ON THE THERMODYNAMICS OF PHOTOLUMINESCENCE

By L. LANDAU

Institute for Physical Problems, Academy of Sciences of the USSR

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The author derives the conditions imposed by thermodynamics upon the total energy yield of photoluminescence and the intensity of radiation in the anti-Stokes region.

Thermodynamics imposes essential restrictions on the process of photoluminescence, giving rise to certain inequalities which must be satisfied in all cases.

According to the second law of thermodynamics the entropy must increase in an isolated system, which in the case under examination is a system consisting of luminescent body + radiation. Therefore, to write these inequalities, the entropy of the radiation as such must be included in the discussion of the problem in question.

The distribution of radiation with respect to frequencies and directions can be described by the density \( \varphi(\nu, n) \) of the energy. \( \varphi(\nu, n) d\nu d\Omega \) is the energy of the radiation, referred to a unit volume, in the interval \( d\nu \) of frequencies, possessing a direction \( n \) in the element \( d\Omega \) of the solid angle. Instead of the function \( \varphi(\nu, n) \) it is convenient to introduce a function \( f(\nu, n) \) defined as follows:

\[
\varphi(\nu, n) d\nu d\Omega = f(\nu, n) h\nu \frac{2\nu^2 d\nu d\Omega}{c^2}, \tag{1}
\]

\( h\nu \) being the energy of the photons and \( 2\nu^2 d\nu d\Omega/c^2 = 2\hbar^2 dk d\Omega \) — the "element of the volume" in the "space" of the wave vector \( \mathbf{k} \). (The factor 2 stands for two possible directions of polarization; for the sake of brevity we shall not consider distribution with respect to polarization altogether, as it does not have a substantial effect on the following discussion.) \( f(\nu, n) \) is the number of photons per unit volume of space, referred to unit volume of the "k-space". The intensity \( dI \) of the radiation emitted by a unit of the surface of the considered body will be determined by

\[
dI = c \cos \theta d\nu d\tau = f(\nu, n) h\nu d\tau, \tag{2}
\]

where we have introduced the notation

\[
d\tau = \cos \theta \frac{2\nu^2 d\nu d\Omega}{c^2} \tag{3}
\]

(\( \theta \) is the angle between \( n \) and the normal to the surface).

The radiation entropy is determined by the well-known formulae of Bose statistics applied to a "photon gas". The entropy \( S \) of the radiation passing through an area of 1 cm² in 1 sec. is equal to

\[
S = k \int (f + 1) \ln (f + 1) - f \ln f \, d\tau, \tag{4}
\]

the integration being extended over the total spectrum of frequencies and over all directions \( n \); \( k \) is the Boltzmann constant.

If the total radiation spectrum is concentrated in a small interval \( \Delta \nu \) of frequencies, and the directions — in the small interval \( \Delta \Omega \) of angles, then, evidently, the total radiation intensity is

\[
I = I \Delta \nu \Delta \tau, \tag{5}
\]

where \( I \) is a certain mean value of \( f \), and

\[
\Delta \tau = \frac{2\nu^2 \cos \theta \Delta \nu \Delta \Omega}{c^2}.
\]
For the entropy we obtain:

\[ S \sim x \left( (\bar{f} + 1) \ln(\bar{f} + 1) - \bar{f} \ln \bar{f} \right) \Delta \tau = \frac{x}{h \nu} \frac{(\bar{f} + 1) \ln(\bar{f} + 1) - \bar{f} \ln \bar{f}}{\bar{f}} I. \]  

(6)

If \( \Delta \tau \) tends to zero for a given total intensity \( I \), \( \bar{f} \) tends to infinity. But in the case of large values of \( \bar{f} \)

\[(\bar{f} + 1) \ln(\bar{f} + 1) - \bar{f} \ln \bar{f}

is approximately equal to \( \ln f + 1 \) and \( (\ln f + 1)/f \) tends to zero. Therefore, it follows from (6) that \( S \) tends to zero. The condition that \( \Delta \tau \) tends to zero does not require that \( \Delta \nu \) and \( \Delta \mathcal{v} \) should simultaneously tend to zero. It is sufficient that one of them should tend to zero. In other words, both the entropy of the strictly monochromatic (\( \Delta \nu = 0 \)) and the entropy of the strictly directed (\( \Delta \mathcal{v} = 0 \)) radiation are equal to zero.

Let us now turn our attention to the process of photoluminescence. We shall assume, for the sake of brevity, that luminescence is accompanied by complete light scattering over all directions, i.e., that the light emitted by the body is isotropic with respect to direction and the luminescence does not depend upon the direction of the incident light. Then the process of luminescence will be specified by a certain function \( w(\nu', \nu) \), which determines the intensity of radiation of light with a frequency \( \nu \) upon irradiation by light with a frequency \( \nu' \).

Let us consider the restrictions imposed by thermodynamics on the properties of this function for a certain value of \( \nu' \). With this purpose in mind we may formally consider the body as being irradiated by a strictly monochromatic light (frequency \( \nu ' \) and intensity \( I_0 \)). The light that is emitted has a spectrum which is determined by the function \( w(\nu', \nu) \). If the emitted light is either sufficiently monochromatic or consist of separate sufficiently narrow spectral lines, then the light entropy will equal zero, and it suffices to consider the change in the body entropy. But this, obviously, in a unit of time (referred to a unit of the body surface) will be

\[ \frac{I_a - I_t}{T}, \]

where \( T \) is the temperature of the body, and \( I_a \) the luminescence intensity. Hence in this case the second law leads to the inequality

\[ I_t \leq I_a, \]  

(7)

i.e., the relative luminescence yield cannot exceed unity.

If, however, upon irradiation by monochromatic light the luminescence does not consist of separate, sufficiently narrow lines, it is necessary to introduce a correction involving the radiation entropy. It should be pointed out that it is possible to disregard the simply reflected light owing to its obviously monochromatic nature.

Let \( \Delta \nu \) be the main interval of frequencies of the luminescence spectrum. The entropy of the incident light is equal to zero, whereas the entropy of the radiated light is approximately equal to

\[ x \left( (\bar{f} + 1) \ln(\bar{f} + 1) - \bar{f} \ln \bar{f} \right) \Delta \tau, \]

where \( f(\nu) \) determines the luminescence spectrum, and we have substituted for the integral (4) the value of the function under the integral sign, corresponding to a certain mean \( \bar{f} \) multiplied by the region \( \Delta \tau \) of integration. The full change of the entropy of the body together with the radiation must be positive:

\[ I_a - I_t + x \left( (\bar{f} + 1) \ln(\bar{f} + 1) - \bar{f} \ln \bar{f} \right) \Delta \tau \geq 0. \]

The intensity \( I_t \) of the luminescent radiation can be expressed by means of \( f \) as follows:

\[ I_t = \int f \nu d\tau \sim \hbar \nu / \Delta \tau. \]  

(8)

Consequently the inequality obtained may be rewritten in the following form:

\[ I_a \geq I_t \left[ 1 - \frac{\nu T}{h} \frac{\ln(\bar{f} + 1) - \bar{f} \ln \bar{f}}{\bar{f}} \right]. \]  

(9)

The expression in the right hand side depends on \( \bar{f} \), i.e., upon the absolute light intensity. On the other hand, as long as the photoluminescence increases linearly with the intensity of the incident light, \( I_t/I_a \) is independent of the intensity. Therefore, we are justified in substituting for \( f \) any value corresponding to the photoluminescence intensity in the linear region. Inasmuch as \( \frac{(\bar{f} + 1) \ln(\bar{f} + 1) - \bar{f} \ln \bar{f}}{\bar{f}} \) is a monotonously decreasing function of \( \bar{f} \), it is evident that the greatest restriction will be imposed when we take the value of \( \bar{f} \) corresponding to the ma-
maximum photoluminescence intensity for which the linearity is still retained.

Let us introduce an "effective temperature" $T_{eff}$ of the luminescent light, as a temperature of black radiation, in the spectrum of which the specified interval $\Delta \nu$ possesses an intensity equal to the greatest intensity of luminescence in the linear region. This temperature is connected with $\tilde{I}$ by Planck's formula:

$$\tilde{I} = \frac{1}{e^{\frac{h\nu}{kT_{eff}}} - 1}. \quad (10)$$

Upon substituting (10) into (9) a rather lengthy expression is obtained; it is sufficient to write $\tilde{I}$ out for the two limiting cases—the large and small values of $h\nu/kT_{eff}$. When $h\nu \gg xT_{eff}$, we have $\tilde{I} \approx e^{-h\nu/kT_{eff}}$ and (9) yields

$$I_a \geq I_1 \left(1 - \frac{T}{T_{eff}}\right). \quad (11)$$

The ratio $T/T_{eff}$ is in general small; therefore, (11) may also be written as follows:

$$I_t \leq I_a \left(1 + \frac{T}{T_{eff}}\right). \quad (12)$$

In the opposite limiting case of small $h\nu/xT_{eff}$, we have $\tilde{I} \approx xT_{eff}/h\nu$, and (9) leads to the inequality

$$I_t \leq I_a \left[1 + \frac{T}{T_{eff}} \left(\ln \frac{xT_{eff}}{h\nu} + 1\right)\right] \quad (13)$$

$(h\nu \ll xT_{eff})$

differing but insignificantly from (12).

The inequalities thus obtained express the thermodynamic limitation of the luminescence yield. The temperature $T_{eff}$ is usually of the order of several tens of thousands of degrees, whereas $T$ is the room temperature. Hence, $T/T_{eff}$ is very small, and we arrive at the conclusion that the consideration of the radiation entropy leads to but an insignificant correction in the simple inequality (7). Thus the relative luminescence yield, even when thermodynamically capable of exceeding unity, does so by an insignificant quantity.

Formulas (12) and (13) do not represent the sole restriction imposed by thermodynamics upon the process of luminescence. Consider a system consisting of the luminescent body and black radiation of the same temperature $T$. We can then assert that the body and the radiation are in thermal equilibrium with respect to one another. This means that in every interval $d\nu$ of frequencies, the intensity of the light emitted by the body is equal to the intensity of the black radiation spectrum in the same interval. But the light emitted by the body consists of two parts: of the light which arises under the influence of the black radiation falling on the body (this part includes photoluminescence) and of the spontaneous emission. Therefore, under these conditions the following inequality must hold for every interval of frequencies:

$$\text{intensity of black radiation} \leq \text{intensity of luminescence intensity}. \quad (14)$$

Let us express this inequality in a mathematical form. We shall assume that for all the considered frequencies the inequality $h\nu' xT$ is valid. According to Wien's formula, for such frequencies the intensity of black radiation is expressed in the form

$$\text{const} \cdot \nu'^3 e^{-h\nu'/xT}.$$

Multiplying by the intensity $\omega(\nu', \nu)$ of the emission of light with a frequency $\nu'$ upon irradiation by light with a frequency $\nu'$, and integrating over $d\nu'$, we obtain the intensity in the left-hand side of inequality (14) in the following form

$$\text{const} \int \omega(\nu', \nu) \nu'^3 e^{-h\nu'/xT} d\nu'.$$

In the right-hand side of inequality (14) we have the expression $\text{const} \cdot \nu^3 e^{-h\nu/xT}$. Thus

$$\int \omega(\nu', \nu) \nu'^3 e^{-h\nu'/xT} d\nu' \leq \nu^3 e^{-h\nu/xT}. \quad (15)$$

Here the integration in the left-hand side does not necessarily have to be extended over all the values of $\nu'$. The inequality can evidently only become stronger if we confine ourselves only to a part of them.

Let us consider a small interval of frequencies $\Delta \nu'$, in which the function $\nu^3 e^{-h\nu/xT}$ does not change considerably. Then (15) may be rewritten in the following form

$$\Delta \nu' \cdot \omega(\nu', \nu) \nu'^3 e^{-h\nu'/xT} \leq \nu^3 e^{-h\nu/xT} \Delta \nu'$$

or

$$\omega(\nu', \nu) \leq \left(\frac{\nu}{\nu'}\right)^3 e^{-h(\nu - \nu')/xT} \cdot \frac{\Delta \nu'}{\Delta \nu}. \quad (16)$$
This inequality shows that the radiation intensity in the anti-Stokes region \( (\nu > \nu') \) for appreciable \( \nu - \nu' \) must become insignificant as compared with the intensity of the incident light.

In the Stokes region \( (\nu < \nu') \) for large \( \nu' - \nu \) the inequality (16) becomes objectless, as it gives merely an upper limit for \( \omega \), which is altogether too high.

I would like to point out here, that this paper arose from discussions with S. I. Varvov, who drew my attention to the importance of the rigorous application of thermodynamics to photoluminescence.