Thermodynamic Limits for Some Light-Producing Devices

P. T. Landsberg and D. A. Evans
Department of Applied Mathematics and Mathematical Physics, University College, Cardiff, Wales
(Received 31 July 1967)

A thermodynamic upper limit for the energy efficiency \( \eta \) of light energy output to pump energy input is obtained. It is of a general form, and is applied to lasers and to electroluminescent diodes when these are in a steady state. The theory generalizes previous work, notably the results \( \eta < 1 - T / T_r \) (Mazurenko, lasers) and \( \eta < (1 - T / T_d) \) (Weinstein, diodes), where \( T_r \) and \( T_d \) are effective temperatures associated with the pumping system and the emitted light, respectively. For a GaAs diode, experimental work at the ambient temperature \( T = 300 \) K has been analyzed to yield \( \eta = 0.1 \) to \( 6 \% \) for various forward currents. The internal entropy generation rate for the same diode, per electron crossing the device, is estimated at 30 to 50 Boltzmann constants.

1. INTRODUCTION

Defining an energy efficiency as luminescent power output in excess of blackbody radiation divided by electrical power input, the experiments of Dousmanis et al. suggest the possibility that an electroluminescent diode may have an energy efficiency greater than unity. Such a diode would necessarily convert some thermal energy of the surroundings into luminescent energy and would therefore act as a refrigerator. Several authors (Tauc, Weinstein, and Gerthsen and Kauer) have discussed the limitations imposed by thermodynamics on the efficiency of any electroluminescent device. Mazurenko has also discussed the thermodynamic upper limit for the efficiency of an optically pumped laser.

The present paper provides a theoretical framework in which the previous work, in particular the diode and the optically pumped laser, has a natural place. Thus, this paper extends the cited earlier work. [See also Landsberg (Ref. 6, Sec. 30, and references cited therein).] Thermodynamic equations are obtained by the introduction of the rate of entropy generation within the device, \( \dot{S}_g \), which is essentially non-negative. Neglect of \( \dot{S}_g \) converts equations into inequalities. It is however possible to do better, and to estimate the value of \( \dot{S}_g \), if sufficient experimental information is available, and this has been done for one diode. The parameters needed include the external quantum efficiency, and also the radiation temperature, which can be calculated using the results of Weinstein.

The present work develops further some results presented at the International Conference on Luminescence in Budapest, 1966, which were, however, directed entirely toward the diode problem.

2. NOTATION AND BASIC THERMODYNAMICS

Consider a device or part of a device, referred to as “the box” in what follows, which absorbs energy from a pumping system and emits energy in the form of light, and is also in thermal contact with a heat reservoir at temperature \( T \). The heat reservoir will normally be the surroundings of the device, while the pumping system may be an electrical circuit in the case of a diode, or an electromagnetic radiation field in the case of an optically pumped laser. The term “light” here means electromagnetic radiation in excess of blackbody radiation at temperature \( T \), and “heat” includes blackbody radiation as well as the thermal motion of particles. It is assumed that the pumping system can be assigned a single effective temperature \( T_p \), so that, for example, the case of a laser with combined electrical and optical pumping is excluded. The remaining notation for the general problem is summarized as follows:

\[ E, S \] is the energy and entropy of the box; \( \dot{E}_p, \dot{S}_p, \dot{P}_p \) are the rates at which the pumping system gives up energy, entropy, and Helmholtz free energy to the box,

\[ \dot{P}_p = \dot{E}_p - T_p \dot{S}_p; \]

\( \dot{S}_g \) is the rate at which entropy is generated in the box;

\( \dot{E}_g, \dot{S}_g \) are the rates at which light emitted by the box carries away energy and entropy; \( T_g = \dot{E}_g / \dot{S}_g \) is the effective temperature of light emitted by the box; and \( Q \) is the rate at which the reservoir supplies heat to the box.

Some further notation is required for the discussion of the diode problem; \( j \) is the particle current of electrons through the diode; \( e \) is the electron charge equals \( | e | \); \( V \) is the applied voltage; \( \theta \) is the external quantum efficiency (equals the mean number of photons emitted per electron passing through the diode); and \( h \nu_0 \) is the mean energy of emitted photons.

The relation between \( \dot{S}_g \) and \( \dot{S}_p \) may be clarified by an example. Suppose that the box is a piece of semiconductor with a characteristic energy gap \( E_g \), and the pumping system is a radiation field of photons with mean energy \( h \nu > E_g \). Then \( \dot{S}_p \) is a function of the randomness, in energy and direction, of the photons,
being zero if the radiation field is perfectly directional or perfectly monochromatic. This randomness will be reproduced in the distribution of the electron-hole pairs created in the semiconductor, so that entropy is automatically generated in the box at a rate \( \dot{S}_p \). However, the electron-hole pairs, being created with an average energy greater than the energy gap, must lose energy in the form of heat to the electron-hole gas and to the lattice before recombining. There will also be some pairs which recombine nonradiatively, and the energy of these pairs appears ultimately as heat. All these causes lead to an additional entropy generation rate, and this is denoted by \( \dot{S}_i \). It appears that \( \dot{S}_i \) is essentially non-negative.

The definition of the effective temperature of light \( T_L \) given above is that used by Weinstein, who calculated the entropy content of the radiation, and thus the effective temperature, explicitly for particular spectral distributions. As noted by him, this temperature is distinct from the brightness temperature, defined as the temperature at which a blackbody would emit radiation of the observed total intensity in the frequency range of interest. In the particular case discussed in Sec. 3, in which \( T_L \) was calculated as approximately 1527K at a current of 5 mA, the brightness temperature is about 1794K.

The two basic equations used express the first and second laws of thermodynamics:

\[ \dot{E} = \dot{E}_p + Q - \dot{E}_L, \]  
\[ \dot{S} = \dot{S}_p + Q/T - \dot{S}_L + \dot{S}_i, \]

(2.1)  
(2.2)

the second law giving rise to the inequality \( \dot{S}_i \geq 0 \). In a steady state \( \dot{E} = \dot{S} = 0 \) and one can substitute for \( Q \) from (2.1) into (2.2), giving

\[ \dot{Q} = \dot{E}_L - \dot{E}_p, \]

(2.3)

\[ T \dot{S}_p + \dot{E}_L - \dot{E}_p - T \dot{S}_L + T \dot{S}_i = 0. \]

(2.4)

With the exception of \( \dot{S}_i \), all entropy rates can be expressed in terms of more easily accessible quantities, using \( \dot{E}_L = T_L \dot{S}_L \) and \( \dot{F}_p = \dot{E}_p - T \dot{S}_p \). Equation (2.4) then becomes

\[ \dot{E}_L (1 - T/T_L) = \dot{E}_p (1 - T/T_p) + (T/T_p) \dot{F}_p - T \dot{S}_L. \]

(2.5)

The energy efficiency is defined as the ratio of light energy output to pumping energy input,

\[ \eta = \dot{E}_L/\dot{E}_p. \]

(2.6)

Hence from (2.5) we obtain the main equation of this work:

\[ \eta = \frac{(1 - T/T_L)^{-1} \{1 - T/T_p + (T/T_p) (\dot{F}_p/\dot{E}_p) - T \dot{S}_L/\dot{E}_p\} - T \dot{S}_i/\dot{E}_p}{1 - T/T_L}. \]

(2.7)

and

\[ \eta < \frac{(1 - T/T_L)^{-1} \{1 - T/T_p + (T/T_p) (\dot{F}_p/\dot{E}_p)\} - T \dot{S}_i/\dot{E}_p}{1 - T/T_L}. \]

(2.8)

Weinstein considered this problem with the restriction that \( T_p = T \), and obtained a much quoted result

\[ \eta < (1 - T/T_L)^{-1}. \]

(2.9)

It is apparent that the additional assumption \( \dot{F}_p = \dot{E}_p \) is implicit in his work. This assumption is in fact contained in Eq. (2) of Ref. 3. As will be shown in Sec. 4 below, the assumption is valid when the pumping system is an electrical circuit, and Weinstein was concerned with this case. But it is not valid generally.

Note that for a monochromatic source \( T_p = \infty \), so that in this case also Eq. (2.8) goes over into Eq. (2.9).

The condition for the box to act as a refrigerator is evidently that the rate of heat supply from the surroundings to the box should be positive, \( Q > 0 \). One can, however, be identified from (2.3), (2.6), and (2.7).

\[ \dot{Q} = (\eta - 1) \dot{E}_p \]

(2.10)

\[ = (1 - T/T_L)^{-1} \times \left[ (T/T_L - T/T_p) \dot{E}_p + (T/T_p) \dot{F}_p - T \dot{S}_i \right]. \]

(2.11)

In the case of a diode, (2.9) applies and leads to

\[ Q < \dot{E}_p (T_p/T - 1)^{-1}. \]

(2.12)

As discussed at the end of Sec. 5 values of \( Q \sim 0.2 \dot{E}_p \) appear to be possible.

### 3. Optically Pumped Laser

In this case the pumping system may be identified with the radiation field of photons incident on the box. Since photons form a gas of zero chemical potential they transfer no Helmholtz free energy to the box, \( \dot{F}_p = 0 \) (or equivalently, \( T_p = \dot{E}_p/\dot{S}_p \) in analogy with the definition of \( T_L \)). Substituting \( \dot{F}_p = 0 \) in (2.8) gives the main result of this section:

\[ \eta < \frac{1 - T/T_p}{1 - T/T_L}. \]

(3.1)

The fact that the limiting efficiency is the ratio of two Carnot efficiencies may be explained as follows. It is, in principle, possible to convert light at an effective temperature \( T_p \) completely to heat at the same temperature, and to convert heat at temperature \( T_L \) completely to light at an effective temperature \( T_L \) by the use of blackbody absorbers and radiators in conjunction with suitable optical systems. One can then imagine a device in which light at temperature \( T_p \) is converted to heat and used to drive a Carnot engine, the mechanical work produced being used to drive a second Carnot engine in reverse. The output of the second engine is heat at temperature \( T_i \) and is converted to light at temperature \( T_L \). If the lower operating temperature of both engines is \( T \), the limiting over-all efficiency of this device is precisely (3.1).

The form of (3.1) is such that an efficiency greater than unity can be obtained only by “degrading”
energy from a higher to a lower temperature \( (T_p > T_L > T) \). It may also be noted that the limiting efficiency obtained by coupling any number of devices in series, the output radiation from one being used to pump the next, is at most equal to that of a single device having the same initial and final temperatures.

As noted by Mazurenko, the light emitted by a laser may approach closely to the ideal of perfectly monochromatic and perfectly directional radiation. Such "ideal" radiation carries energy but no entropy and must therefore be assigned an effective temperature \( T_L = \infty \). In this case (3.1) becomes

\[
\eta < 1 - T/T_p,
\]

a result obtained in Ref. 5.

4. DIODE

A number of interpretations of the basic formalism are possible in this case:

(a) The box is interpreted as containing the entire diode, including the contacts. The pumping system is then the external electrical circuit, and the rate at which it does work on the box is

\[
E_p = j e V,
\]

where \( j \) is the particle current of electrons in the circuit and \( V \) the applied voltage. It is then reasonable to assume that the external circuit is at the same (lattice) temperature as the diode,

\[
T_p = T.
\]

(b) The diode can be divided into regions, each region in turn being considered as the box, and the regions adjacent to it being considered as the pump. We have investigated this procedure, which was suggested to us in Budapest by Professor F. E. Williams, University of Delaware. It leads, however, to a rather complicated formalism.

(c) The box is interpreted as the solid structure of the diode and the pump as the electron and hole gas in the diode. One then has \( T_p = T \) and \( E_p = j e V \), where \( E_p \) is the average energy lost by an electron in crossing the diode. \( E_p \) can be estimated from the energy band diagram of the diode, and some work in this direction was done by Landsberg and Evans.\(^7\)

Approaches (b) and (c) involve a more detailed study of the particular case than does (a), and may lead to correspondingly deeper insights. In the remainder of this paper, however, the interpretation (a) will be used exclusively. It has the advantage that the technical efficiency of a lamp is usually defined as

\[
\eta = E_L/eV,
\]

so that if (4.1) is valid, (4.3) and (2.6) are identical, \( \eta = \eta_\text{eff} \). This would not be true for interpretations (b) or (c). However (4.3) represents the more useful definition of efficiency even in these interpretations.

Given (4.1) and (4.2), it remains to evaluate \( E_p \) and \( E_L \) and \( E_p \) is obtained by introducing \( h v_0 \), the mean energy of an emitted photon, and \( \theta \), the mean number of emitted photons produced per electron passing through the device, so that

\[
E_L = \hbar \theta v_0.
\]

\( \theta \) is also called the external quantum efficiency. In practice the mean energy \( \hbar v_0 \) is not directly observed. Rather one observes a peak in the emission spectrum at \( v = v_{\max} \), say. If the spectrum is a narrow line, the error involved in identifying \( \theta \) with \( v_{\max} \) (as is done in Sec. 5 below) will be small.

To calculate \( E_p \), consider that each electron, in passing through the diode, goes from a region at chemical potential \( \mu_i \) to a region at chemical potential \( \mu_j \), where, provided that the contacts at each end are made of the same metal, \( \mu_i - \mu_j = e V \). If the regions are numbered 1 and 2, the change in free energy of each region can be written generally as

\[
dF_i = -\mu_i n_i + p_i v_i, \quad (i=1 \text{ or } 2),
\]

where \( n_i \) denotes number of electrons, \( p_i \) the pressure, and \( v_i \) the volume of region \( i \). Consider now the transfer of a single electron from region 1 to region 2, the volumes remaining fixed. Evidently

\[
dF_1 = -\mu_1, \quad dF_2 = +\mu_2, \quad dF_p = \mu_1 - \mu_2,
\]

where \( dF_p = -(dF_1 + dF_2) \) is the free energy lost by the external circuit in the transfer of one electron. Thus, since \( j \) electrons are transferred in unit time,\(^8\)

\[
\dot{F}_p = j \hbar \dot{F}_p = j (\mu_1 - \mu_2) = j e V
\]

so that, for this interpretation, \( \dot{F}_p = E_p \).
Substituting (4.1), (4.2), and (4.7) into (2.8) leads to the upper limit for the technical efficiency of a diode as
\[ \eta < (1 - T/T_s)^{-1}, \] (4.8)
reproducing the Weinstein result (2.9). Like most inequalities in this field, this result comes from neglecting the internal entropy generation rate \( S_i \). One can alternatively use (2.5), together with (4.1), (4.2), and (4.7), to estimate this rate in terms of observable quantities:
\[ T S_i = k T / (1 - T/T_s) \theta \text{hv}_0. \] (4.9)
It is convenient to introduce the internal entropy production per electron crossing the device as
\[ s_i = S_i / j, \] (4.10)
so that
\[ T S_i = k T / (1 - T/T_s) \theta \text{hv}_0. \] (4.11)
Numerical values for \( s_i \) are presented in Sec. 5 below. Before leaving the general formulas, however, some further comparison with earlier results will be made. Tauc\(^8\) defines an efficiency \( \eta \) by
\[ \eta = E_0 / eV, \] (4.12)
where \( E_0 \) is the band-gap energy of the diode material. Comparison with (4.1), (4.4), and (2.6), which lead to
\[ \eta = \theta \text{hv}_0 / eV, \] (4.13)
shows that (4.12) is appropriate if the external quantum efficiency is unity and if the mean energy of emitted photons is the band-gap energy. Gerthsen and Kauer\(^4\) also make both these assumptions and obtain the result
\[ T/T_s = 1 - (eV/E_0) = 1 - (1/\eta^*), \] (4.14)
while (4.11) without these assumptions gives
\[ T/T_s = 1 - [(eV - T S_i) / \theta \text{hv}_0]. \] (4.15)
It is apparent that (4.14) contains the further assumption of no entropy generation within the device. Since \( s_i > 0 \), (4.14) should be replaced by (4.15) or by
\[ (T/T_s) > 1 - (1/\eta), \]
where \( \eta \) is given by (4.13).

5. CALCULATION OF RADIATION TEMPERATURES AND ENTROPY GENERATION RATES FROM EXPERIMENTAL DATA

Experimental spectra of light emitted from diodes usually show an approximately Gaussian variation of light intensity \( I(\nu) \) with frequency \( \nu \) (Dousmanis et al.\(^4\) and Rupprecht\(^9\) of the general form
\[ I(\nu) = I_0 \exp\{- (\nu - \nu_0)^2 / (\Delta \nu)^2\}. \] (5.1)

If this form is assumed for the spectral density, the further assumptions that light is emitted uniformly from a flat emitting area and is spatially isotropic (within a solid angle of 2\( \pi \)) allow one to use the expression of Weinstein\(^8\) for the radiation temperature:
\[ T_L = (\mu_0 / k) [1.5 - \ln \rho_L(\nu_0)]^{-1}. \] (5.2)

Here \( \rho_L(\nu_0) \) is the mean number of photons per electromagnetic mode in the emitted radiation at the peak frequency \( \nu_0 \), and is given by
\[ \rho_L(\nu_0) = j \theta c^2 / 2 \pi^2 A \nu_0^2 \Delta \nu, \] (5.3)
where \( c \) is the velocity of light, \( j \) and \( \theta \) are as defined in Sec. 2, and \( A \) is the emitting area of the diode. [In Ref. 3, which was not specifically concerned with diodes, (5.3) was expressed in terms of the energy flux density of emitted photons \( \phi_L \), which for an electroluminescent device is clearly \( j \theta c / A \).]

The data to be analyzed refer to a GaAs diode optically pumped with \( S_i \) and operated at 300°K, and are partly contained in Ref. 8. The emitting area, peak frequency, and linewidth were found to be essentially independent of applied voltage:
\[ A = 3.6 \times 10^{-4} \text{ cm}^2, \quad \mu_0 = 1.325 \text{ eV}, \quad \Delta \nu = 1.9 \times 10^8 \text{ sec}^{-1}, \]
the light being emitted from an approximately rectangular area of 75 \( \mu \times 120 \mu \) on each of four faces. The light intensity and forward current were measured over a range of applied voltage in which the current varied from 3 \( \times 10^{-4} \) to 20 mA, a maximum quantum efficiency of 5.7% being achieved at 20 mA.

The first three columns of Table I give experimental data. The values of \( T_L \) calculated from (5.2) and of the internal entropy production \( s_i \) calculated from (4.11) for five typical values of current are also given. A comparison of columns 2 and 6 shows that the internal entropy produced is equivalent to the conversion into heat at lattice temperature \( T = 300^\circ \text{K} \) of almost all the electrical energy \( eV \) supplied. This was to be expected from (4.11) since the quantum efficiency is much smaller than unity. In the last column the internal entropy production per electron is expressed as a multiple of Boltzmann’s constant \( k \).

Comparison of the applied voltage (column 2) with the peak photon energy \( \mu_0 \) (which is equal to the mean photon energy for a Gaussian spectrum) shows that \( \mu_0 > eV \) for \( J < 5 \) mA. It follows from (2.10), (4.1), and (4.13) that a diode with \( \mu_0 > eV \) and \( \theta = 1 \) will act as a refrigerating device, the refrigerating power being
\[ \dot{Q}(\theta = 1) = j (\mu_0 - eV), \] (5.4)
and will have a technical efficiency \( \eta = \mu_0 / eV \) which is greater than unity. The question now arises whether, for particular values of current, voltage, etc., a quantum efficiency \( \theta = 1 \) is in fact thermodynamically possible. To illustrate this, consider the experimental data for \( J = 1 \) mA in Table I, and suppose that, while \( J, V, A, \)

\[^8\] H. Rupprecht, J. M. Woodall, K. Konnerth, and D. G. Pettit, Appl. Phys. Letters 9, 221 (1966). We are indebted to Dr. Rupprecht (private communication) for supplying additional numerical information not contained in this paper.
and \( p_0 \) remain unchanged, \( \theta \) is increased from 0.0312 to 1. This means that all nonradiative processes are made radiative, so that it is reasonable to assume that \( \Delta \nu \) remains the same or increases. The resulting values of \( T_L \) and \( \eta \) are as follows:

\[
T_L \leq 1759^\circ K, \\
\eta = 1.325/1.101 = 1.203, \\
(1 - T/T_L)^{-1} \geq 1.206.
\]

Thus the thermodynamic upper limit \( \eta < (1 - T/T_L)^{-1} \) is not violated. Under these conditions the diode would have an electrical power consumption of \( P_e = ieV = 1.101 \times 10^{-4} \) W, and a refrigerating power of \( Q = 0.203E_g = 2.2 \times 10^{-4} \) W. It appears, therefore, that the laws of thermodynamics do not preclude the construction of a diode having a measurable refrigerating effect and a technical efficiency significantly greater than unity.

Since quantum efficiencies at 300 K are of order 6% or less, the thermodynamic limits are at present of only academic interest at this temperature. Conditions at low temperatures are very different. Recently, quantum efficiencies of 36% have been recorded at 77 K, and of 40% at 20 K (Carr). It seems possible that in these cases the internal quantum efficiency \( \eta \), i.e., the number of photons produced in the device per electron crossing it, is near unity, the losses being accounted for by internal absorption and reflection. Pilkhuin and Rupprecht have estimated that \( \eta \approx 100\% \) for epitaxial GaAs diodes used as lasers at 4.2 K. One can therefore expect that improved experimental techniques may lead to external quantum efficiencies near 100%, and in such a case the thermodynamic limit would become a realistic restriction. External quantum efficiencies of 95% at 77 K have recently been reported by Lamorte et al., but this refers to a pulsed laser which is not a steady-state device and to which therefore the thermodynamic arguments of this paper do not apply.


---

**Physical Review** Volume 166, Number 2 10 February 1968

**Quantum Theory of an Optical Maser. II. Spectral Profile**

**Marlan O. Scully† and Willis E. Lamb, Jr.**

*Department of Physics, Yale University, New Haven, Conn.*

(Received 26 July 1967)

In Paper I of this series, we derived equations of motion for a quantum-laser field interacting with atomic reservoirs. In the usual region of sustained oscillation, the off-diagonal elements of the radiation density matrix \( \rho_{n+1,n} \) were found to have an exponential decay associated with phase diffusion. In I we found the spectrum of the laser radiation by calculating the single time-ensemble average electric field implied by \( \rho_{n+1,n} \). This electric field was then treated as a classical variable whose Fourier analysis gave the spectrum. In the present paper, we establish the validity of this procedure by analyzing a simple model for a spectrometer. It is also shown that the same spectrum can be obtained from a two-time correlation function derived from the equations of motion.

**I. INTRODUCTION**

In the first paper of this series, we derived the equation of motion for the density matrix of the laser field as it evolved under the influence of excited atoms (lasing medium) and a dissipation mechanism (cavity \( Q \)). We found that the elements of the density matrix in the \( n \) representation were coupled only along lines parallel to the main diagonal. The diagonal elements of the density matrix were seen to approach a steady state while the off-diagonal terms decayed in time. It was shown, to a good approximation, that the density matrix for a laser in sustained oscillation sufficiently above threshold obeys the equation

\[
(\langle dp/dt\rangle)_{n,n+1} = -i(n-n')\nu \rho_{n,n+1} - \mu(0) \rho_{n,n+1},
\]

where \( \nu \) is the laser frequency. We have included the first term on the right since it is more convenient for the present purposes to work in the Schrödinger picture. The damping constant \( \mu(0) \) had the form \( 1/2D \), where \( D \) is given by

\[
D = \frac{1}{2}(\nu/Q)/(n),
\]

and \( n \) is the average number of quanta at steady state. It was seen in I that the decay of the off-diagonal elements implied by Eq. (1) is associated with phase diffusion.

The density matrix \( \rho_{n,n'} \) represents our knowledge of the state of the system of interest and thus contains