)$ for large ω, which then also places a restriction on the spectral energy density $\rho_{\text{in}}(\omega/T)=\omega^3 f_{\text{in}}(\omega/T)$ for small T. The restriction is such that the Nernst-Simon form of the third law of thermodynamics must be satisfied for classical electric dipole oscillators interacting with classical electromagnetic thermal radiation, thereby providing a derivation of the third law for this system.

Surprisingly, perhaps, but the possibility of thermal radiation being nonzero at $T=0$ did not actually enter into this derivation. Instead, the consideration of ZP radiation only helped to motivate us to examine the required restriction on the thermal spectrum for $C_{\mathcal{V}}$ to be finite. The restriction we obtained on $g(\Theta)$ was independent of the value of κ. Even for no radiation being present at $T=0$, or $\kappa=0$, we still must have the stronger condition of $x>4$ than the $x>1$ condition required by the third law. In hindsight, this result agrees with the usual view in physics that the change in energy between two equilibrium states should be the important physical quantity rather than the total energy at a particular state.

Our work here on the third law extends the earlier work on this subject in Ref. 1. As we have already seen, ZPP radiation possesses a finite specific heat. Hence we immediately recover our earlier result that the system of dipole oscillators will obey the third law if ZPP radiation is present. The case of RJ radiation, which has an infinite specific heat, must be examined separately, as was done at the end of Sec. VIII A.

C. Observation about parallel to Nernst's analysis

This rather surprising deduction of the Nernst-Simon form of the third law for our system of dipole oscillators, starting from the physical demand of a finite specific heat, has some similarities to Nernst's attempt at deriving the third law for general systems. His analysis was based only on the second law of thermodynamics and the assumption that specific heats vanish at $T=0$.[45,46] Like Nernst's analysis, our derivation involved the second law of thermodynamics, i.e., our derivation was based on Eq. (27), which in turn was obtained from the second law. Also, our derivation was based on an assumption about the specific heat, i.e., that $C_{\mathcal{V}}$ be finite. Consequently, $C_{\mathcal{V}}\rightarrow 0$ as $T\rightarrow 0$ [Eq. (48)], which is related to the assumption made by Nernst. Of course, our derivation holds only for a very specific system, whereas Nernst was considering thermodynamic systems in general; nevertheless, it is interesting to see that a parallel does exist here.

Indeed, despite Einstein's objection,[45] Nernst's argument represents an interesting physical observation. Specifically, Nernst argued that *if* a Carnot engine could be constructed with its lower isothermal at $T=0$, then a perpetual motion machine of the second kind could be constructed. Since the existence of such a machine conflicts with the second law of thermodynamics, Nernst concluded that one can never fully reach the absolute zero temperature, which is essentially the unattainability statement of the third law.

D. Observations about the physical significance of the third law for classical systems

The unattainability statement is traditionally expressed as follows: "By no finite series of processes is the absolute zero attainable."[47,48] This form of the third law reflects what experimentalists find to be true: ". . . the fundamental feature of all cooling processes is that the lower the temperature achieved, the more difficult it is to go lower."[47] Thus a thermodynamic barrier exists to prevent us from ever actually reaching the $T=0$ state. Consequently, the ZP state is really a very highly idealized state that cannot exist in nature, but that forms a useful construct for us to think in terms.

This result will help us to understand the answers to the following questions: if a classical system can have a nonzero fluctuating motion at $T=0$, what prevents us from being able to reduce these fluctuations and thereby lower the average energy? Indeed, why can't we continue to extract energy, or "heat," and lower the energy content of a classical system until no fluctuating motion is present? Here we should note that, in contrast, this problem does not arise with the traditional viewpoint that no fluctuating motion and no fluctuating fields exist at $T=0$ for classical systems, since no energy is then available to be extracted in the form of heat.

Nevertheless, the results we have obtained enable us to recognize two important barriers to extracting heat energy from a classical system possessing fluctuating motion at $T=0$. First, according to the definition of $T=0$, no reversible, isothermal process can result in heat flow; i.e., $\Delta Q=0$ at $T=0$. Reference 1 gave a particular instance where nonzero fluctuating motion existed, but no matter what isothermal, quasistatic displacement operations were performed, no heat could be made to flow into or out of the system. Second, the Nernst-Simon form of the third law demands that $\lim_{T\rightarrow 0}\Delta Q/T=0$ (see Ref. 1, Sec. VII), which places an even stronger constraint on the behavior of ΔQ as $T\rightarrow 0$, and which also gives rise to the unattainability statement.[48] Thus the third law acts as an even stronger protector of the energy contained in the $T=0$ state: namely, we cannot reduce the energy below what is present in the $T=0$ state, because "by no finite series of processes is the absolute zero attainable."[47]

Moreover, other important physical reasons exist for suspecting that nonzero fluctuating motion at $T=0$ may be a critical part of the equilibrium between charged particles and random radiation. Some of these suggestive reasons were discussed in Ref. 1. In particular, for a classical atom consisting of electrons orbiting a pointlike nucleus, a nonfluctuating equilibrium state is not possible; rather, the only equilibrium state possible is a fluctuating one that arises from a balance, on the average, between the energy picked up by the electrons from the thermal radiation field and by the energy radiated by the electrons.[49]

At this point we cannot help but notice the following significant distinction that exists between quantum and classical systems. In the quantum case, the ground state of a physical system is the state with the lowest possible quantized energy level; also, the ground state is equivalent to the state of the system at $T=0$, namely, the ZP state (here we assume that the ground state of a system is nondegenerate, which is the usual assumption made). However, the thermodynamic significance of the ground state in quantum mechanics plays a far less prominent role in the development of quantum mechanics than does the property of quantization. Indeed, the thermodynamic role of the quantum-mechanical ground state is usually deduced as almost an afterthought, once the quantization of states is deduced, and the existence is established of a lowest energy level for the bound states of a system. Using statistical-mechanics notions, a thermal equilibrium state of the system at some temperature T is formed by taking an incoherent superposition of bound states, where the weighting factor is $\exp(-E_i/kT)$ for each quantized energy level E_i.[50] As $T\rightarrow 0$, only the ground state remains in this summation, so that the ZP state is obtained.[51]

For classical systems, the ZP energy state is not quantized; rather the energy of the system fluctuates in value about some average amount. Hence we can certainly conceive of the energy of the system being lowered by reducing the fluctuations, whereas in the quantum case, quantization effects prevent the energy from being lowered. Nevertheless, roughly speaking, as $T\rightarrow 0$ a classical system "resists" having the average of its fluctuating energy reduced via heat extraction because (i) heat does not flow during reversible operations at $T=0$, and (ii) we can never quite attain the $T=0$ state. Thus, although the energy of the system is not "quantized," as we approach $T=0$ there can still exist a nonzero, lowest average energy for the fluctuating motion of a classical system: i.e., the ZP energy.

IX. QUASISTATIC AND NONQUASISTATIC PROCESSES

Before concluding this article, let us put into perspective the relationship of the quasistatic thermodynamic processes we have examined for our system of dipole particles to more general nonquasistatic processes. After all, a natural question to ask is how do we extend the thermodynamic analysis involving these fluctuating dipole oscillators so that we can describe the very important area of nonquasistatic processes, which are, indeed, the only processes that are actually physically realizable in nature.

In Ref. 1, the electric dipole oscillator particles were assumed to have been separated at an infinitesimally slow rate. We were then able to simplify the calculation in Ref. 1 for the expectation value of the work done in displacing the fluctuating electric dipole particles (i.e., $\langle \mathcal{W} \rangle$). Specifically, the assumption of slowly moving the particles apart allowed a quasistatic approximation to be made in Eq. (64) in Ref. 1.

If the particles are not quasistatically displaced, this calculation of $\langle \mathcal{W} \rangle$ can become much more difficult. Nevertheless, we can certainly recognize a few qualitative points for such a situation.

In general, nonquasistatic displacements will constitute irreversible thermodynamic operations since the motion of the dipole particles will involve non-negligible accelerations that will result in irrecoverable energy being radiated off to infinity. Moreover, if the velocity of the dipole particles is not kept nearly equal to zero, as in a quasistatic operation, then for most incident radiation spectra, the incident radiation acts via the Lorentz force to oppose the motion of the dipole particles. This resulting force is a frictional dissipative one that must be overcome by the external forces that move the dipole particles. For a dipole particle moving at a constant velocity, the only nonzero radiation spectrum that will not result in this dissipative force is one with $(h_{\text{in}})^2=\kappa\omega$, as occurs for ZP radiation.[9,10,52] In this case, the incident radiation possesses Lorentz invariant stochastic properties,[9,53] so that the average force on an electric dipole simple harmonic oscillator moving at any constant velocity through ZP radiation can indeed be shown to equal zero [see Eq. (9) in Ref. 54 or Eq. (51) in Ref. 9].[52]

For a nonquasistatic motion of the dipole particles, our calculation of ΔU_{int} in Ref. 1 will still be valid, provided we always ensure that t_{II} in Eq. (1) of Ref. 1 is sufficiently larger than the time when the displacements of the dipole particles are stopped so that the internal motions of the oscillators have lost their memory of the previous displacements, and so that the electromagnetic fields in the volume $\mathcal{V}$ are again only due to the incident fields and the fields of the electric dipoles in their steady-state motion. However, additional work than what we calculated in Sec. V in Ref. 1 will be required be external forces to carry out the full process of starting, executing, and stopping the dipole particles for nonquasistatic motion. Consequently, via Eq. (1) in Ref. 1, additional heat will be radiated out of the volume $\mathcal{V}$ for such an irreversible thermodynamic process.

Clearly, an in depth analysis that goes beyond this qualitative discussion on irreversible processes would be very desirable, but also quite complicated. Consequently, Ref. 1 and the present article concentrated exclusively on calculations for quasistatic processes of the system of fluctuating electric dipoles. However, we can easily justify this attention to quasistatic processes since this procedure is precisely what is done in the usual study of thermodynamics. More specifically, as discussed in thermodynamic textbooks, reversible operations serve a fundamental role for analyzing changes, including irreversible ones, in the thermodynamic state of all systems.

X. CONCLUDING REMARKS

A number of thermodynamic properties have been found here for classical electromagnetic thermal radiation. As far as I know, the rather surprising situation exists that such basic thermodynamic properties as changes in internal energy and entropy have never before been explicitly calculated (e.g., as a function of temperature) for a classical electrodynamic system involving *both* electromagnetic fields and a set of charged particles. Such calculations were carried out here. A motivating factor for pursuing this work was that thermodynamic equilibrium and thermodynamic processes of electrodynamic systems found in nature naturally involve the interaction of both particles and fields.

Most of the results in this article were found by extending the work in Ref. 1 on the thermodynamic behavior of a set of electric dipole simple harmonic oscillators in equilibrium with classical electromagnetic thermal radiation. The major advance here was the analysis of thermodynamic reversible processes where the temperature can vary. In this way, a general state of entropy was obtained for the system of fluctuating dipoles. The calculation of changes in entropy was based on the traditional thermodynamic definition involving heat flow during a reversible, thermodynamic process. Here the heat appeared in the form of stochastically fluctuating electromagnetic radiation that flowed into or out of a large volume enclosing the dipole oscillators.

In addition to entropy, other quantities calculated were changes in internal energy and work done on the system. With these quantities, changes in other thermodynamic functions can readily be calculated as well.

An important point in this article has been that some of the traditional views about the thermodynamic properties of classical systems are not in general valid, since we should not *a priori* exclude the possibility of fluctuating motion and fluctuating classical electromagnetic fields from being present at $T=0$.[55] Indeed, the laws of thermodynamics do not exclude this possibility.

The traditional expectation that fluctuating motion should not exist for classical systems at $T=0$ is probably due, at least in part, to the analysis of a classical "ideal gas" of N particles. Here the internal energy due to random motion is given by $3Nk_BT/2$, so at $T=0$, this energy vanishes and all particles are at rest with respect to each other. However, as was clearly discussed in Ref. 10, a classical ideal gas fails to account for the required electromagnetic interaction between electromagnetic thermal radiation and the real electrodynamic atomic systems found in nature.

The recognition of the thermodynamic possibility of ZP motion for classical systems emphasizes that changes in internal energy are the important thermodynamic quantities rather than the net internal energy. We saw that classical electromagnetic thermal radiation could possess a finite specific heat if the thermal radiation spectrum obeyed a particular asymptotic restriction, which was shown to be satisfied by ZPP radiation, but not by RJ radiation. Indeed, satisfying this criterion also meant that our system of dipoles would obey the third law of thermodynamics. We saw that this law acts as an effective barrier to prevent the average energy of a system from being reduced below the average energy the system would attain at $T=0$.

A second major point here has been that despite the fact that traditional views on thermodynamic *properties* change once a fluctuating ZP state is admitted, the basic thermodynamic *laws* do not change. The first and second laws still hold for classical systems, and entropy can still be discussed in the traditional manner. Even the third law can hold for our system.

Finally, a third important point here (see Sec. VIII D) has been the contrast in the nature of a classical system at $T=0$ and the ZP state of a system as described by quantum mechanics. Thermodynamics plays the prominent role in the classical case for understanding the ZP state, whereas quantization plays the prominent role in quantum mechanics.

We should now probably conclude by noting some of the outstanding problems remaining with the present analysis. First, some of the traditional ideas on applying statistical mechanics to classical systems needs to be revisited in light of the present work. In some of Boyer's early work, he already noted the inadequacy of many of these statistical-mechanics notions for classical charged particles interacting with radiation.[10] Further clarification of these ideas is desirable, but has not been pursued in the present article.[56] Instead, the entropy was calculated via a "safe" way: namely, by explicitly evaluating the heat flow due to radiation rather than by introducing *ad hoc* assumptions on thermodynamic probability. Using this heat flow method, we were able to discuss the thermodynamic situations for both the RJ spectrum and the ZPP spectrum.

A second problem has to do with the spectrum of the energy radiated by the dipole oscillators while they are displaced. This problem was not analyzed in Ref. 1, nor in the present article, but it does represent an important factor that should be considered to ensure that thermal equilibrium conditions are fully met between the dipole oscillators and the radiation. In particular, this point is critical when the oscillators are situated within a cavity, with walls that are approximately adiabatic. This point was mentioned in Sec. I in Ref. 1 (in particular, see footnote 39 in Ref. 1). Let us now clarify this point further.

The net energy within each frequency interval that is transferred to infinity does equal zero for a stationary nonrelativistic simple harmonic oscillator. This fact is true regardless of the spectral form of $\rho_{\text{in}}(\omega,T)$, as was proved in Appendix B in Ref. 2. (Also see Sec. IV in Ref. 57. Using the method in Sec. III of Ref. 57, the proof can be extended to an arbitrary number N of these dipole oscillators.)

However, the problem in the present article and in Ref. 1 involves oscillators that are slowly displaced from each other. Other researchers have treated the spectral decomposition of the net radiated energy for certain classes of electrodynamic systems bathed in random radiation (see Refs. 32–34 and 36), but only for systems that can be described by a stationary stochastic process. Systems that are quasistatically displaced do not follow a stationary stochastic process. Hence the problem encountered here and in Ref. 1 is quite different from the one analyzed by others. Indeed, as far as I am aware, the thermodynamics involved in displacement operations have not been treated by other researchers for any of the systems considered in Refs. 32–36.

Actually, in terms of thermal equilibrium conditions being ensured, the emitted spectra during the displacement does not really appear to be a critical problem for the present situation, where the oscillators are situated in free space, but bathed in thermal radiation. Indeed, after completing the displacement, the emitted radiation has no effect on the spectrum of the radiation in which the oscillators are immersed, nor does it effect the behavior of the oscillators. However, we can easily conceive of a hypothetical situation where the emitted spectra will be quite critical.

Suppose a slab of material exists that is composed of N of these oscillators, where N may be quite large. Furthermore, suppose we insert this slab within a cavity, with walls that are approximately adiabatic during the following thermodynamic operation: namely, where we slowly compress the slab. Here the emitted radiation of the oscillators will reflect back off the walls of the cavity, as will all the radiation in the cavity, and in this way continually interact with the N oscillators. Hence the emitted radiation will be critically important in determining the spectral form of the resulting radiation within the cavity, as well as the behavior of the oscillators.

In general, we expect the temperature of the radiation and the slab will change during the compression. An exception to this rule is when the compression is performed at $T=0$, since here adiabatic and isothermal conditions are equivalent. Nevertheless, regardless of what the temperature becomes, we still expect the spectrum of the radiation within the cavity to remain of a thermal spectral form. Only under this condition will the net entropy of the system be a function of state, as is demanded by the second law of thermodynamics.[58]

For experiments performed on real systems in nature, the thermal spectral form is that found for blackbody radiation. This observed spectrum agrees with the classical case if ZPP radiation is the appropriate thermal equilibrium spectrum for classical electrodynamic systems.

Of course, we already know that RJ radiation, rather than ZPP radiation, forms an equilibrium state with the nonlinear electrodynamic oscillator systems studied in Refs. 32–36, under the constraint that these oscillator systems follow a stationary stochastic process in time. Hence, before we even consider a displacement operation for these oscillator systems, we already see that ZPP radiation cannot form a thermal equilibrium state with them. On the other hand, we also have the following strange problem observed in Sec. VI: RJ radiation results in singular behavior for simple thermodynamic operations like changes in temperature. Thus the thermodynamic behavior of the electrodynamic systems studied in Refs. 32–36 is far different from the familiar thermodynamic behavior of real, physical systems we find in nature.

Thus we return to the point made a number of times in Refs. 1, 38, and 39. The classical electrodynamic systems that have been studied in stochastic electrodynamics[2–6] need to reflect the physical character of real atomic systems if we expect to obtain truly meaningful comparisons between the behavior of classical systems and the behavior of systems found in nature. In the past,[32–34,36] the electromagnetic nature of the binding potential of real atomic systems has not been adequately taken into account when deducing the emitted electromagnetic radiation of classical oscillating systems of charged particles.[38,39] This point needs to be corrected in future studies, and may be critical when comparing the emitted spectra and the general behavior of classical systems with corresponding properties of physical systems.

The present study is also subject to the same criticism.[59] Nevertheless, the analysis discussed here does contribute to the understanding of the appropriate thermodynamic behavior of classical systems. Although ZP energy for classical systems has been discussed in the physics literature for over 30 years now,[60] as far as I am aware, calculations such as those in Ref. 1 had not been carried out to specifically address appropriate thermodynamic operations corresponding to the definition of absolute zero temperature. The present article extended this analysis to nonzero temperatures. Indeed, the thermodynamics of the retarded van der Waals forces were treated, which has some general theoretical interest, since all atomic systems interact with each other to some extent via van der Waals forces. More significant, however, is that the calculations presented here for finding the change in internal energy, work done, heat flow, and change in entropy represent the type of analysis that is essential in deducing the appropriate thermodynamic behavior of classical electrodynamic systems in general.

Consequently, when mathematical methods are developed that enable the treatment of classical atomic models that more realistically represent atomic systems found in nature, then similar analyses involving heat flow should be repeated for these systems. Such analyses should not necessarily be restricted to quasistatic displacement operations, since other quasistatic operations are certainly possible, important, and perhaps closer to the quasistatic operations that might be approximated by experiment, such as when weak, applied electromagnetic fields are slowly switched on.

APPENDIX: ASYMPTOTIC RESTRICTIONS ON THERMAL SPECTRUM

A key point to much of our analysis in this article has been the asymptotic limits on the thermal radiation spectrum. The "displacement law" we deduced in Eq. (27) provided the means to deduce the asymptotic limit of $\omega \rightarrow \infty$ for the thermal spectrum, via the following method. First, from Ref. 1, we found the required $T \rightarrow 0$ spectral form for thermal radiation. Since ω and T must combine as in Eq. (27), then this $T \rightarrow 0$ limitation gave us the appropriate $\omega \rightarrow \infty$ restriction. Both limits are expressed in the single form of Eq. (35). Second, in Sec. VI D we deduced the required asymptotic rate of change of $f_{\text{in}}(\omega/T)$ as $\omega/T \rightarrow \infty$, in order for changes in temperature to yield finite changes in electromagnetic thermal energy. This restriction was sufficient to show that RJ radiation is unsuitable for certain fundamental thermodynamic processes, like changes in temperature. We also saw in Sec. VIII B that this restriction was sufficient to deduce the Nernst-Simon form of the third law of thermodynamics for thermal radiation interacting with electric dipole oscillators.

Now we need to prove the statement following Eq. (54). In the process, we will find the appropriate $\omega/T \to 0$ limiting spectral form for thermal radiation. Also, we will be able to prove that Eq. (66) in Ref. 1 must hold for classical electromagnetic thermal radiation.[16]

Let us first deal with the $\omega \to \infty$ limit. From Eqs. (49) and (50), we have that as $(\omega/T) \to \infty$, then

$$h^2_{\rm in}(\omega,T) \approx \kappa\omega + c^2\omega g\left[\frac{\omega}{T}\right] , \tag{A1}$$

where $g(\Theta) \to 0$ faster than $1/\Theta^4$, as $\Theta \to \infty$. Hence, for a fixed value of T, $\partial h^2_{\rm in}(\omega,T)/\partial T$ must go to zero faster than $1/\omega^3$ as $\omega \to \infty$.

In Appendix B of Ref. 1, we saw that

$$\operatorname{Im}\ln\det(\underline{M}) \approx \frac{\mathcal{B}}{\omega^2} \tag{A2}$$

for large ω, where $\mathcal{B}$ is a constant. Consequently, for any fixed temperature value, electromagnetic thermal radiation must satisfy

$$\lim_{\omega\to\infty} [h^2_{\rm in}(\omega,T)\operatorname{Im}\ln\det(\underline{M})] = 0 \tag{A3}$$

and

$$\lim_{\omega\to\infty}\left[\frac{\partial h^2_{\rm in}(\omega,T)}{\partial T}\operatorname{Im}\ln\det(\underline{M})\right] = 0 , \tag{A4}$$

which provides the $\omega \to \infty$ part of Eq. (66) in Ref. 1, and the $\omega \to \infty$ part of the first term in the statement following Eq. (54).

Turning to the second and third terms in the statement following Eq. (54), since

$$C(\omega) = -\omega^2 + \omega_0^2 - i\Gamma\omega^3 , \tag{A5}$$

then

$$\operatorname{Im}\ln C(\omega) = \tan^{-1}\left[\frac{-\Gamma\omega^3}{-\omega^2+\omega_0^2}\right] \underset{\omega\to\infty}{\Longrightarrow} \frac{3\pi}{2} . \tag{A6}$$

Since $\partial h^2_{\rm in}(\omega,T)/\partial T$ must go to zero faster than $1/\omega^3$ as $\omega \to \infty$, we see that both the second and third terms in the statement following Eq. (54) must vanish as $\omega \to \infty$.

Turning now to the $\omega \to 0$ limit of the above quantities, we should first note that from Appendix B of Ref. 1, as $\omega \to 0$, $\operatorname{Im}\{\ln[\det(\underline{M})]\} \to 0$. From Eq. (A5), $\operatorname{Im}[\ln(C)] \to 2\pi$ as $\omega \to 0$. If we assume that $h^2_{\rm in}(\omega,T)$ and $\partial h^2_{\rm in}(\omega,T)/\partial T$ remain finite as $\omega \to 0$, then we see that the $\omega \to 0$ limit of Eq. (66) in Ref. 1 and the $\omega \to 0$ limit of the statement following Eq. (54) must both equal zero.

We can probably come up with several reasons for making what appears to be a very natural assumption that $h^2_{\rm in}(\omega,T)$ and $\partial h^2_{\rm in}(\omega,T)/\partial T$ should not diverge as $\omega \to 0$. Indeed, if they did diverge as $\omega \to 0$, the energy per unit mode of the thermal radiation would diverge at small frequencies, which seems physically unreasonable. However, a more definitive argument can be constructed by noting from Eq. (50) that the $\omega \to 0$ limit is related to the $T \to \infty$ limit, and by analyzing the energy dependence on temperature of a single electric dipole oscillator bathed in thermal radiation. As we will see, in order for a three-dimensional oscillator to possess the usual energy of $3(k_BT)$ at large temperatures, then $h^2_{\rm in}(\omega,T)$ must reduce to the nondivergent result of k_BT/π^2 at small frequencies.

Specifically, for N such electric dipole oscillators that are separated infinitely far apart in space, the average of the sum of the (i) kinetic, (ii) potential, and (iii) electromagnetic energies associated with these N oscillators can be deduced from Eq. (58) of Ref. 1, and from the paragraph immediately following Eq. (58). Thus

$$\begin{aligned} U_N(T) &= -3N\pi\int_0^\infty d\omega\, h^2_{\rm in}(\omega,T)\frac{d}{d\omega}[\operatorname{Im}\ln C] \\ &= +3N\pi\int_0^\infty d\omega\, h^2_{\rm in}(\omega,T)\frac{\Gamma(3\omega_0^2\omega^2-\omega^4)}{|C|^2} . \end{aligned} \tag{A7}$$

Dividing by N, and using the standard resonance argument on pp. 569 and 570 of Ref. 61, or pp. 1653 and 1654 of Ref. 28, then

$$U_1(T) \approx 3[\pi^2 h^2_{\rm in}(\omega_0,T)] . \tag{A8}$$

From Eq. (A1) at $T=0$,

$$U_1(T=0) = 3\pi^2\kappa\omega_0 , \tag{A9}$$

which for ZPP radiation is the familiar $3(\hbar\omega_0/2)$ quantity for an oscillator with three spatial degrees of freedom.

At the other extreme, for large enough temperatures we expect to find the usual result of $3k_BT$ for the average energy of the oscillator. Hence, from Eq. (A8), for large T

$$h^2_{\rm in}(\omega_0 T) \approx \frac{k_BT}{\pi^2} , \tag{A10}$$

which is equivalent to the RJ spectrum via Eqs. (16) and (28). As will be seen shortly, the RJ spectrum serves as the natural limiting spectral form for the classical electromagnetic thermal radiation spectrum when $(\omega/T) \to 0$.

We expect that the $T=0$ energy of Eq. (A9) will be much less than the energy of $3k_BT$, provided that T is sufficiently large. More precisely, $U_1(T=0) \ll 3k_BT$ is obtained provided that

$$\frac{\pi^2\kappa\omega_0}{k_B} \ll T . \tag{A11}$$

If $\kappa \neq 0$, so that zero-point energy is present, the condition of Eq. (A11) can always be achieved if the ratio of ω_0/T is taken to be small enough. Thus the low-temperature energy limit in Eq. (A9) and the high-temperature energy limit of $3k_BT$ are dictated not just by the value of T, but by the ratio of (ω_0/T). Consequently, as $\omega/T \rightarrow 0$, the appropriate spectrum for classical electromagnetic thermal radiation should reduce to the RJ spectrum, as shown in Eq. (A10). Indeed, from Eqs. (28) and (29), we see that ZPP radiation does satisfy this property, since $\coth(\hbar\omega/2k_BT) \rightarrow 2k_BT/\hbar\omega$ as $\omega/T \rightarrow 0$.

Thus Eq. (A10) is the correct limiting form for $h_{\text{in}}^2(\omega,T)$ when T is held fixed and $\omega \rightarrow 0$. Consequently,

$$f_{\text{in}}(\Theta) \approx \frac{k_B}{c^3\pi^2}\left[\frac{1}{\Theta}\right], \qquad \text{(A12)}$$

as $\Theta \rightarrow 0$.

Hence not only have we verified our assumption above that $h_{\text{in}}^2(\omega,T)$ and $\partial h_{\text{in}}^2(\omega,T)/\partial T$ should not diverge as $\omega \rightarrow 0$, but we have also obtained the specific limiting forms of k_BT/π^2 and k_B/π^2 for these quantities.

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[9] T. H. Boyer, Phys. Rev. **182**, 1374 (1969).

[10] T. H. Boyer, Phys. Rev. **186**, 1304 (1969).

[11] In particular, see M. W. Zemansky and R. H. Dittman, Ref. 7, Secs. 7-7 to 7-10.

[12] See, for example, F. W. Sears and G. L. Salinger, *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics*, 3rd ed. (Addison Wesley, Reading, MA, 1975), p. 131.

[13] A clear discussion on this point can be found in Secs. 7-7 to 7-9 of Ref. 7, or, for example, F. W. Sears, Am. J. Phys. **31**, 747 (1963). Quoting p. 170 of Ref. 7, "It is only because of the second law that the differential form for dQ referring to a physical system of any number of independent coordinates possesses an integrating factor." As will be seen shortly, the electrodynamic system we are analyzing in the present article has $1+3N$ independent thermodynamic coordinates.

[14] Again quoting Ref. 7, p. 173: "Since $f(\sigma)d\sigma$ is an exact differential, the quantity $1/\phi(T)$ is an integrating factor for dQ. It is an extraordinary circumstance that not only does an integrating factor exist for the dQ of any system, but this integrating factor is a function of temperature only and is the same function for all systems! This universal character of $\phi(T)$ enables us to define an absolute temperature."

[15] See, for example, F. W. Sears and G. L. Salinger, Ref. 12, Sec. 2.10.

[16] In Ref. 1, Eq. (66) was shown to hold for RJ and ZPP radiation, and the conjecture was made that the equation should hold true for any other reasonable candiate for classical electromagnetic thermal radiation. In the Appendix, we prove that Eq. (66) in Ref. 1 must hold for classical electromagnetic thermal radiation obeying certain physically imposed restrictions. (For best continuity, a close reading of the Appendix should probably be postponed until after reading Sec. VII.)

[17] M. Planck, *The Theory of Heat Radiation* (Dover, New York, 1959).

[18] T. S. Kuhn, *Black-Body Theory and the Quantum Discontinuity 1894-1912* (Oxford University Press, New York, 1978), bottom p. 6.

[19] For a clear presentation of the traditional derivation of these two laws, see Planck's treatment in Ref. 17. Some variations on this derivation can be found in the literature. In particular, see S. Tomonaga, *Quantum Mechanics, Vol. 1* (North-Holland, Amsterdam, 1962), pp. 20–31.

[20] See, for example, T. H. Boyer, Ann. Phys. (N.Y.) **56**, 474 (1970).

[21] In our notation, the second line after Eq. (96) in Ref. 17 reads

$$\Delta U = \frac{\Delta\mathcal{V}}{3}\left[[\omega\rho(\omega,T)]|_0^\infty - \int_0^\infty \rho(\omega,T)d\omega\right].$$

Here ΔU is the change in the electromagnetic energy within a cavity of volume $\mathcal{V}$, due to an adiabatic change in volume $\Delta\mathcal{V}$. In the paragraph that follows the above line in Ref. 17, Planck assumed that the first term above equals zero, which is an invalid assumption for ZP radiation. Indeed, if we insert here Planck's final result of $\rho(\omega,T)=\omega^3 f(\omega/T)$, we explicitly see that the assumption is made that

$$\lim_{\omega\rightarrow\infty} f(\omega/T) = \lim_{\Theta\rightarrow\infty} f(\Theta) = 0 .$$

If nonzero radiation is present at $T=0$, the above limit should equal κ/c^3, where $\kappa \neq 0$ [see Eq. (35)].

[22] In Ref. 17, the usual expression for the Stéfan-Boltzmann law is deduced in two ways. One way directly involves the change in entropy associated with thermal radiation in a cylinder of volume $\mathcal{V}$, with one wall of the cylinder being a movable piston (see Chap. 2 in Ref. 17). As mentioned earlier, to properly generalize this derivation to allow for the possible existence of nonzero radiation at $T=0$, requires that the thermodynamics of Casimir-like forces be taken into account. A second method in Ref. 17 for obtaining the Stéfan-Boltzmann law starts with the same result we obtained here of Eq. (27) (see p. 84, Sec. 86 in Ref. 17). In the present article, this second derivation is the one we will generalize. However, here we will restrict our attention to the electromagnetic energy in a volume $\mathcal{V}$ of free space that lies far from material boundaries rather than discussing the electromagnetic energy within a cavity of volume $\mathcal{V}$. In future work, I plan to discuss this last problem: namely, the thermodynamics of radiation enclosed by conducting parallel plates.

[23] Other researchers investigating the effects of classical electromagnetic ZP radiation have long recognized that the usual form of the Stéfan-Boltzmann law must be generalized when classical electromagnetic ZP radiation is present at $T=0$. For example, see Ref. 10, Eq. (23). The development in the present article complements this earlier recognition by providing a deeper analysis, plus an argument that demands the form of this generalized law.

[24] Another form for the Stéfan-Boltzmann law is $R_B(T)=\sigma T^4$, where $R_B(T)$ is the radiant emittance of a blackbody at any

temperature T. Here $\sigma=\sigma' c/4$. See, for example, Ref. 17, Sec. 64 for further information and for a discussion on an early experimental measurement of σ.

[25] See, for example, the discussion on the Casimir effect by T. H. Boyer in Sci. Am. **253** (2), 70 (1985). References 4 and 6 contain additional information and references.

[26] Equation (41) can be seen to be equivalent to Eq. (39) by integrating Eq. (41) by parts and by using Eq. (35). From Eq. (41)

$$\sigma' = -\tfrac{1}{4}[\Theta^4 f_{\text{in}}(\Theta)]|_0^\infty + \int_0^\infty d\Theta\, \Theta^3 f_{\text{in}}(\Theta)$$
$$= \int_0^\infty d\Theta\, \Theta^3 \left[f_{\text{in}}(\Theta) - \frac{\kappa}{c^3} \right] + \lim_{\Theta\to 0} \tfrac{1}{4}\Theta^4 f_{\text{in}}(\Theta) ,$$

which agrees with Eq. (39), except for the presence of the last term. From Eq. (A12) in the Appendix, this last term equals zero.

[27] I. S. Gradshteyn and I. M. Ryzhik, in *Table of Integrals, Series, and Products,* edited by A. Jeffrey (Academic, New York, 1980). See integral No. 3.4112 and Sec. 9.71. Alternatively, Eq. (41) could be used to evaluate σ', which then requires integral No. 3.5272 in Gradshteyn and Ryzhik.

[28] T. H. Boyer, Phys. Rev. A **11**, 1650 (1975), Sec. V.

[29] J. Mehra, Physica **37**, 145 (1967).

[30] See, for example, F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), p. 120.

[31] For a deeper understanding why the third law of thermodynamics is usually viewed as not being applicable for classical systems, see the two sections starting on p. 1528 in T. H. Boyer, Phys. Rev. D **1**, 1526 (1970). Indeed, for a classical ideal gas, the third law does not hold because the specific heat does not reduce to zero as $T\to 0$.

[32] T. H. Boyer, Phys. Rev. D **13**, 2832 (1976).

[33] J. H. Van Vleck and D. L. Huber, Rev. Mod. Phys. **49**, 939 (1977).

[34] T. H. Boyer, Phys. Rev. A **18**, 1228 (1978).

[35] R. Blanco, L. Pesquera, and E. Santos, Phys. Rev. D **27**, 1254 (1983).

[36] R. Blanco, L. Pesquera, and E. Santos, Phys. Rev. D **29**, 2240 (1984).

[37] We should note that the simple expediency of putting some sort of cutoff factor into the RJ spectrum does not easily alleviate our problems. Here we briefly mention this point without pursuing it too far. First, there exists the obvious difficulty that such a procedure interferes with the reasoning upon which the RJ spectrum is based of assigning an average energy of $k_B T$ for each electromagnetic standing wave in a cavity [see, for example, R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Nuclei, and Particles* (Wiley, New York, 1974), p. 14]. More importantly, perhaps, is the following second difficulty. In order for the spectrum to cut off at some upper frequency so as to yield a finite result for Eq. (43), a factor f' must be introduced into Eq. (28) such that $f'\to 0$ as $\omega\to\infty$. If we still demand that Eq. (27) holds, then f' must be a function of ω/T. Hence f' must also go to zero as $T\to 0$. Thus the low-temperature behavior of the RJ spectrum will be significantly altered with this cutoff factor. Indeed, at low temperatures this altered spectrum will no longer yield the equilibrium behavior found in Refs. 32–36 for certain classes of classical electrodynamic systems interacting with RJ radiation. Only if Eq. (27) is in error at large values of ω/T can we escape this difficulty; of course, then we must also face the complication of understanding, and determining, this hypothetical correction to Eq. (27).

[38] T. H. Boyer, Found. Phys. **19**, 1371 (1989).

[39] D. C. Cole, Found. Phys. **20**, 225 (1990).

[40] See, for example, R. Resnick, *Relativity and Early Quantum Theory* (Wiley, New York, 1972), Sec. 4.3.

[41] See R. Resnick, Ref. 40, p. 119.

[42] For an explanation of this assumption, see M. Planck, Ref. 17, Sec. 22, Eq. (21).

[43] See, for example, F. Reif, Ref. 30, pp. 119 and 120.

[44] D. ter Harr, *Elements of Thermostatics,* 2nd ed. (Holt, Rinehart, and Winston, New York, 1966), Chap. 9, particularly Sec. 9.2.

[45] Nernst's derivation is described by F. E. Simon in Z. Naturforsch. **6A**, 397 (1951). Also, Simon discusses in this article some possible objections to the derivation; he considers Einstein's objection to be the most serious, but not without some reservations. Also see P. T. Landsberg, Rev. Mod. Phys. **28**, 363 (1956). Landsberg is in basic agreement with Simon; Landsberg's comments in the left column of p. 391 significantly help to clarify the situation.

[46] W. Nernst, Ber. S.-B. Preuss. Akad. Wiss. Phys. Math. Kl. Feb. 1 (1912); *Die theoretischen und experimentellen Grundlagen des neuen Warmesatzes* (Knapp, Halle, 1918), p. 72.

[47] M. W. Zemansky and R. H. Dittman, *Heat and Thermodynamics,* Ref. 7, p. 515.

[48] For what is usually taken to be the traditional proof of the equivalence between the Nernst-Simon form of the third law and the unattainability statement of the third law, see, for example, M. W. Zemansky and R. H. Dittman, Ref. 7, Sec. 19-6. For the purposes of our present article, let us remain at this level of discussion on the relationship between different versions of the third law, and simply make a few notes on deeper and more subtle points. For example, see D. ter Haar, Ref. 44, Sec. 9.1, which expresses these forms of the third laws somewhat differently. Here ter Haar states on p. 289, "As Simon has emphasized in his discussion of the third law, it should not be surprising that there are some restricting clauses in the formulation of the third law, but these clauses do not mean that the third law is not a general thermodynamical law. Indeed, one sees immediately that the restrictions are equivalent to the statement that the third law is valid as long as we are dealing with systems to which thermodynamics applies at all." This last statement is probably too strong, since we can discuss the thermodynamics of a hypothetical classical ideal gas, even though such a system is not found in nature and does not obey the third law of thermodynamics. Nevertheless, ter Haar certainly is correct in that many restricting clauses are often implicitly assumed and not fully stated when discussing the basis of the third law, since all real physical systems found in nature have been found to satisfy these implicit requirements. Indeed, for a discussion on such relevant restricting clauses that are required to make the Nernst-Simon form of the third law rigorously deducible from the unattainability statement, see P. T. Landsberg, *Thermodynamics and Statistical Mechanics* (Oxford University Press, New York, 1978), p. 71. Also, as Landsberg points out in Sec. 6.3.3 (see p. 73), ". . . a rigorous deduction of the unattainability principle from Nernst's theorem is not possible," since the proof has not been demonstrated for all possible thermodynamic processes. For more detail, see Landsberg's article in Ref. 45, particularly Theorem 23.

[49] A qualitative analysis on how this balance might be achieved, as well as an estimate on the size of a classical hydrogen atom, was first given by Boyer in Ref. 2. Also see H. E.

Puthoff, Phys. Rev. D **35**, 3266 (1987).

[50] For a more precise discussion, see, for example, R. C. Tolman, *The Principles of Statistical Mechanics* (Dover, New York, 1979), Chap. IX.

[51] Very often in the textbooks on quantum physics, as well as in the physics literature, the terminology of the "ZP state" and the "ZP energy" of a system is used interchangeably with the "ground state" and the "ground-state energy," without ever mentioning temperature or thermal equilibrium conditions. [See, for example, the undergraduate textbook A. P. French and E. F. Taylor, *An Introduction to Quantum Physics* (Norton, New York, 1978), pp. 134 and 170, or the graduate textbook L. I. Schiff, *Quantum Physics,* 3rd ed. (McGraw-Hill, New York, 1968), p. 69.] Since in quantum mechanics the two concepts are really equivalent, then this terminology does indeed seem quite appropriate. However, historically, the terminology of "zero point" appears to have been first due to the observed nonvanishing kinetic energy of systems near the point of absolute *zero* temperature, rather than to the *zeroth* quantum energy level of a system. [See, for example, T. S. Kuhn, Ref. 18, pp. 246 and 247, or the footnote on p. 73 in L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (Dover, New York, 1985).] Nevertheless, probably most students in physics today first and foremost associate the "zero" in "zero point" with the lowest ("zeroth") energy quantum state, rather than with the state of a system at $T=0$.

[52] For information on this velocity-dependent force for systems other than an electric dipole simple harmonic oscillator, see C. Díaz-Salamanca and A. Rueda, Phys. Rev. D **29**, 648 (1984). A number of other relevant articles are also cited there.

[53] T. W. Marshall, Proc. Cambridge Philos. Soc. **61**, 537 (1965).

[54] A. Einstein and L. Hopf, Ann. Phys. (Leipzig) **33**, 1105 (1910).

[55] Certainly the general view in physics is that at $T=0$, classical systems must exhibit no fluctuating motion. See, for example, Eisberg and Resnick, Ref. 37, p. 235. Nevertheless, Ref. 1 provided a contrary example. Thus, even within the context of classical physics, all molecular and atomic motion may not necessarily cease at $T=0$. On a related subject, some elementary textbooks clearly err in their discussion on thermodynamics by saying that the meaning of $T=0$ is when molecular motion ceases. As noted by Zemansky and Dittman on p. 18 of Ref. 7, this statement is "... entirely erroneous. First, such a statement involves an assumption connecting the purely macroscopic concept of temperature and the microscopic concept of molecular motion. If we want our theory to be general, this is precisely the sort of assumption that must be avoided." Their point is certainly true. Indeed, the thermodynamic definition of $T=0$ given in Ref. 7 was the one used in Ref. 1 for investigating the $T=0$ behavior of the oscillators. However, Zemansky and Dittman go on to say that, "Second, when it is necessary in statistical mechanics to correlate temperature to molecular activity, it is found that classical statistical mechanics must be modified with the aid of quantum mechanics ... ." As pointed out here and in Ref. 1, this second point is not a closed problem in physics.

[56] Some other researchers have attempted to explore certain statistical-mechanics ideas on classical electromagnetic thermal radiation. See A. M. Cetto and L. de la Peña, Found. Phys. **19**, 419 (1989).

[57] D. C. Cole, Phys. Rev. D **33**, 2903 (1986). Note that Ref. 11 in this 1986 article refers to unpublished work; this work has since been published and is listed as Ref. 61 below.

[58] See the related discussion by Planck in Ref. 17 that starts with the following statement in italics on p. 69, namely, "... the radiation always retains the character of black radiation...," and that ends at the bottom of p. 70. Some of Planck's discussion is not quite accurate, but the main point is certainly correct. (An example of Planck's discussion that is inaccurate is his statement on p. 70 that" ... the radiation pressure depends only on the total energy density u of the energy of radiation, not on its spectral distribution." As discussed in Sec. IV A, Planck is thinking that $p=\frac{1}{3}\int_0^\infty \rho_{\rm in}d\omega=u/3$, which is used throughout his analysis. He treats u as being independent of the volume $\mathcal{V}$, which is not valid, since the shape and volume of the cavity determine the distribution of the normal modes of the radiation within the cavity.)

[59] The simple harmonic-oscillator system treated here is easy to describe mathematically, which is why it has been analyzed so extensively in the literature. Moreover, despite the simplicity of this classical system, it exhibits such interesting physical effects as van der Waals forces, diamagnetic effects, and the thermal effects of acceleration (see Refs. 1, 3, 4, and 6 for further discussion and references). Indeed, this system has even been used to obtain some understanding into excited states: see the clear discussion and analysis by H. M. Franca and T. W. Marshall in Phys. Rev. A **38**, 3258 (1988).

[60] See the references cited in Refs. 4 and 6. A particularly important early reference is T. W. Marshall, Proc. R. Soc. London Ser. A **276**, 475 (1963).

[61] D. C. Cole, Phys. Rev. D **35**, 562 (1987).