MINIMUM ENTROPY PRODUCTION AND STEADY STATE PHOTOCONDUCTIVITY

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ABSTRACT

The principle of minimum entropy production is applied to an intrinsic photoconductor exposed to constant intensity monochromatic radiation. The steady state and the state of extremum entropy production are formulated in terms of the average number of electrons or holes in a given energy state by using the methods of statistical mechanics. It is shown that, for small deviations from thermal equilibrium, steady state photoconductivity is characterized by a minimum rate of entropy production, provided that the intrinsic gap of the photoconductor is small compared to the product of the Boltzmann constant and the absolute temperature.

I. INTRODUCTION

A. NATURE OF THE PROBLEM

It is well known that the entropy of an isolated system in thermodynamic equilibrium is a constant and has its maximum value subject to given constraints. Such a system can be characterized by a vanishing rate of increase of entropy. On the other hand, if we prevent a system from reaching equilibrium by imposing external constraints, the system will undergo irreversible changes and the entropy will increase. For the special case in which these constraints are held constant, a steady non-equilibrium state will be reached which, under certain conditions, will also be characterized by a particular rate of entropy production, that of minimum entropy production.

The concept of minimum entropy production was first introduced by Prigogine[1] and has been extensively studied by workers in the field of non-equilibrium thermodynamics. This concept can be restated more completely in the following

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1. I. Prigogine, Etude Thermodynamique des Phénomenés Irreversibles (Editions Dosoer, Liege, 1947), Chap. V.

principle:[2] "the steady state is that state in which the rate of production of entropy has its minimum value consistent with the constraints which prevent the system from reaching equilibrium."

This principle has only limited validity as shown by examples in the literature and by the present example as well. Generally, the domain of validity includes those steady states whose departure from thermal equilibrium is small. A possible extension of the domain of validity, made by one worker in the field, will be reviewed in the following section.

The system chosen for the present example is that of an intrinsic photoconductor illuminated by constant intensity radiation. Since it will involve electronic transitions between the valence and conduction bands of the photoconductor, the problem is most naturally treated by the methods of statistical mechanics.

B. EXAMPLES IN THE LITERATURE

The principle of minimum entropy production has had frequent application in the literature. It is not our

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2. M. J. Klein and P. H. E. Meijer, Phys. Rev. 96, 250 (1954).

intention to trace completely its historical development but to mention and describe some of its more recent applications.

Klein and Meijer[3] gave a proof of the principle by using a system of two identical containers of ideal gas connected by a capillary tube to allow transfer of molecules. Each container was in contact with its own heat reservoir. Entropy was produced by the process of transferring heat from the higher to the lower temperature reservoir. For the proof to be valid, it was necessary to assume that the temperatures of the reservoirs differed by a small amount, i.e., the steady state was close to equilibrium.

Klein[4] later applied the principle to the Overhauser Effect. This effect concerns the polarization of the nuclear spins of a crystal via changes in the coupled electronic spins. Changes in the electronic spins are induced by absorption of external microwave radiation. The proof depended upon the assumption that the electronic spin states were approximately equally occupied, a condition for small departure from high temperature equilibrium. In this example, as well as in the one we wish to consider, the applied radiation serves as the constraint which prevents the system from reaching equilibrium.

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3. Ibid.

4. M. J. Klein, Phys. Rev. 98, 1736 (1955).

The principle was extended to include Fermi-Dirac and Bose-Einstein particles in a paper by Meijer[5] in which he considered systems with variable numbers of particles.

An investigation into the domain of validity of the principle was carried out by Klein[6] by using a system which is a degenerate form of the one we will consider. He proposed a system of N particles each of which had two energy states 0 and ϵ. The system was exposed to external radiation of photon energy $h\nu = \epsilon$. The usual condition for validity required approximately equal distribution of the N particles between the two states. It was shown, however, that even for situations where this condition was seriously violated, the steady state and the state of minimum entropy production were nearly equal and that the agreement improved as the intensity of the radiation was increased.

Generalizations of the principle have been made by Callen[7] and by Blount,[8] who formulated entropy production in terms of a variational approach.

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5. P. H. E. Meijer, Phys. Rev. 103, 839 (1956).

6. M. J. Klein, Proceedings of the International Symposium on Transport Phenomena in Statistical Mechanics, (Interscience Publishers, Inc., New York, 1958) p. 311.

7. H. B. Callen, reference 6, p. 327.

8. E. I. Blount, Phys. Rev. 131, 2354 (1963).

II. APPLICATION TO A PHOTOCONDUCTOR

A. GENERAL PROPERTIES OF PHOTOCONDUCTORS

Photoconductors are substances whose electrical conductivity is increased by exposure to external radiation of a particular frequency. Virtually all semiconductors and insulators are, to some extent, photoconductors. For such substances, the conductivity increases as valence band electrons are optically excited into the conduction band leaving behind vacancies which are free to move as positive charges. Collectively they are referred to as free electron-hole pairs.

For an illuminated photoconductor, free electron-hole pairs are produced in excess of those normally produced by thermal excitation. Photoconductive phenomena are concerned with these excess charge carriers and, in particular, with their rate of recombination. The rate of recombination of free electrons with free holes partially determines the response of a photoconductor to the applied radiation.

In most instances, recombination occurs via impurity states which may exist within the intrinsic gap between the valence and conduction bands. Although direct band to band recombination can also occur, it is dominant only in extremely pure substances or under conditions where the free carrier density greatly outnumbers the density of impurity states.

Because of the importance of the recombination process, a characteristic parameter of a photoconductor is the lifetime of a free pair, τ. The lifetime may be defined to be the average time required for either the electron or hole of an optically created pair to recombine. The lifetime shows a strong dependence on the physical structure of a photoconductor. In this connection, the width of the intrinsic gap and the energy distribution and density of impurity states within this region are of first importance.

A fundamental, although somewhat idealized equation describing a steady photoconductive process is

$$n = f\tau$$

where n is the increase in the number density of free electrons due to the constant volume excitation rate, f, caused by the radiation. Written in the form

$$f = n/\tau$$

it expresses the steady state criterion that the rate of excitation, f, equals the rate of recombination, $\frac{n}{\tau}$. Corresponding expressions exist for the number densities of free holes.

The increase in conductivity arising from electrons and due to absorption of radiation can be written

$$\Delta\sigma = ne\mu$$

where n is defined as before, e is the magnitude of the electronic charge and μ is the electron mobility, defined to be the electron drift velocity per unit electric field.

For the case in which the photoconductivity varies with time, it is no longer true that $f = n/\tau$. The simplest modification of this equation would be to write

$$\frac{dn}{dt} = -n/\tau + f$$

In order to write this equation in such simple form, we must make the following assumptions: (a) the volume excitation rate, f, is constant throught the body of the photoconductor, (b) the photoconductor is homogeneous and is without shallow trapping states,[9] (c) the lateral dimensions of the

9. As opposed to deeper lying impurity states, an electron in a shallow trapping state is more likely to be re-excited back into the conduction band than to recombine with a free hole.

photoconductor are large enough, compared to its thickness, that edge effects causing diffusion and inhomogeneities of carrier densities can be neglected and (d) any applied electric field is uniform and constant.

As drastic as these assumptions may seem, it is worth noting that the above simple equation is one of the few for which a complete solution can be obtained for arbitrary light intensities.[10] It is sometimes necessary to include the fact that τ itself depends on n in a manner dictated by the dominant type of recombination mechanism.

With the exception that we will not consider an applied field, the physical model we will use is very similar to that implied by the equation $(dn/dt) = (-n/\tau) + f$.

B. ENTROPY PRODUCTION

For all the calculations which follow, the physical model used will be that of a homogeneous, intrinsic photoconductor illuminated by constant intensity monochromatic radiation. We will assume that the photoconductor is thin enough

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10. E. S. Rittner, Photoconductivity Conference (John Wiley and Sons, Inc., New York, 1954), p. 216.

to allow approximately uniform absorption of photons and, compared to its thickness, its lateral dimensions are large enough that edge effects may be neglected. We will also assume that the photoconductor is in contact with a heat reservoir at temperature T.

Since we are dealing with a system of electrons, entropy production can be calculated from the expression

$$\frac{S}{k} = \sum_i \left[(n_i - 1) \ln (1 - n_i) - n_i \ln n_i \right] \qquad (1)$$

where n_i is the average number of electrons in the i^{th} energy state. The n_i may also be thought of as being proportional to the probability that an electron occupies state i. The rate of entropy production of the photoconductor can be written as the sum of the contributions due to the valence and conduction bands since these bands are the only ones where significant changes occur. Hence for the conduction band we have

$$\frac{S_c}{k} = \sum_{\substack{i \\ \left(\text{cond. band}\right)}} \left[(n_i - 1) \ln (1 - n_i) - n_i \ln n_i \right]$$

and entropy production becomes

$$\frac{\dot{S}_c}{k} = \sum \left[\ln \left(\frac{1 - n_i}{n_i} \right) \right] \dot{n}_i \qquad (2)$$

For the valence band, entropy production can be described in terms of holes, or the absence of electrons. We define p_j to be the average number of holes in the j^{th} state of the valence band. By definition

$$p_j = 1 - n_j \tag{3}$$

It is easily seen from (2) and (3) that, for the valence band, we have

$$\frac{\dot{S}_v}{k} = \sum_j \left[\ln\left(\frac{1-n_j}{n_j}\right)\right]\dot{n}_j = \sum_j \left[\ln\left(\frac{1-p_j}{p_j}\right)\right] \dot{p}_j \tag{4}$$

It remains to find more explicit expressions for the n_i and p_j. These quantities can be expressed in terms of the probability per unit time that an electronic transition will occur from a given initial state to a final state and vice versa. Consequently, we define a_{ji} to be the probability per unit time that a transition will occur from state j of the valence band to state i of the conduction band due to absorption of a photon. Similarly, we let b_{ji} be the probability per unit time that a transition will occur between the same two states by thermal excitation. The quantities a_{ij} and b_{ij} represent the reverse transition probabilities and correspond physically to induced emission and electron-hole recombination, respectively. The $\dot{n}_i$ and $\dot{p}_j$ may therefore be written as

$$\frac{dn_i}{dt} = \sum_j \left[(a_{ji}+b_{ji})(1-p_j)(1-n_i) - (a_{ij}+b_{ij})\, n_i p_j \right]$$

$$\frac{dp_j}{dt} = \sum_i \left[(a_{ji}+b_{ji})(1-p_j)(1-n_i) - (a_{ij}+b_{ij})\, n_i p_j \right] \tag{5}$$

The product terms $(1-p_j)(1-n_i)$ and $n_i p_j$ are required by the Pauli Exclusion Principle. For example, $a_{ji}(1-p_j)$ is the probability per unit time that an electron will undergo an optical transition from the j^{th} to the i^{th} state and $(1-n_i)$ is the probability that there is a vacancy in the i^{th} state.

Substituting equations (5) into (2) and (4), we obtain

$$\frac{\dot{S}_c}{k} = \sum_{i,j} \left[\ln\left(\frac{1-n_i}{n_i}\right) \right] \left[(a_{ji}+b_{ji})(1-p_j)(1-n_i) - (a_{ij}+b_{ij})\, n_i p_j \right] \tag{6}$$

$$\frac{\dot{S}_v}{k} = \sum_{i,j} \left[\ln\left(\frac{1-p_j}{p_j}\right) \right] \left[(a_{ji}+b_{ji})(1-p_j)(1-n_i) - (a_{ij}+b_{ij})\, n_i p_j \right] \tag{7}$$

Since the photoconductor is assumed to be in contact with a heat reservoir, entropy is produced in the reservoir also. The composite of the photoconductor plus the reservoir is assumed to be thermally isolated. Consequently, any exchange of energy required to maintain the temperature of the photoconductor constant must occur with the reservoir. Hence, we can calculate the entropy production in the reservoir as follows

$$\frac{\dot{S}_R}{k} = \frac{1}{kT}\frac{dU_R}{dt} = -\frac{1}{kT}\left[\frac{dU_c}{dt} + \frac{dU_v}{dt}\right]$$

$$= -\frac{1}{kT}\left[\sum_i \varepsilon_i \dot{n}_i' + \sum_j \varepsilon_j \dot{n}_j'\right]$$

$$= -\frac{1}{kT}\left[\sum_i \varepsilon_i \dot{n}_i' - \sum_j \varepsilon_j \dot{p}_j'\right]$$

The primes on the $\dot{n}_i$ and $\dot{p}_j$ indicate that terms proportional to a_{ji} and a_{ij} are to be omitted since the reservoir offers only thermal coupling. Using equations (5) with the a's equal to zero, we obtain

$$\frac{\dot{S}_R}{k} = -\sum_{i,j}\left(\frac{\varepsilon_i - \varepsilon_j}{kT}\right)\left[b_{ji}(1-p_j)(1-n_i) - b_{ij}\, n_i\, p_j\right] \tag{8}$$

The total entropy production is the sum of these contributions

$$\frac{\dot{S}_t}{k} = \frac{\dot{S}_c}{k} + \frac{\dot{S}_v}{k} + \frac{\dot{S}_R}{k} ,$$

or, using (6), (7) and (8),

$$\frac{\dot{S}_t}{k} = \sum_{i,j} \left\{ \left[\ln \left(\frac{1-n_i}{n_i} \right) \left(\frac{1-p_j}{p_j} \right) \right] \left[(a_{ji} + b_{ji})(1-p_j)(1-n_i) - (a_{ij} + b_{ij}) n_i p_j \right] \right.$$

$$\left. - \left(\frac{\varepsilon_i - \varepsilon_j}{kT} \right) \left[b_{ji}(1-p_j)(1-n_i) - b_{ij} n_i p_j \right] \right\} \qquad (9)$$

C. THE STEADY STATE

It was previously mentioned that the steady state requires that the rate of upward transitions from the valence to the conduction band equals the rate of downward transitions from the conduction to the valence band. An alternate method of describing the steady state would be to require that the average number of electrons or holes in a given state is independent of time. This latter condition can be expressed in the two sets of equations

$$\frac{dn_i}{dt} = 0 \quad , \qquad \text{and} \qquad \frac{dp_j}{dt} = 0 \qquad (10)$$

For later use, we consider the equation $dn_r/dt = 0$, which by (5) is equivalent to

$$\sum_j a_{jr}\left[(1-P_j)(1-n_r) - n_r P_j\right] = \sum_j b_{jr}\left[n_r P_j e^{\frac{\varepsilon_r-\varepsilon_j}{kT}} - (1-P_j)(1-n_r)\right] \quad (11)$$

Here we have used the quantum mechanical result that the radiative transition probabilities are symmetric,

$$a_{jr} = a_{rj} \quad (12)$$

and that the thermal transition probabilities are related by

$$b_{rj} = b_{jr}\, e^{\frac{\varepsilon_r-\varepsilon_j}{kT}} \quad (13)$$

Equation (13) can be made plausible by referring to the first of equations (5). If we set the a's equal to zero in this equation (which corresponds physically to zero light intensity) we obtain, changing i to r, the thermal equilibrium condition

$$\frac{dn_{ro}}{dt} = \sum_j \left[b_{jr}(1-P_{jo})(1-n_{ro}) - b_{rj}\, n_{ro} P_{jo}\right]$$

where n_{r0} and P_{j0} represent the thermal equilibrium values of n_r and P_j, respectively. But since n_{r0} is not time dependent,

$$\sum \left[b_{jr}(1-P_{j0})(1-n_{r0}) - b_{rj}\, n_{r0}\, P_{j0} \right] = 0$$

Thus a sufficient condition for thermal equilibrium can be written

$$b_{rj} = b_{jr} \frac{(1-P_{j0})(1-n_{r0})}{n_{r0}\, P_{j0}}$$

We now use the fact that, for thermal equilibrium, n_{r0} and P_{j0} are given by the Fermi-Dirac distribution. Therefore,

$$n_{r0} = \frac{1}{e^{\frac{\varepsilon_r - \zeta}{kT}} + 1} \qquad \text{and} \qquad P_{j0} = \frac{e^{\frac{\varepsilon_j - \zeta}{kT}}}{e^{\frac{\varepsilon_j - \zeta}{kT}} + 1} \tag{14}$$

where ζ is the Fermi energy. Using (14) we can write

$$b_{rj} = b_{jr} \frac{(1-P_{j0})(1-n_{r0})}{n_{r0}\, P_{j0}} = b_{jr} \frac{e^{\frac{\varepsilon_r - \zeta}{kT}}}{e^{\frac{\varepsilon_j - \zeta}{kT}}}$$

$$= b_{jr}\, e^{\frac{\varepsilon_r - \varepsilon_j}{kT}}$$

which is identical to (13).

D. CORRESPONDENCE BETWEEN MINIMUM ENTROPY PRODUCTION AND THE STEADY STATE

We now wish to find the conditions on the n_i and p_j for which $\dot{S}_t/k$ is an extremum. The n_i and p_j are not independent but are connected by the equation of constraint

$$G(n_i, p_j) = \sum_i n_i - \sum_j p_j = 0 \tag{15}$$

Equation (15) simply expresses the fact that, for an intrinsic photoconductor, the number of electrons in the conduction band equals the number of holes in the valence band. Since we have an equation of constraint, we introduce a Lagrange multiplier, μ, and write the conditions for an extremum in the form

$$\frac{\partial}{\partial n_r}\left(\frac{\dot{S}_t}{k} + \mu G\right) = 0$$

$$\frac{\partial}{\partial p_\ell}\left(\frac{\dot{S}_t}{k} + \mu G\right) = 0$$

or, using (15)

$$\begin{aligned} \mu &= -\frac{\partial}{\partial n_r}\left(\frac{\dot{S}_t}{k}\right) \\ \mu &= \frac{\partial}{\partial p_\ell}\left(\frac{\dot{S}_t}{k}\right) \end{aligned} \tag{16}$$

If we substitute from (9) and perform the indicated operations, we obtain

$$\mu = \sum_j \Bigg\{ \left[\frac{1}{n_r(1-n_r)}\right]\Big[(a_{jr}+b_{jr})(1-P_j)(1-n_r) - (a_{rj}+b_{rj})\, n_r P_j\Big]$$

$$+ \left[\ln\left(\frac{1-n_r}{n_r}\right)\left(\frac{1-P_j}{P_j}\right)\right]\Big[(a_{jr}+b_{jr})(1-P_j) + (a_{rj}+b_{rj}) P_j\Big] \tag{17}$$

$$- \left(\frac{\varepsilon_r-\varepsilon_j}{kT}\right)\Big[b_{jr}(1-P_j) + b_{rj} P_j\Big]\Bigg\}$$

$$\mu = -\sum_i \Bigg\{ \left[\frac{1}{P_\ell(1-P_\ell)}\right]\Big[(a_{\ell i}+b_{\ell i})(1-P_\ell)(1-n_i) - (a_{i\ell}+b_{i\ell})\, n_i P_\ell\Big]$$

$$+ \left[\ln\left(\frac{1-n_i}{n_i}\right)\left(\frac{1-P_\ell}{P_\ell}\right)\right]\Big[(a_{\ell i}+b_{\ell i})(1-n_i) + (a_{i\ell}+b_{i\ell})\, n_i\Big] \tag{18}$$

$$- \left(\frac{\varepsilon_i-\varepsilon_\ell}{kT}\right)\Big[b_{\ell i}(1-n_i) + b_{i\ell}\, n_i\Big]\Bigg\}$$

It will now be shown that if all $\dot{n}_i = 0$ and $\dot{P}_j = 0$, then equations of the form (17) and (18) are satisfied with

$\mu = 0$. Or to state it another way, $\dot{n}_i = 0$ and $\dot{P}_j = 0$ imply from (16) that

$$\frac{\partial}{\partial n_i}\left(\frac{\dot{S}_t}{k}\right) = 0$$

and

$$\frac{\partial}{\partial P_j}\left(\frac{\dot{S}_t}{k}\right) = 0$$

Since equations (17) and (18) are very similar in form it will suffice to deal with just one of them. We will confine our attention to proving that $\dot{n}_r = 0$ implies that (17) is satisfied with $\mu = 0$. Using the relations (12) and (13), equation (17) may be re-written

$$\begin{aligned}\mu = \sum_j a_{jr}\Bigg\{&\left[\frac{1}{n_r(1-n_r)}\right]\left[(1-P_j)(1-n_r) - n_r P_j\right] + \left[\ln\left(\frac{1-n_r}{n_r}\right)\left(\frac{1-P_j}{P_j}\right)\right]\Bigg\} \\ + \sum_j b_{jr}\Bigg\{&\left[\frac{1}{n_r(1-n_r)}\right]\left[(1-P_j)(1-n_r) - n_r P_j\, e^{\frac{\varepsilon_r-\varepsilon_j}{kT}}\right] \\ &+ \left[\ln\left(\frac{1-n_r}{n_r}\right)\left(\frac{1-P_j}{P_j}\right) - \frac{\varepsilon_r-\varepsilon_j}{kT}\right]\left[(1-P_j) + P_j\, e^{\frac{\varepsilon_r-\varepsilon_j}{kT}}\right]\Bigg\}\end{aligned} \qquad (19)$$

The condition $\dot{n}_r = 0$ will be re-written here for ease of reference

$$\sum a_{jr}\left[(1-p_j)(1-n_r) - n_r p_j\right] = \sum b_{jr}\left[n_r p_j e^{\frac{\varepsilon_r-\varepsilon_j}{kT}} - (1-p_j)(1-n_r)\right] \quad (11)$$

If we multiply (11) by $1/n_r(1-n_r)$, it can easily be seen that the first terms in each summation of (19) cancel. We now show that second terms in each summation can be made to cancel with the use of (11). To accomplish this, it is necessary to assume that the steady state does not differ greatly from the state of thermal equilibrium. This can be expressed in the form

$$n_i = n_{io}(1+\delta_n) \quad \text{and} \quad p_j = p_{jo}(1+\delta_p) \quad (20)$$

where n_{io} and p_{jo} are again the thermal equilibrium values of n_i and p_j, respectively, and δ_n and δ_p are assumed to be small compared to one.

Before we proceed further it is worthwhile reviewing some consequences of the thermal equilibrium state. If we set the a's equal to zero in the first of equations (5) we obtain, changing i to r, and using (13), that

$$\frac{dn_{ro}}{dt} = \sum b_{jr}\left[(1-p_{jo})(1-n_{ro}) - n_{ro} p_{jo} e^{\frac{\varepsilon_r-\varepsilon_j}{kT}}\right] = 0 \quad (21)$$

Other properties which will be useful are the explicit expression for n_{r0} and P_{j0} given by (14).

Using (20), the left hand side of (11) becomes, to the first order in δ_n and δ_p,

$$\sum_j a_{jr}\left[(1-P_j)(1-n_r) - n_r P_j\right] = \sum_j a_{jr}\left[(1-P_{j0}-n_{r0}) - n_{r0}\delta_n - P_{j0}\delta_p\right] \quad (22)$$

Similarly the right hand side of (11) becomes

$$\begin{aligned}\sum_j b_{jr}\left[n_r P_j\, e^{\frac{\varepsilon_r-\varepsilon_j}{RT}} - (1-P_j)(1-n_r)\right] = \sum_j b_{jr}\Big[&\Big\{n_{r0}P_{j0}\, e^{\frac{\varepsilon_r-\varepsilon_j}{RT}} - (1-P_{j0})(1-n_{r0})\Big\}\\ &+\Big\{n_{r0}P_{j0}\, e^{\frac{\varepsilon_r-\varepsilon_j}{RT}} + (1-P_{j0})\,n_{r0}\Big\}\delta_n\\ &+\Big\{n_{r0}P_{j0}\, e^{\frac{\varepsilon_r-\varepsilon_j}{RT}} + P_{j0}(1-n_{r0})\Big\}\delta_p\Big]\end{aligned} \quad (23)$$

$$= \sum_j b_{jr}\left[(1-P_{j0})\delta_n + (1-n_{r0})\delta_p\right]$$

with the use of (14) and (21). Multiplying (22) and (23) by $1/n_{r0}(1-n_{r0})$ we can write the steady state condition, to the first order in δ_n and δ_p as,

$$\sum_j a_{jr}\left[\frac{(1-P_{jo}-n_{ro})}{n_{ro}(1-n_{ro})} - \frac{\delta_n}{1-n_{ro}} - \frac{P_{jo}\,\delta_p}{n_{ro}(1-n_{ro})}\right]$$

$$= \sum_j b_{jr}\left[\frac{(1-P_{jo})}{n_{ro}(1-n_{ro})}\,\delta_n + \frac{\delta_p}{n_{ro}}\right] \qquad (24)$$

We now look at the second term of (19) whose coefficient is a_{jr}. It follows from (20) and (14) that

$$\ln\left(\frac{1-n_r}{n_r}\right) \simeq \frac{\varepsilon_r-\zeta}{kT} - \frac{\delta_n}{1-n_{ro}}$$

and

$$\ln\left(\frac{1-P_j}{P_j}\right) \simeq \frac{\zeta-\varepsilon_j}{kT} - \frac{\delta_p}{1-P_{jo}}$$

therefore,

$$\sum_j a_{jr}\left[\ln\left(\frac{1-n_r}{n_r}\right)\left(\frac{1-P_j}{P_j}\right)\right] \simeq \sum_j a_{jr}\left[\frac{\varepsilon_r-\varepsilon_j}{kT} - \frac{\delta_n}{1-n_{ro}} - \frac{\delta_p}{1-P_{jo}}\right] \qquad (25)$$

The second term of (19) whose coefficient is b_{jr} becomes

$$\sum b_{jr}\left[\ln\left(\frac{1-n_r}{n_r}\right)\left(\frac{1-P_j}{P_j}\right) - \frac{\varepsilon_r-\varepsilon_j}{kT}\right]\left[(1-P_j) + P_j\, e^{\frac{\varepsilon_r-\varepsilon_j}{kT}}\right]$$

$$\simeq -\sum b_{jr}\left[\frac{(1-P_{jo})\,\delta_n}{n_{ro}(1-n_{ro})} + \frac{\delta_p}{n_{ro}}\right] \qquad (26)$$

Comparing (24), (25) and (26), we see that the second terms in each summation of (19) cancel with the use of (11) if

$$\frac{1 - P_{j0} - n_{r0}}{n_{r0}(1-n_{r0})} \simeq \frac{\varepsilon_r - \varepsilon_j}{kT}$$

and

$$\frac{P_{j0}}{n_{r0}(1-n_{r0})} \simeq \frac{1}{1 - P_{j0}}$$

The above relations can be shown to hold using (14) and by assuming that terms of the form $\frac{\Delta\varepsilon}{kT}$ are small compared to one. It follows that

$$\frac{1 - P_{j0} - n_{r0}}{n_{r0}(1-n_{r0})} = \frac{\left(e^{\frac{\varepsilon_r - \varepsilon_j}{kT}} - 1\right)\left(1 + e^{-\frac{(\varepsilon_r - \zeta)}{kT}}\right)}{\left(1 + e^{-\frac{(\varepsilon_j - \zeta)}{kT}}\right)} \simeq \frac{\frac{\varepsilon_r - \varepsilon_j}{kT}\left(2 - \frac{\varepsilon_r - \zeta}{kT}\right)}{\left(2 - \frac{\varepsilon_j - \zeta}{kT}\right)}$$

$$\simeq \frac{\varepsilon_r - \varepsilon_j}{kT}$$

and

$$\frac{P_{j0}}{n_{r0}(1-n_{r0})} = \frac{\left(e^{\frac{\varepsilon_r - \zeta}{kT}} + 1\right)\left(1 + e^{-\frac{(\varepsilon_r - \zeta)}{kT}}\right)}{\left(1 + e^{-\frac{(\varepsilon_j - \zeta)}{kT}}\right)} \simeq \frac{2\left(1 + \frac{\varepsilon_r - \zeta}{kT}\right)\left(1 - \frac{\varepsilon_r - \zeta}{kT}\right)}{\left(1 - \frac{\varepsilon_j - \zeta}{kT}\right)}$$

$$\simeq \left(1 + \frac{\varepsilon_j - \zeta}{kT} + 1\right) \simeq \left(e^{\frac{\varepsilon_j - \zeta}{kT}} + 1\right)$$

$$= \frac{1}{1 - P_{j0}}$$

Thus we have shown that $\dot{n}_r = 0$ implies that (19) is satisfied with $\mu = 0$. It can be shown that similar results follow for all p_j as well.

Proceeding in the other direction, we can prove to the same approximation that for all n_i and p_j which satisfy equations of the form (17) and (18), it follows that $\mu = 0$, $\dot{n}_i = 0$ and $\dot{p}_j = 0$. We have shown above that, to the first order in δ_n and δ_p,

$$\sum_j a_{jr}\left[\ln\left(\frac{1-n_r}{n_r}\right)\left(\frac{1-p_j}{p_j}\right)\right] \simeq \sum_j a_{jr}\left[\frac{1}{n_{r0}(1-n_{r0})}\right]\left[(1-p_j)(1-n_r) - n_r p_j\right]$$

and

$$\sum_j b_{jr}\left[\ln\left(\frac{1-n_r}{n_r}\right)\left(\frac{1-p_j}{p_j}\right) - \frac{\varepsilon_r - \varepsilon_j}{kT}\right]\left[(1-p_j) + p_j\, e^{\frac{\varepsilon_r-\varepsilon_j}{kT}}\right]$$

$$\simeq \sum b_{jr}\left[\frac{1}{n_{r0}(1-n_{r0})}\right]\left[(1-p_j)(1-n_r) - n_r p_j\, e^{\frac{\varepsilon_r-\varepsilon_j}{kT}}\right]$$

If we use the fact that $n_{r0} \simeq n_r$ for small deviations from thermal equilibrium, (19) may be written

$$\mu \simeq \left[\frac{2}{n_r(1-n_r)}\right] \sum_j \Big\{ a_{jr}\left[(1-P_j)(1-n_r) - n_r P_j\right] + b_{jr}\left[(1-P_j)(1-n_r) - n_r P_j\, e^{\frac{\varepsilon_r-\varepsilon_j}{kT}}\right]\Big\} \tag{27}$$

$$= \left[\frac{2}{n_r(1-n_r)}\right] \sum_j \left[(a_{jr}+b_{jr})(1-P_j)(1-n_r) - (a_{rj}+b_{rj})\, n_r P_j\right]$$

$$= \left[\frac{2}{n_r(1-n_r)}\right] \frac{dn_r}{dt}$$

where we have used (12), (13) and the first of equations (5) with i replaced by r.

Similarly, it can be shown that

$$\mu \simeq -\left[\frac{2}{P_\ell(1-P_\ell)}\right] \frac{dP_\ell}{dt} \tag{28}$$

Multiplying (27) by $n_r(1-n_r)$, summing over r and performing a similar operation on (28) we have, changing r to i and ℓ to j,

$$\mu\left\{\sum_i n_i(1-n_i) + \sum_j P_j(1-P_j)\right\} \simeq 2\left\{\sum_i \frac{dn_i}{dt} - \sum_j \frac{dP_j}{dt}\right\}$$

But by (5) we have

$$\sum_i \frac{dn_i}{dt} = \sum_j \frac{dP_j}{dt}$$

Therefore,

$$\mu \left\{ \sum_i n_i(1-n_i) + \sum_j P_j(1-P_j) \right\} \simeq 0$$

and $\mu = 0$, since the quantity in brackets is non-zero. It follows from (27) and (28), changing r to i and λ to j , that $\dot{n}_i = 0$ and $\dot{P}_j = 0$.

Summarizing, we have proved, for small deviations from equilibrium and for quantities $\frac{\Delta\mathcal{E}}{kT}$ small compared to one, that an extremum of entropy production is a necessary and sufficient condition for the existance of the steady state.

E. PROOF OF MINIMUM

We would now like to prove that the extremum of entropy production is actually a minimum. To do this we consider small changes δn_i and δP_j from the steady state values n_i^s and P_j^s . We wish to prove that

$$\delta\left(\frac{\dot{S}_t}{k}\right) = \left\{ \left.\frac{\dot{S}_t}{k}\right|_{n_i^s+\delta n_i,\, P_j^s+\delta P_j} - \left.\frac{\dot{S}_t}{k}\right|_{n_i^s,\, P_j^s} \right\} \geq 0 \qquad (29)$$

Since we are calculating changes from an extremum value, we need only consider second order terms in δn_i and δp_j . Substituting (9) into (29) we obtain

$$\delta\left(\frac{\dot{S}_t}{k}\right) = \sum_{i,j} a_{ji}\Big[\left(\frac{1}{n_i^s} + \frac{1}{1-n_i^s}\right)(\delta n_i)^2 + \left(\frac{1}{n_i^s} + \frac{1}{1-n_i^s} + \frac{1}{p_j^s} + \frac{1}{1-p_j^s}\right)\delta n_i\, \delta p_j$$

$$+ \left(\frac{1}{p_j^s} + \frac{1}{1-p_j^s}\right)(\delta p_j)^2\Big] + \sum_{i,j} b_{ji}\Big[\left(\frac{1-p_j^s}{n_i^s} + \frac{1-p_j^s}{1-n_i^s} + \frac{\sigma_{ij}\, p_j^s}{n_i^s}\right.$$

$$\left. + \frac{\sigma_{ij}\, p_j^s}{1-n_i^s}\right)(\delta n_i)^2 + \left(\frac{1}{n_i^s} + \frac{1}{p_j^s} - \ln \frac{n_i^s\, p_j^s\, \sigma_{ij}}{(1-n_i^s)(1-p_j^s)}\right. \tag{30}$$

$$\left. + \frac{\sigma_{ij}}{1-n_i^s} + \frac{\sigma_{ij}}{1-p_j^s} + \sigma_{ij} \ln \frac{n_i^s\, p_j^s\, \sigma_{ij}}{(1-n_i^s)(1-p_j^s)} \right)\delta n_i\, \delta p_j$$

$$+ \left(\frac{1-n_i^s}{p_j^s} + \frac{1-n_i^s}{1-p_j^s} + \frac{\sigma_{ij}\, n_i^s}{p_j^s} + \frac{\sigma_{ij}\, n_i^s}{1-p_j^s}\right)(\delta p_j)^2 \Big]$$

where $\sigma_{ij} = e^{\frac{\varepsilon_i - \varepsilon_j}{kT}} = b_{ij}/b_{ji}$. If we can write (30) in the form of a sum of squares, then (29) will be satisfied and the extremum will be a minimum. Towards this end we again resort to the restrictions that the steady state is not far from equilibrium and that quantities of the form $\frac{\Delta\varepsilon}{kT}$ are small compared to one. These restrictions can be expressed in the form

$$\frac{n_i^s \, P_j^s \, \sigma_{ij}}{(1-n_i^s)(1-P_j^s)} \simeq 1 \tag{31}$$

and

$$\frac{n_i^s \, P_j^s}{(1-n_i^s)(1-P_j^s)} \simeq 1 \tag{32}$$

Applying (31) and (32), equation (30) may be re-written

$$\begin{aligned}
\delta\left(\frac{\dot{S}_t}{k}\right) = \sum_{ij} a_{ji}\left[\frac{1}{n_i^s P_j^s}\right]\Bigg[&\left(P_j^s + \frac{n_i^s P_j^s (1-P_j^s)}{(1-n_i^s)(1-P_j^s)}\right)(\delta n_i)^2 + \left(P_j^s + \frac{n_i^s P_j^s (1-P_j^s)}{(1-n_i^s)(1-P_j^s)}\right. \\
&\left. + n_i^s + \frac{n_i^s P_j^s (1-n_i^s)}{(1-P_j^s)(1-n_i^s)}\right)\delta n_i \delta P_j + \left(n_i^s + \frac{n_i^s P_j^s (1-n_i^s)}{(1-P_j^s)(1-n_i^s)}\right)(\delta P_j)^2 \Bigg] \\
+ \sum_{ij} b_{ji}\Bigg[&\left(\frac{1-P_j^s}{n_i^s} + \frac{1-P_j^s}{1-n_i^s} + \frac{(1-P_j^s)(1-n_i^s)}{(n_i^s)^2} + \frac{1-P_j^s}{n_i^s}\right)(\delta n_i)^2 \\
&+ \left(\frac{1}{n_i^s} + \frac{1}{P_j^s} + \frac{1-P_j^s}{n_i^s P_j^s} + \frac{1-n_i^s}{n_i^s P_j^s}\right)\delta n_i \delta P_j + \left(\frac{1-n_i^s}{P_j^s} + \frac{1-n_i^s}{1-P_j^s}\right. \\
&\left. + \frac{(1-n_i^s)(1-P_j^s)}{(P_j^s)^2} + \frac{1-n_i^s}{P_j^s}\right)(\delta P_j)^2 \Bigg]
\end{aligned}$$

It follows after some manipulation, that

$$\delta\left(\frac{\dot{S}_t}{k}\right) = \sum_{i,j}\left\{ a_{ji}\left[\frac{1}{n_i^s p_j^s}\right]\left[\delta n_i + \delta p_j\right]^2 \right.$$

$$\left. + \; b_{ji}\left[\frac{(1-p_j^s)^{1/2}}{n_i^s(1-n_i^s)^{1/2}}\,\delta n_i + \frac{(1-n_i^s)^{1/2}}{p_j^s(1-p_j^s)^{1/2}}\,\delta p_j\right]^2\right\} \geq 0 \quad (33)$$

Thus we have proved that entropy production in a steady state obeying the restrictions (31) and (32) has its minimum value.

F. CALCULATION OF MINIMUM ENTROPY PRODUCTION

In the steady state, we can give an interesting physical interpretation to the entropy production process. Since $\dot{n}_i = 0$ and $\dot{p}_j = 0$ for the steady state, it follows from (2) and (4) that $\frac{\dot{S}_c}{k} = 0$ and $\frac{\dot{S}_v}{k} = 0$; consequently,

$$\left(\frac{\dot{S}_t}{k}\right)_{min} = \frac{\dot{S}_R}{k} = -\sum_{i,j}\left(\frac{\varepsilon_i - \varepsilon_j}{kT}\right)\left[b_{ji}(1-n_i^s)(1-p_j^s) - b_{ij}\, n_i^s p_j^s\right] \quad (34)$$

But from (5), the steady state also implies that

$$\sum_j\left[a_{ji}(1-p_j^s)(1-n_i^s) - a_{ij}\, n_i^s p_j^s\right] = -\sum_j\left[b_{ji}(1-p_j^s)(1-n_i^s) - b_{ij}\, n_i^s p_j^s\right] \quad (35)$$

and

$$\sum_i \left[a_{ji}(1-p_j^s)(1-n_i^s) - a_{ij}\, n_i^s\, p_j^s\right] = -\sum_i \left[b_{ji}(1-p_j^s)(1-n_i^s) - b_{ij}\, n_i^s\, p_j^s\right] \quad (36)$$

If we multiply (36) by $\frac{\varepsilon_j}{kT}$, sum over j and subtract the result from a similar modification of (35) involving $\frac{\varepsilon_i}{kT}$, we find that (34) may be re-written in the form

$$(\dot{S}_t)_{min} = \sum_{i,j} \left(\frac{\varepsilon_i - \varepsilon_j}{T}\right)\left[a_{ji}(1-p_j^s)(1-n_i^s) - a_{ij}\, n_i^s\, p_j^s\right] = \dot{S}_R \quad (37)$$

The quantity $\frac{\varepsilon_i - \varepsilon_j}{T}$ may be interpreted as the increase in entropy, at temperature T, per transition between states i and j. The expression

$$\left[a_{ji}(1-p_j^s)(1-n_i^s) - a_{ij}\, n_i^s\, p_j^s\right]$$

represents the net rate of electronic transitions induced by the absorbed radiation. We may conclude that in the steady state, the photoconductor takes only an indirect part in the production of entropy. Entropy is, in fact, produced by the process of transforming coherent electromagnetic radiation absorbed by the system into incoherent thermal energy of the heat reservoir at temperature T.

III. CONCLUSION AND DISCUSSION

We may conclude that the principle of minimum entropy production can be applied to an illuminated photoconductor provided certain restrictions are met. These restrictions require that only small departures from high temperature equilibrium be allowed. It can be seen from the introduction that these results are very consistent with those obtained for similar systems.

It is interesting to consider how these restrictions can be realized. Since we can consider only small departures from thermal equilibrium, the rate of entropy production will be small. Or, more precisely, the rate of entropy production is of second order in the small quantities δ_n and δ_p. This follows from the fact that the Lagrange multiplier, μ, may be physically interpreted as being proportional to the negative of the entropy production, and μ was shown to be zero to the first order in δ_n and δ_p.

It is worthwhile to consider the expression for entropy production written in a different form. Applying (12) and (13) to (9) and using $\sigma_{ij} = e^{\frac{\varepsilon_i - \varepsilon_j}{kT}}$, we obtain

$$\frac{\dot{S}_t}{k} = -\sum \left\{ a_{ji} \left[\ln \frac{n_i P_j}{(1-n_i)(1-P_j)} \right] \left[(1-n_i)(1-P_j) - n_i P_j \right] \right. \tag{38}$$

$$\left. + \; b_{ji} \left[\ln \frac{n_i P_j \sigma_{ij}}{(1-n_i)(1-P_j)} \right] \left[(1-n_i)(1-P_j) - n_i P_j \sigma_{ij} \right] \right\}$$

From (38) we can see that conditions for small entropy production could be written as

$$\frac{n_i P_j}{(1-n_i)(1-P_j)} \simeq 1$$

and

$$\frac{n_i P_j \sigma_{ij}}{(1-n_i)(1-P_j)} \simeq 1$$

These are recognized as equations (31) and (32), the conditions for a minimum of $\frac{\dot{S}_t}{k}$. Virtually the only way (31) and (32) can be satisfied is for $n_i \simeq \frac{1}{2}$, $P_j \simeq \frac{1}{2}$ and $\sigma_{ij} \simeq 1$. The restrictions on the values of the n_i and P_j imply that the available electrons are approximately equally distributed among the levels of the valence and conduction bands. The last restriction, of course, implies high temperature. Thus, the physical situation in which the principle is valid is one in which the Fermi-Dirac distribution function

$$n = \frac{1}{e^{\frac{E-\zeta}{kT}} + 1}$$

is approximately equal to $1/2$ for all energies of the valence and conduction bands. This is highly unlikely. For example, if we take the average width of the intrinsic gap to be 1 e.v., a temperature required for $n \simeq \frac{1}{2}$ is around 300,000°K. Hence for most photoconductors the principle does not apply in the strict form we have used it.

However, it was mentioned in the introduction that the domain of validity of the principle was extended by Klein using a system similar to our own. By analogy, it seems conceivable that the state of minimum entropy production might provide a rough criterion for the existence of the steady state in our system when lower temperatures and higher light intensities are considered.

As can be seen from the present example, the way is open for more intensive research in the theory of non-equilibrium thermodynamics as related to the steady state. A possible direction of further research might be in the attempt to develop a new thermodynamic function, perhaps related to the entropy, whose extremum would insure the existence of the steady state under more general conditions.

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