Entropy concepts in classical electrodynamics

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Abstract. Aspects of entropy and related thermodynamic analyses are discussed here that have been deduced in recent years in the area of classical electrodynamics. A motivating factor for most of this work has been an attempted theory of nature often called, "stochastic electrodynamics" (SED). This theory involves classical electrodynamics (Maxwell's equations plus the relativistic version of Newton's second law of motion for particles), but with the consideration that motion and fluctuations should not necessarily be assumed to reduce to zero at temperature $T = 0$. Both fairly subtle and rather blatant assumptions were often imposed in early thermodynamic analyses of electrodynamic systems that prevented the analyses from being sufficiently general to account for these "zero-point" properties, which hindered classical physics from being able to better account for quantum mechanical phenomena observed in nature. In turn, such thermodynamic considerations have helped motivate many of the key ideas of SED.

INTRODUCTION

This article examines some relatively recent work on the thermodynamic analysis of classical electrodynamic systems that necessarily involves concepts about entropy. An early analysis on classical electromagnetic thermal radiation will be outlined and contrasted to a more recent classical modern derivation that takes into account factors overlooked in this early work. As will be seen, some rather subtle and apparently innocuous assumptions were made that end up being quite critical for deducing the correct thermodynamic equilibrium conditions between charges and radiation. In the process of this discussion, a brief review will be given of an attempted theory of nature often referred to as "stochastic electrodynamics" (SED); investigations of this theory have helped to stimulate the thermodynamic ideas discussed in the present article.

The development of the concept of entropy, and its relationship to the second law of thermodynamics, clearly has had a very interesting history. Key early contributors to the development of this topic, consisting in particular of Carnot, Clausius, Kelvin, Boltzmann, Planck, and Carathéodory, helped to guide much of our present thinking. However, there are still important open questions, as evidenced by the interest in the present conference. In particular, open issues exist regarding irreversible processes, as well as systems in the quantum mechanical regime that interact with systems of large degrees of freedom (*i.e.*, radiation) that can be modified via applied constraints.

Much of introductory thermodynamics deals with very specific and idealistic systems, such as an ideal gas of uncharged point mass particles, or a container with perfectly conducting walls filled with blackbody radiation. Far more interesting and relevant physical systems are ones that involve both electrodynamic particles as well as radiation. Only by considering the two together, namely, the sources of charge (particles) plus the generated electromagnetic fields that in turn act back upon the particles, can one really expect to obtain a clear understanding of the thermodynamics of electrodynamic systems.

CORRECTIONS TO THERMODYNAMIC ANALYSIS

Here we will outline one of the more famous and early thermodynamic analyses of thermal radiation and then indicate some of the subtle, but important, points that were originally not taken into account. A more extensive explanation is contained in Ref. [1], with full details in Refs. [2] and [3]. The early work that we are reexamining here was first advanced by Wien and then later developed in considerable detail by Planck [4]; it involves the compression and expansion of thermal radiation within a chamber by means of a mechanical piston. We will begin by quickly reviewing the steps that are traditionally followed in the derivation of the Stéfan-Boltzmann relationship.

If one considers a cylinder of volume V, with the walls of the cylinder maintained at temperature T, then blackbody radiation should exist within the cylinder. If one of the walls of the cylinder is taken to be a piston that can be moved, so as to change the volume of the cylinder, then work can be done as the piston is displaced. Wien's and Planck's analyses assumed that the time average of the electromagnetic radiation energy could be expressed as $U = Vu$, where V is the volume of the cavity or cylinder, and u is an electromagnetic energy density that is independent of position within the cavity, and only dependent on temperature. Thus, U was taken to be an extensive thermodynamic quantity. The first law of thermodynamics is written as [5],

$$dU = d(Vu) = d'Q - PdV \quad , \tag{1}$$

where $d'Q$ is the heat flow *into* the cavity during such a process, $-PdV$ is the work done *on* the radiation in the cavity, and P is the radiation pressure on the piston.

Thus, a key assumption made in this early work was that the radiation in the cavity was uniform and isotropic within the cavity. A second key step involved equating the radiation pressure, P, to $u/3$. The second law of thermodynamics then allows us to equate that $d'Q = TdS$, where dS is called the caloric entropy and is an exact differential. From Eq. (1),

$$dS = \frac{1}{T}\left[\frac{4}{3}udV + V\frac{du}{dT}dT\right] \quad . \tag{2}$$

Equating $\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T}$, which is a consequence of the second law, then yields a simple first-order differential equation of $\frac{1}{T}\frac{du}{dT} = \frac{1}{T^2}4u$ that can be solved to yield the usual form of the Stéfan-Boltzmann relationship of $u = \sigma T^4$. Further early thermodynamic analyses involving, in particular, Kirchhoff's and Wien's work, are also of interest, and involve additional subtle points [2],[3]. However, for the purposes of the present discussion, the above outline quickly reveals some of the key points of interest.

Although it has taken some time for the following points to be recognized, investigations into Casimir forces, begun in 1948 [6],[7],[8],[2], have enabled the limitations of the early thermodynamic analysis to be better understood. One key point can immediately be brought out, namely, that the internal electromagnetic thermal energy of a cavity at temperature T was treated as being an extensive quantity that is proportional to the volume of the cavity ($U = Vu$). From the study of Casimir forces, and, indeed, even from the study of microwave resonators [9],[10], we know that this assumption is not in general valid. For example, in a microwave resonant cavity, where the dimensions of the cavity are typically close to the wavelength of the radiation being manipulated, the electromagnetic energy density inside the cavity is certainly not a constant at all points in the cavity, but varies depending on the location in the cavity. To correct this assumption of $U = Vu$ made in early blackbody radiation analysis, the full normal mode analysis must be carried out and the difference in energy between the sum of normal mode energies due to the change in volume must be calculated, before continuum approximations are made [2].

Moreover, early thermodynamic analysis was not sufficiently general to include the situation that $\lim_{T\to 0} \rho(\omega, T)$ might not equal zero, or, that "zero-point" (ZP) electromagnetic radiation might exist. The piston surface was only explicitly calculated in the case of a perfectly reflecting surface [4], and, in that case, only when an isotropic and uniform radiation was assumed. Researchers then made the assumption that the pressure on other walls in the chamber were equal to this calculated value, independent of the material and relatively independent of the geometry of the wall. However, if we compare two cavities of the same shape and size, but made of different materials, the pressure in the two cavities are in general different, even when the walls of both cavities are held at the same temperature. For example, the Casimir force between two conducting plates is attractive, but between a perfectly conducting and an infinitely permeable plate, the force is repulsive [11]. Changing the shape of the cavity can change the magnitude and sign of the radiation force even more dramatically.

The key steps needed in the normal mode analysis are somewhat similar to the steps outlined earlier here for the Stéfan-Boltzmann law, just much more involved. More specifically, the first law of thermodynamics still needs to be imposed, as in Eq. (1), but without the assumption of a uniform electromagnetic energy density. Next the second law of thermodynamics needs to be imposed, just as in the Stéfan-Boltzmann analysis reviewed earlier, that $d'Q = TdS$, where dS is an exact differential. As shown in Refs. [2] and [3], this condition can be satisfied if the functional form of the radiation spectrum is given by $\rho(\omega, T) = \omega^3 f\left(\frac{\omega}{T}\right)$. We can call this relationship a generalized Wien displacement law, since the functional form is the same, but now the steps in the derivation also apply in the situation where the restriction of $\lim_{T\to 0}\rho(\omega,T)=0$ is not imposed, so that the possibility of ZP radiation is taken into account. Following this analysis farther then leads to a generalized Stéfan-Boltzmann relationship.

Further thermodynamic analysis has been carried out for the case of electric dipole oscillators and cavity radiation. In both cases, one can actually derive the functional form for ZP radiation, based on the thermodynamic definition of no heat flow at $T=0$ during reversible thermodynamic operations [12],[2],[13],[14],[15]. Moreover, these systems were explored regarding the restrictions of the third law of thermodynamics, the requirement of a finite specific heat, and the ultraviolet catastrophe. In addition, one can examine other thermodynamic questions, such as whether extracting energy from ZP radiation violates physical laws [16],[17],[18].

STOCHASTIC ELECTRODYNAMICS

Probably most physicists will find the above points curious, and of some interest, but will also wonder about the need to examine these points at this late date. After all, nearly every physicist accepts that classical physics cannot explain quantum mechanical phenomena and that new physical ideas need to be invoked, outside of classical electrodynamics, to achieve agreement with nature. The above points may extend the domain of classical physics, but the program still appears to be doomed, so why even consider it?

There are at least two reasons. First, the early thermodynamic arguments, which are reported in many quantum mechanics textbooks, do need to be modified for understanding the thermodynamics of small cavities, where Casimir-like forces become important. Second, the investigation of most of the ideas discussed here was motivated from the attempted theory of nature, SED, which a very small group of researchers still pursue, including myself.

This theory of nature was aimed at providing a causal and, depending somewhat on how one wants to define the term, a "deterministic" description of quantum mechanical phenomena, by examining in detail the deficiencies, such as atomic collapse, that made physicists turn from classical physics after about 1900. Trevor Marshall [19],[20] and Timothy Boyer [21],[22] are the two key initial founders of SED, although, as nicely described in Ref. [8], a number of earlier researchers had ideas that clearly relate to SED notions. Since the 1960s there have been some notable accomplishments in SED, such as regarding van der Waals and Casimir forces, blackbody radiation, Bell's theorem, locality, photon measurements, thermal effects of acceleration, quantum cavity electrodynamics, nonlinear optical effects, ideas on a wide variety of astrophysical tests and phenomena, and basic thermodynamic issues [8],[23],[24],[25]. Subtle issues in thermodynamics and statistical mechanics have been probed in much of this work. For example, in Ref. [22], Boyer pointed out that in as simple a physical world as one governed by classical physics, it appears to be necessary to make a distinction between Boltzmann's probabilistic entropy idea of the logarithm of the number of microstates, and Clausius' thermodynamic definition of entropy based on heat flow.

Nevertheless, SED has not yet yielded a satisfactory account of even the simplest of atoms, namely, hydrogen, despite some fairly vigorous attempts [25],[26],[27],[28],[29],[30],[31]. Most researchers have abandoned the original ideas and only a small group remains that thinks the theory may yet prove to be successful if sufficiently close attention is made to restrict the theory to real physical systems that occur in nature [32],[30],[33],[31].

Despite the disagreement with nature that has been found to date, there are still several reasons for further investigations. Perhaps none of these motivations will instill much incentive to divert researchers from more conventional matters, but, these reasons should make the pursuit at least respectable and reasonable, of practicality for some regimes, and potentially of great interest if some of these directions are successful. First, on the "respectable" end, there are a host of questions still to be examined more deeply, such as: "If the world really did operate via classical physics, what would happen? Is there any equilibrium condition that can be achieved between classical charged particles and radiation? What becomes of the 'laws' of statistical mechanics and thermodynamics as applied to a universe that operates via classical physics, particularly when ZP motion is recognized to not be in violation of classical ideas?" Second, from a "practical" perspective, the theory does work well for "linear" systems, such as for a fairly wide variety of systems of electric dipole simple harmonic oscillators [23], as well as for electromagnetic fields interacting linearly with macroscopic media boundaries, like conducting walls and dielectric plates, that occur in most experiments to date with Casimir and van der Waals forces [2],[15]. Consequently, for someone doing simulation work on complicated systems in solid state physics, where Casimir-like forces are involved, the use of SED for the description seems reasonable. Third, if some of the difficulties discussed in Refs. [32] and [30] are overcome, then there is the exciting, but admittedly remote, possibility that SED will turn out to be a successful theory of nature for electromagnetic-interaction-governed phenomena.

CONCLUDING REMARKS

Thermodynamic analyses can be both incredibly powerful in their generality and conclusions, as well as limited, as they can overlook some very subtle points that in the end turn out to be quite critical. It seemed appropriate to briefly review the ideas of SED at the present conference on the second law of thermodynamics, since much of the physical concepts in SED are very closely intertwined with notions of thermodynamics and statistical mechanics.[1]

Clearly, early blackbody thermodynamic analysis contained some very innocuous and physically appealing assumptions that resulted in significant differences than what has been observed in nature. In particular, by not taking into account the

[1] I greatly appreciate Prof. Sheehan's invitation and support to be a part of this conference.

possibility of electromagnetic ZP radiation in the analysis, effects such as due to Casimir-like forces and van der Waals forces could not be taken into account, and investigations on the Stéfan-Boltzmann law, the third law of thermodynamics, the ultraviolet catastrophe, specific heats, and other effects and properties, were significantly hindered in the early analysis. We should at the very least keep such cautions in mind when probing questions on the second law of thermodynamics.

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