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Thermodynamics of Radiative Emission Processes

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A basic assumption implicit in the application of thermodynamics to the electromagnetic field is that the laws of thermodynamics are *locally* valid for radiative emission and absorption processes. This means that a certain minimum amount of entropy must be created by the radiative process itself. It is shown, by considering the extreme case in which the spontaneous emission of a natural spectral line is the only process taking place, that this assumption is correct, and that its validity is essentially a consequence of the uncertainty principle as expressed by the reciprocal relationship between natural line breadth and lifetime.

INTRODUCTION

RECENTLY the methods of irreversible thermodynamics have been applied, in an elementary way, to a number of problems involving the emission of luminescence radiation.¹⁻³ A basic assumption implicit in these applications (and, indeed, in the very idea of applying thermodynamics to the electromagnetic field⁴) is that not only the first, but also the second law of thermodynamics is *locally* valid for radiative emission and absorption processes. Expressed somewhat more precisely, the assumption is: In any process, the net rate at which the electromagnetic field carries entropy away from a system (or any element of a system) must equal or exceed the difference between the rate at which the entropy of the system⁵ (or element) decreases, and the net rate at which entropy is carried away from the system (or element) by any mechanism other than radiation.⁶ For this to

be possible, however, a certain minimum amount of entropy must be created by the radiative process itself, and in terms of the mechanism of the radiative process it is not immediately obvious how this comes about nor, indeed, that it can be so. The difficulty is illustrated by the following rather convincing counter-argument, due to Klein.⁷

Consider a closed system consisting of a collection of noninteracting particles, each of which has two energy states. At a given time, let a certain fraction of the particles be in the excited state, and suppose that the system at no time receives energy from the outside. Then the excited particles will eventually drop to the ground state by the spontaneous emission of radiation, and the energy of the system will decrease as this radiation leaves. If the states are sufficiently sharp and we wait long enough, however, the emitted radiation will be essentially monochromatic and will therefore carry off no entropy. Yet, because the system loses energy, it will cool, and its entropy will therefore decrease. Hence, at first sight, the behavior of this system appears to contradict the basic assumption outlined above.

The trouble with this type of argument is a familiar one in the thermodynamics of irreversible processes, namely, that it attempts to deal with the over-all changes brought about by an irreversible process

enters into thermodynamics, the same degree of physical reality it enjoys in other branches of physics; instead, one would have to conclude that thermodynamics is essentially a theory of action at a distance.

⁷ M. J. Klein (private communication).

¹ M. A. Weinstein, J. Opt. Soc. Am. (to be published).

² F. E. Williams, Bull. Am. Phys. Soc. **5**, 70 (1960).

³ L. D. Landau, J. Phys. (U.S.S.R.) **10**, 503 (1946).

⁴ M. Planck, *The Theory of Heat Radiation* (P. Blakiston's Son and Company, Philadelphia, Pennsylvania, 1914). In this classic text, the question to be treated below is already considered in some detail, but from a somewhat different point of view than the one adopted here.

⁵ One must, of course, include the entropy of the radiation inside the system as part of the entropy of the system.

⁶ If this were not so, one would have to assume that the presence of absorbing matter external to a radiating system (or element) is necessary for the validity of the second law. Hence, in applying thermodynamics to a system radiating at a given time, one would have to take into account the *later* changes in entropy which accompany the ultimate absorption of the radiated energy. One could not, therefore, ascribe to the electromagnetic field, as it

without considering the relationships among the various rates involved in the process. As soon as we think in terms of rates, it becomes apparent that the flaw in the argument is that it does not take into account the effect of the lifetime of the excited state. For while it is true that we can, in principle, make the emitted radiation as nearly monochromatic as we please, the essential point here is that because of the uncertainty principle we must, at the same time, make the lifetime of the excited state correspondingly long. The longer the lifetime of the excited state, however, the slower will be the rate at which the entropy of the system decreases, and hence the smaller the rate at which the field needs to carry off entropy, i.e., the longer the lifetime, the more nearly monochromatic the radiation can be and still satisfy the second law. The object of the present note is to show, by an elementary calculation on Klein's system, that when one takes into account the reciprocal relationship between natural line breadth and lifetime, the second law is indeed satisfied, and thus to show that the local validity of the second law of thermodynamics for radiative emission processes is essentially a consequence of the uncertainty principle.

ENTROPY CHANGE OF THE PARTICLES

We consider a closed system composed of a collection of noninteracting particles confined to a volume V . Each particle is to have two (nondegenerate) energy states separated by an energy E , and is to be capable of making radiative transitions between these states; we calculate first the rate at which the entropy of the system changes as a result of these transitions.

Let N be the total particle density, and n the density of particles in the excited state; the entropy of the system of particles is then⁸

$$S_p = -kNV[(n/N) \ln(n/N) + (1-n/N) \ln(1-n/N)], \quad (1)$$

where k is Boltzmann's constant. Then if τ is the lifetime of the excited state against spontaneous emission, the average rate at which the density of excited particles changes because of spontaneous emission processes is

$$dn/dt = -n/\tau, \quad (2)$$

and the average rate at which the entropy of the system changes because of spontaneous emission processes is therefore

$$dS_p/dt = -(knV/\tau) \ln[(N/n)-1]. \quad (3)$$

Thus, the entropy of the system decreases with time as soon as $n < N/2$, which we assume to be the case.⁹

⁸ C. Kittel, *Elementary Statistical Physics* (John Wiley and Sons, Inc., New York, 1958).

⁹ $N/2 < n$ corresponds, of course, to the negative temperature region for the two-state particle system, and will not be considered here.

ENTROPY CHANGE OF THE FIELD

Next, we calculate the rate at which the spontaneously emitted radiation carries entropy away from the system. To avoid having to solve an irrelevant transport problem, we assume from the start that the density of particles is sufficiently small that we can neglect reabsorption and stimulated emission. This means that if d_m is the maximum linear dimension of the containing volume, we assume N small enough that $\alpha(\nu)d_m \ll 1$, where $\alpha(\nu)$ is the absorption coefficient of the system of particles for radiation of frequency ν . Now, if the emission line has only its natural breadth, the maximum value of the absorption coefficient will be¹⁰

$$\alpha_0 = \alpha(\nu_0) = (N-n)c^2/(2\pi\nu_0^2), \quad (4)$$

where $\nu_0 = E/h$ is the central frequency of the line. We therefore restrict ourselves to particle densities such that

$$N \ll 2\pi\nu_0^2/(c^2d_m). \quad (5)$$

When this condition is satisfied, the spontaneously emitted radiation will escape directly from the containing volume and spontaneous emission will be the only process by which n changes, so that Eq. (3) will actually represent the total rate at which the entropy of the system of particles changes.

To calculate the rate at which the field carries off entropy, we observe that if, in the neighborhood of the point \mathbf{r} in space,

$$f(\nu, \hat{k}, \mathbf{r})$$

is the total number of quanta per unit volume per unit frequency range moving per unit solid angle about the direction of the unit vector \hat{k} , the specific intensity of entropy¹¹ will be,¹²⁻¹⁶ for unpolarized radiation,

$$s(\nu, \hat{k}, \mathbf{r}) = \frac{2k\nu^2}{c^2} \left[\left(1 + \frac{c^3 f}{2\nu^2}\right) \ln \left(1 + \frac{c^3 f}{2\nu^2}\right) - \left(\frac{c^3 f}{2\nu^2}\right) \ln \left(\frac{c^3 f}{2\nu^2}\right) \right]. \quad (6)$$

Hence, in terms of the density of quanta, f , the net rate at which the field carries off entropy is

$$\frac{dS_f}{dt} = \int_0^\infty d\nu \int dA \int d\omega \hat{k} \cdot \hat{n} s(\nu, \hat{k}, \mathbf{r}_A), \quad (7)$$

¹⁰ W. Heitler, *The Quantum Theory of Radiation* (The Clarendon Press, Oxford, 1954), 3rd ed. It should be noted that the absorption coefficient at the peak of a natural line is independent of the lifetime.

¹¹ I.e., the entropy crossing unit projected area per unit time per unit frequency range per unit solid angle.

¹² M. Planck, reference 4, p. 169.

¹³ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., New York, 1958), p. 155.

¹⁴ P. Rosen, *Phys. Rev.* **96**, 555 (1954).

¹⁵ A. Ore, *Phys. Rev.* **98**, 887 (1955).

¹⁶ For an interesting discussion of the validity of expressions like Eq. (6) in nonequilibrium situations, see P. T. Landsberg, *Proc. Phys. Soc. (London)* **74**, 486 (1959).

where dA is the element of surface area of the containing volume at the surface point \mathbf{r}_A , \hat{n} is the outward normal to dA , and $d\omega$ is the element of solid angle. The integral, of course, is to cover the entire surface area (assumed non-re-entrant) and the hemisphere of solid angle of the outward normal to each element of area ($\hat{k} \cdot \hat{n} \geq 0$).

To calculate f , we first note that if $g(\nu)d\nu$ is the probability that spontaneous emission gives a quantum with frequency between ν and $\nu+d\nu$, the total number of quanta emitted per unit time per unit volume per unit frequency range per unit solid angle will be $ng(\nu)/(4\pi\tau)$. Since we are neglecting reabsorption and stimulated emission, the equation of continuity for quanta is therefore

$$\partial f / \partial t + c \hat{k} \cdot \text{grad} f = ng / (4\pi\tau). \quad (8)$$

To simplify the problem still further, we now assume that the linear dimensions of the containing volume are sufficiently small that we can neglect the effects of retardation, which are irrelevant to the question with which we are concerned. Since n does not change appreciably in times small compared with τ , retardation effects will be negligible if

$$c\tau \gg d_m; \quad (9)$$

when this condition is satisfied, we can neglect $\partial f / \partial t$ in Eq. (8),¹⁷ and it is then readily shown that the solution of Eq. (8) is

$$f(\nu, \hat{k}, \mathbf{r}) = nd(\hat{k}, \mathbf{r})g(\nu)/(4\pi c\tau), \quad (10)$$

where $d(\hat{k}, \mathbf{r})$ is the distance from the point \mathbf{r} to the boundary of the containing volume looking in the direction $-\hat{k}$, i.e., looking back along the line of propagation of the quanta considered.

In what follows we will not need to know the precise form of $g(\nu)$; we assume only that $g(\nu)$ is a positive definite function with a single sharp peak at ν_0 , that

$$\int_0^\infty d\nu g(\nu) = 1, \quad (11)$$

and that, from the uncertainty principle,

$$\Delta\nu = (2\pi\tau)^{-1}, \quad (12)$$

where $\Delta\nu$ is the width of the peak,¹⁸ i.e., the difference between the frequencies at which $g(\nu)$ drops to half

its peak value. From this, it follows that¹⁹

$$g(\nu_0)\Delta\nu/2 = g(\nu_0)/(4\pi\tau) < 1. \quad (13)$$

Now, from Eqs. (6) and (10), there will be appreciable contributions to the integral over frequency in Eq. (7) only when $g(\nu)$ is large, i.e., only in the neighborhood of ν_0 . In this region, however, we have

$$\frac{c^3 f}{2\nu^2} \sim \frac{nc^2 dg}{8\pi\tau\nu_0^2} = (\alpha_0 d) \left(\frac{n}{N-n} \right) \left(\frac{g}{4\tau} \right) \ll 1. \quad (14)$$

We can therefore write, approximately,

$$s \sim (2k\nu_0^2/c^2)(c^3 f/2\nu_0^2)[1 - \ln(c^3 f/2\nu_0^2)], \quad (15)$$

so that Eq. (7) becomes

$$\begin{aligned} \frac{dS_f}{dt} \sim \frac{kn}{4\pi\tau} \int_0^\infty d\nu g(\nu) \int dA \int d\omega \hat{k} \cdot \hat{n} d(\hat{k}, \mathbf{r}_A) \\ \times \left[1 - \ln \left(\frac{\alpha_0 d n g(\nu)}{4\tau(N-n)} \right) \right]. \end{aligned} \quad (16)$$

But since we will underestimate dS_f/dt if we replace d by d_m and $g(\nu)$ by $g(\nu_0)$ in the logarithm in Eq. (16), and since it is readily shown that

$$\int dA \int d\omega \hat{k} \cdot \hat{n} d(\hat{k}, \mathbf{r}_A) = 4\pi V, \quad (17)$$

we obtain, using Eqs. (11), (13), and (17),

$$\frac{dS_f}{dt} > \frac{knV}{\tau} \left[1 - \ln \left(\frac{\pi n \alpha_0 d_m}{N-n} \right) \right]. \quad (18)$$

NET ENTROPY CHANGE

Combining Eqs. (3) and (18), we obtain, for the difference between the rate at which the spontaneously emitted radiation carries entropy away from the system and the rate at which the entropy of the system decreases because of spontaneous emission processes,

$$\frac{dS_f}{dt} + \frac{dS_p}{dt} > \frac{knV}{\tau} [1 - \ln(\pi \alpha_0 d_m)]. \quad (19)$$

The right-hand side of this inequality is positive as long as $\alpha_0 d_m < e/\pi$. Thus, since the analysis leading to Eq. (19) is valid only for $\alpha_0 d_m \ll 1$, it follows that the second law of thermodynamics is locally valid for radiative emission processes even in the extreme case in which the spontaneous emission of a natural spectral line is the only process taking place.

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I am indebted to Professor M. J. Klein for a helpful and stimulating discussion.

¹⁹ Actually, this is readily shown to be a considerable overestimate of $g(\nu_0)/\tau$.

¹⁷ We can then also neglect the contribution of the entropy of the radiation inside the system to the rate at which the entropy of the system changes.

¹⁸ It should be noted that, strictly speaking, the distribution function, f , refers to wave packets, and that in order to localize a wave packet within a domain of size d_m we must utilize in its construction a range of wave numbers $\Delta k \gtrsim d_m^{-1}$ and hence a range of frequencies $\Delta\nu \gtrsim c/(2\pi d_m)$. Hence, if we take $d_m \ll c\tau$, we must use a range of frequencies much greater than the natural linewidth in order to be sure that the wave packet is even within the containing volume. The rates calculated with the function f are, of course, only average rates.