Some remarks about extremum principles involving the rate of entropy production
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The minimum rate of entropy production (MREP) and the least dissipation energy (LDE) principles are re-examined concerning continuous systems in stationary nonequilibrium states. By means of simple considerations on coefficients of phenomenological laws and by taking into account balance equations, an Onsager-like potential density for the stationary state is obtained. In the case of a single state variable it is found that the potential density describes a saddle-shaped surface around the stationary point in the domain of the force (state variable) and the flux. The saddle point may be considered a maximum along a LDE path (fixed force) and a minimum along a MREP path (fixed phenomenological coefficient). The latter allow for the Glansdorff-Prigogine local potential.

I. INTRODUCTION

Thermodynamics establishes that, under certain conditions, systems in stationary nonequilibrium states (SNES) have a minimum rate of entropy production (MREP) compatible with system constraints. The MREP principle (or criterion) requires that linear phenomenological relations between generalized fluxes and forces hold. This condition is satisfied when slight deviations from equilibrium take place uniformly in the whole system volume. Beyond this range some additional assumptions are required in order to apply a suitably modified principle. The matter is not so well defined in continuous systems when deviations from equilibrium are not uniformly distributed. Remaining near equilibrium, several problems can be assessed successfully provided the flux laws are suitably linearized. But in most case the linearization procedure presents some difficulties. Actually, according to statistical mechanics, linear laws hold when local thermodynamic equilibrium (LTE) conditions are satisfied. But, in this case linearity is meant in the sense of deviations from the local equilibrium. Thus, in general, phenomenological laws are not strictly linear. The matter is further complicated by a certain freedom in the choice of forces and conjugated fluxes. Thus, for example, in the case of heat conduction the MREP principle apparently works or fails according to the used conventions.

Glansdorff and Prigogine formulated a general evolution criterion for irreversible processes which is independent of the actual form of the phenomenological coefficients. Based on this criterion, they devised a procedure to define a
potential for the SNES which coincides (unless a numeric factor) with the entropy production functional in the strictly linear range. Beyond this range, the local potential allows for a (generalized) MREP principle provided certain restrictions to the entropy production functional are assumed.\textsuperscript{9}

To give a thermodynamic framework to phenomenological laws, Onsager and Machlup proved a least dissipation energy (LDE) principle for near-equilibrium processes.\textsuperscript{10,11} In the assumption of Gaussian behaviour of extensive state variables, the nonequilibrium processes are Markovian. A system displaced from equilibrium by a fluctuation decays back to equilibrium by following, on the average, the same empirical laws for the decay of the system displaced by an external constraint.\textsuperscript{11} According to this theory, the probability associated with a given decay path is to be searched for by means of an extremum principle of a suitable functional. The most probable path (with fixed forces) is the one established by phenomenological laws, i.e., by the LDE principle.

The theory developed by Onsager and Machlup has given insights for the formulation of several Hamilton-based variational principles in the field of hydrodynamics. We do not give accounts of the many works devoted to this topic (see for example ref. 9). In this paper we are interested in the possible connection between the Onsager (LDE) and the Glansdorff-Prigogine (extended MREP) principles for continuous systems. Specifically, we ask for a variational criterion including both the two principles to give a unified and concise representation of our knowledge about the SNES. To achieve its formulation we will pursue a simple task: the criterion must account for the (entropy and mass) balance equations regardless of the actual form of phenomenological coefficients.

To deal with this matter the paper is planned as follows. In Section 2 we will examine some features concerning the rate of entropy production as established by thermodynamics. In section 3 we will derive the variational criterion for the SNES. The extremum properties of a functional dependent on forces (state variables) and fluxes will be investigated. In the simplest case of a single (state) variable the density of the functional describes a saddle-shaped surface in the domain of force and flux. The extended MREP and LDE principles will be apparent by restrictions of the potential to special deviation paths. In the field of thermodynamics, restriction of the functional to the MREP path allows for the Glansdorff-Prigogine local potential.

### II Entropy production

The definition of entropy production follows from the thermodynamic construction of the local entropy balance equation\textsuperscript{2,5}

\[
\sigma_S = \frac{\partial \rho s}{\partial t} + \nabla \cdot J_{STOT}
\]  

(1)

where \(s\) stands for the specific entropy, \(\rho\) for mass density, \(J_{STOT}\) for total entropy flux. The time derivative in the local frame is connected to the barycentre derivative by the relation.
\[
\frac{\partial \rho_s}{\partial t} = \rho \frac{ds}{dt} - \nabla \cdot \rho_s v
\]  
(2)

where \(v\) stands for the centre of mass velocity. By inserting eq. (2) in eq. (1) we define entropy flux

\[
J_s = J_{STOT} - \rho s v .
\]  
(3)

The starting point of the construction procedure is the Gibbs equation (assumed to hold in LTE conditions) in which energy and mass balance equations have been inserted. These latter read

\[
\frac{\partial \rho_i}{\partial t} + \nabla \cdot (j_i + \rho_i v) = \sum_j \nu_{ij} \xi_j
\]  
(4)

where \(\rho_i\) stands for the density of the \(i\)-th system component, \(j_i\) for diffusion flow, \(\nu_{ij}\xi_j\) is the rate of mass production of the \(i\)-th component in the \(j\)-th chemical reaction with reaction rate \(\xi_j\) and stoichiometric coefficient \(\nu_{ij}\). The entropy flux can be written in general as

\[
J_s = \left( J_Q - \sum_i \phi_i j_i \right) / T
\]  
(5)

where \(J_Q\) stands for the heat flux and \(\phi_i\) for electrochemical potential of the \(i\)-th component\(^{13}\). We are interested in those states where the barycentre derivatives vanish. Moreover, we consider the case of mechanical equilibrium where derivatives of \(v\) vanish everywhere in the system\(^6\). In these conditions, the density of entropy production is\(^{12}\)

\[
\sigma_s = - \sum_i j_i \cdot \nabla \varphi_i + J_Q \cdot \nabla \frac{1}{T} - \sum_i \xi_i \Gamma_i / T
\]  
(6)

where \(\Gamma_i = \sum_j \nu_{ij} \varphi_j\) stands for the affinity of the set of reactions involved in the production of the \(i\)-th component. When the centre of mass motion is determined by flows \(j_i\), we have the condition \(\sum j_i = 0\). In this case the entropy production should be re-written in order to present only independent flows\(^{12}\).

Equation (6) can be used, for example, to investigate thermoelectric processes in semiconductors. In this case, chemical reactions are replaced by electron and hole excitation processes.

Formally, \(\sigma_s\) can be written as a product of generalized fluxes \(\mathbf{J}\) and forces \(\mathbf{X}\)

\[
\sigma_s = \sum_k \mathbf{J}_k \cdot \mathbf{X}_k .
\]  
(7)

Fluxes are assumed to be functions of the forces (phenomenological laws):

\[
\mathbf{J}_k = \sum_l L_{kl} \mathbf{X}_l .
\]  
(8)
By inversion of eqs. (8) we have

\[ X_k = \sum_l M_{kl} J_l \]  (9)

where \( M = L^{-1} \). According to Curie’s theorem, phenomenological coefficients are scalars in isotropic systems so that only fluxes and forces of the same vectorial (or tensorial) character are related. The requirement of microscopic time reversibility of processes near equilibrium allow for symmetry of coefficients associated with cross effects (this does not hold in cases of magnetic and Coriolis forces) :

\[ L_{ik} = L_{ki} \]  (10)

Owing to the detailed balance not all the possible definitions of forces and conjugated fluxes are allowed (two important conventions consider "energy transport per molecule" or the "entropy transport per molecule"). In this connection, we point out that a variational principle correctly formulated must not depend on the convention adopted.

The entropy production of the whole system is (integrated over the system volume)

\[ P = \int \sum_k J_k \cdot X_k d^3x \]  (11)

By considering the steady state as a reference state \((J_0 = \delta J_k, X_0 = X_0 + \delta X_k)\), the first variation of \(P\) at the point \((X_0, J_0)\) due to small deviations of forces is (constant Onsager’s coefficients)

\[ \delta^{(1)} P = \int \sum_k X_0 \cdot \delta J_k d^3x + \int \sum_k J_0 \cdot \delta X_k d^3x \]  (12)

The second variation is

\[ \delta^{(2)} P = \int \sum_k \delta J_k \cdot \delta X_k d^3x \]  (13)

Thus \( \Delta P = \delta^{(1)} P + \delta^{(2)} P \); no higher terms appear with the settings dealt with (see next section). Equation (13) defines the excess of entropy production. If we consider equilibrium as the reference state \((X_0 = 0; J_0 = 0)\), we remain with \( \Delta P = P = \int \sum_k J_k \cdot X_k d^3x \) so that \( \Delta P \geq 0 \) and \( d\Delta P/dt \leq 0 \) (= 0 at the stationary state) which explains the MREP principle.

Let us consider a simple example to clarify some points presented in the introduction. The diffusion under uniform temperature (for simplicity’s sake we do not consider the Dufour and Soret effects) in absence of sources shows \( \sigma_S = -j \nabla \rho / \rho^\alpha \) (we leave unspecified exponent \( \alpha \)). A possible choice of the force and the conjugated flux is
\begin{equation}
X = - \frac{1}{\rho^n} \nabla \rho \quad J = \frac{L}{\rho^n} \nabla \rho
\end{equation}

The variational calculus is applied to the functional $P[\rho] = \int X(\rho)J(\rho)d^3x$ by keeping fixed the variable at the system boundary:

$$
\delta P(\rho) = \delta \int \frac{L}{\rho^{2n}} (\nabla \rho)^2 d^3x = \int \left[ \left( \frac{\partial}{\partial \rho} - \nabla \frac{\partial}{\partial \nabla \rho} \right) \frac{L}{\rho^{2n}} (\nabla \rho)^2 \right] \delta \rho d^3x = 0
$$

that is,

$$
\int \left\{ \left[ \frac{d}{d\rho} \left( \frac{L}{\rho^{2n}} \right) + 2n \frac{L}{\rho^{2n+1}} \right] (\nabla \rho)^2 - \frac{2}{\rho^n} \nabla \left( \frac{L}{\rho^n} \nabla \rho \right) \right\} \delta \rho \ d^3x = 0 \quad \text{(15)}
$$

Equation (15) is apparently written in a complicated form, but it clearly shows that to account for the right transport equation ($L\nabla \rho/\rho^n = \text{const}$) we require $dL/d\rho = 0$. The latter condition appears excessively restrictive since in some important cases (Fourier’s law, Fick’s law) $L \propto \rho^n$. A better choice may be:

$$
X = -\nabla \rho \quad J = \frac{j}{\rho^n} = -L' \nabla \rho \quad \text{(16)}
$$

where $L'$ is a suitable constant coefficient. However, this choice does not match the transport features if the actual diffusion process requires $L'$ to be dependent on variable $\rho$.

III. STATIONARY STATES BEYOND SMALL DEVIATIONS FROM EQUILIBRIUM.

Henceforth, we will take SNES as the reference state from which deviations of variables are considered. To represent deviations of fluxes one can use expansions with respect to forces. But in this way information about phenomenological coefficients are lost. In a more conservative representation deviations of coefficients are explicitly considered. Thus, by taking into account of expansions

$$
X_j(\rho) = X_{0j} + \delta^{(1)}X_j(\rho) + \delta^{(2)}X_j(\rho) + ...
\quad \text{(17)}
$$

and

$$
L_{ij}(\rho) = L_{0ij} + \delta L_{ij}(\rho) + \delta^{(2)}L_{ij}(\rho) + ...
\quad \text{(18)}
$$

we obtain from eq. (5):

$$
\delta^{(1)}J_i(\rho) = \sum L_{0ij} \delta^{(1)}X_j(\rho) + \sum X_{0ij}^{(1)} \delta L_{ij}(\rho) \quad \text{(19)}
$$

For convenience, in eqs (17) and (18) we have indicated the functional dependence on state variables (for brevity symbolized by $\rho$) of all terms except the
quantities \( X_{ij} \) and \( L_{0ij} \) which pertain to the reference state. By taking into account that

\[
\int \sum_k J_{0k} \cdot \delta^{(1)} X_k (\rho) \, d^3x = 0
\]

(20)
eqs (19) and (12) provide a way to represent SNES whatever conventions are used. Based on eq. (20) we may write

\[
\delta^{(1)} P[\rho] = \int \sum_k X_{0k} \delta^{(1)} J_k (\rho) \, d^3x
\]

(21)
which represents the variation of entropy production at the point \( \rho_0 \). In general, variation \( \delta^{(1)} P[\rho] \) is different from 0 at the stationary state. To search for a potential showing vanishing variation at this state it is convenient to use the transformation

\[
\int \sum_k X_{0k} \cdot \delta^{(1)} J_k (\rho) \, d^3x = \delta^{(1)} \frac{1}{2} \sum_{kl} M_{0kl} J_k (\rho) \cdot J_l (\rho) \, d^3x
\]

(22)
where \( M_0 = L_0^{-1} \). Thus, by taking into account of eqs (12), (20) and (22) we obtain

\[
\delta^{(1)} \left\{ P[\rho] - \frac{1}{2} \sum_{kl} M_{0kl} J_k (\rho) \cdot J_l (\rho) \, d^3x \right\} = 0
\]

(23)
from which we define the functional

\[
\Psi[\rho] = \int \sum_k J_k (\rho) \cdot X_k (\rho) \, d^3x - \frac{1}{2} \sum_{kl} M_{0kl} J_k (\rho) \cdot J_l (\rho) \, d^3x
\]

(24)
and the associated density

\[
\psi(\rho) = \sum_k J_k (\rho) \cdot X_k (\rho) - \frac{1}{2} \sum_{kl} M_{0kl} J_k (\rho) \cdot J_l (\rho)
\]

(25)
According to definition (24), we can rewrite eq. (22) as \( \delta^{(1)} \Psi[\rho] = 0 \) (at SNES). It is worth to point out that the second deviation \( \delta^{(2)} \psi (\rho) \) does not present terms such as \( \sum_k X_{0k} \cdot \delta^{(2)} J_k (\rho) \). This can be verified from eq. (25), by taking into account eq. (9) written for the stationary state point, that is,

\[
\delta^{(2)} \psi (\rho) = \sum_k \delta^{(1)} J_k (\rho) \cdot \delta^{(1)} X_k (\rho) - \frac{1}{2} \sum_{kl} M_{0kl} \delta^{(1)} J_k (\rho) \cdot \delta^{(1)} J_l (\rho)
\]

(26)
where the sums \( \sum_k X_{0k} \cdot \delta^{(2)} J_k (\rho) \) multiplied by opposite signs are canceled out. In eq. (20) we have omitted the sum \( \sum_k J_{0k} \cdot \delta^{(2)} X_k (\rho) \) since its integral vanishes as in eq. (20). On these grounds, we can define the functional \( \Psi[\rho, J] \) which has the form (24) but in which the function \( J_k (\rho) \) is replaced by the
variable $J_k$. Analogously, we follow the same rule to define the density $\psi(\rho, J)$ from eq. (25). Thus, the variational equation

$$\delta \Psi = 0$$

$$\text{(27)}$$

($\Psi$ be stationary at the SNES) can be solved with respect to the state variables (see eqs 17 to 19) or also with respect to the fluxes. In this case, the associated Euler-Lagrange equations are

$$\left(\frac{\partial \psi}{\partial J_l}\right)_{SNES} = 0 .$$

$$\text{(28)}$$

which go back to the phenomenological laws at the SNES. The set of eqs (28) devises a local extremum problem of the function $\psi$ with respect to the fluxes by keeping the forces (state variables) fixed to their reference state values. To assure the existence of such an extremum it is sufficient for a general quadratic form $f(\eta) = \sum_{kl} M_{0kl} \eta_k \eta_l$ to have a definite sign. In particular, $\psi(\rho, J)$ has a maximum (fixed forces) if the quadratic form is positive definite.

In general, the functional $\Psi$ does not show an extremum at SNES. However, as seen above, we can search for some special variation paths, crossing the SNES point in the domain of forces (state variables) and fluxes where this can be established in a restricted sense. To this end, we extend the problem (28) to any set of fixed forces lying within a small interval around the SNES point. The locus of maxima thus found satisfies the relation

$$X_k = \sum_l M_{0kl} J_l$$

$$\text{(29)}$$

which by inversion gives

$$J_k = \sum_l L_{0kl} X_l .$$

$$\text{(30)}$$

Note that the points represented by eqs (30) does not satisfy the LTE conditions which are fitted by eq. (8). Thus, deviations of fluxes defined by

$$\delta J_k (\rho) = \sum_l L_{0kl} \delta X_l (\rho)$$

$$\text{(31)}$$

does not introduce any additional condition such as $\delta L_{kl} (\rho) = 0$. In the view of a local LDE principle, deviations (31) may be considered as fluctuations from the (SNES) local equilibrium. From substitution of eq. (30) into eq. (25) we obtain

$$\tilde{\psi} (\rho) = \frac{1}{2} \sum_{kl} L_{0kl} X_k (\rho) \cdot X_l (\rho)$$

$$\text{(32)}$$

Accordingly, we define the functional

$$\Psi [\rho] = \frac{1}{2} \int \sum_{kl} L_{0kl} X_k (\rho) \cdot X_l (\rho) d^3x$$

$$\text{(33)}$$
Variations of \( \tilde{\Psi}[\rho] \) imply variations of \( \Psi[\rho, J] \) along paths defined by eq. (31). Now, the extremum property of \( \tilde{\Psi}[\rho] \) depends on the sign of \( \delta^{(2)} \tilde{\psi}(\rho) \), that is,

\[
\delta^{(2)} \tilde{\psi}(\rho) = \frac{1}{2} \sum L_{0ij} \delta X_i(\rho) \delta X_j(\rho). \tag{34}
\]

The same arguments presented for the problem (28) can be used for eq. (34). If \( f(\eta) \) is positive definite it follows that \( \delta^{(2)} \tilde{\psi}(\rho) \geq 0 \) so that \( \tilde{\Psi}[\rho] \) shows a minimum at the SNES. Thus the extremum properties of the functional \( \Psi[\rho, J] \) along the two paths dealt with are determined uniquely by the sign of the form \( f(\eta) \) which can be established only by thermodynamics. In this connection, we note that functional (33) represent in a general form a Glansdorff-Prigogine local potential. Thus, if the extended MREP principle establishes the minimum of \( \tilde{\Psi}[\rho] \), automatically, it also establishes the maximum of \( \Psi[\rho, J] \) along the fixed force path, thus allowing for an extended LDE principle.

Let us consider the simplest case of a functional dependent on a single state variable. In the domain \( \{X, J\} \) we have \( \psi = J \cdot X - (1/2)M_0 J^2 \) where \( M_0 > 0 \) because of the second thermodynamic law. The function \( \psi \) describes a saddle-shaped surface where the saddle point \( \{X_0, J_0\} \) is a maximum along the path \( \delta X = 0 \) and a minimum along the path \( \delta J = M_0 \delta X \). In the important case of the heat conduction we have \( X = \nabla(1/T) \) and \( L = \lambda(T)T^2 \) where \( \lambda(T) \) is a temperature-dependent coefficient of thermal conductivity. The restricted functional is

\[
\tilde{\Psi}[T] = \frac{1}{2} \int \lambda(T_0)T_0^2 |\nabla(1/T)|^2 d^3x
\]

which is the local potential for heat conduction\(^8\).

**IV SOME EXAMPLES**

**Bulk thermoelectricity in intrinsic semiconductors.** We apply the above variational procedure to the case of bulk thermoelectricity in semiconductors where cross effects between electron-hole and heat transport are to be taken into account. The entropy production is (compare with eq. (6) where \( -\xi \) is replaced by \( v \))

\[
\sigma_S = -j_n \cdot \nabla \varphi_n \frac{1}{T} - j_p \cdot \nabla \varphi_p \frac{1}{T} + J_Q \cdot \nabla \frac{1}{T} + \frac{\nu \Gamma}{T} \tag{35}
\]

where \( \varphi_n \) and \( \varphi_p \) are the electrochemical potentials of electrons and holes, respectively, (\( \varphi_n = \mu_n + eV \) and \( \varphi_p = \mu_p - eV \), \( V \) standing for electric potential, \( e \) for the absolute value of electron charge and \( \mu \) for chemical potentials), \( v \) for the generation-recombination rate (\( v > 0 \) for recombinations) and \( \Gamma = \varphi_n + \varphi_p \) for the carrier affinity (or, equivalently, for the differences of quasi-Fermi levels\(^4\)). On these grounds, by taking into account of eq. (24) (with fluxes as variables) we have
\[ \Psi(\varphi, T, J, \upsilon) = -\int \left( \frac{1}{2}M_{0nn} j_n^2 + \frac{1}{2}M_{0pp} j_p^2 + \frac{1}{2}M_{0QQ} J_Q^2 + M_{0nQ} j_n \cdot J_Q + + M_{0np} j_n \cdot j_p + \frac{1}{2}M_{0ev} \upsilon^2 \right) d^3x \]

\[ -\int \left[ j_n \cdot \nabla \varphi_n + j_p \cdot \nabla \varphi_p - J_Q \cdot \nabla \frac{1}{T} - \frac{\upsilon}{T} \right] d^3x \]  

By varying potential \( \Psi \) with respect to temperature we obtain

\[ \nabla \cdot \frac{\partial \sigma}{\partial \nabla T} - \frac{\partial \sigma}{\partial T} = 0 \]

that is

\[ \nabla \cdot \frac{\mathbf{J}_Q}{T^2} + 2 \frac{\mathbf{J}_Q}{T^3} \cdot \nabla T + \mathbf{j}_n \cdot \nabla \varphi_n + \mathbf{j}_p \cdot \nabla \varphi_p - \frac{\upsilon T}{T^2} = 0 \]

where \( \mathbf{J}_Q = \mathbf{J}_Q - \sum_i \varphi_i \mathbf{j}_i \) so that (see eqs 5-6)

\[ \nabla \cdot \mathbf{J}_S = \sigma_S \]

As for the flux balance equations (variations with respect to \( \varphi \)), it is easy to verify that \( \nabla \cdot \mathbf{j}_n = -\upsilon \) and \( \nabla \cdot \mathbf{j}_p = -\upsilon \)

Now, let us consider the flux laws (variations with respect to fluxes). As for electron and hole fluxes, it is to be pointed out that we does not expect direct cross effect. In this connection, later we will use (even if not explicitly shown) \( L_{np} = (M^{-1})_{np} = 0 \), that is, \( M_{0QQ} M_{0np} = M_{0nQ} M_{0pQ} \). The stationary fluxes are

\[ \mathbf{j}_n = -\frac{1}{M_{0nn}} \nabla \varphi_n - \frac{M_{0nQ}}{M_{0nn}} \mathbf{J}_Q - \frac{M_{0np}}{M_{0nn}} \mathbf{j}_p \]  

(37)

\[ \mathbf{j}_p = -\frac{1}{M_{0pp}} \nabla \varphi_p - \frac{M_{0pQ}}{M_{0pp}} \mathbf{J}_Q - \frac{M_{0np}}{M_{0pp}} \mathbf{j}_n \]  

(38)

\[ \mathbf{J}_Q = -\frac{1}{M_{0QQ}} \frac{1}{T^2} \nabla T - \frac{M_{0nQ}}{M_{0QQ}} \mathbf{j}_n - \frac{M_{0pQ}}{M_{0QQ}} \mathbf{j}_p \]  

(39)

where the Onsager reciprocity relations will appear when the forces are explicitly shown. To write the flux equations in a more compact form it is convenient to define

\[ e^2 \sigma_n = \left( 1 - \frac{M_{0nQ}^2}{M_{0nn} M_{0QQ}} \right) M_{0nn} \]  

(40)

\[ e^2 \sigma_p = \left( 1 - \frac{M_{0pQ}^2}{M_{0pp} M_{0QQ}} \right) M_{0pp} \]  

(41)

Note that \( 1 - M_{0nQ}^2/M_{0nn} M_{0QQ} > 0 \) and \( 1 - M_{0pQ}^2/M_{0pp} M_{0QQ} > 0 \) due to positiveness of the quadratic form. Here \( \sigma_n \) and \( \sigma_p \) stand for the electron and
hole conductivities, respectively. Thus, current densities of electrons and holes are respectively
\[
\frac{I_n}{-e} = j_n = -\frac{\sigma_n}{e^2} \left( T \frac{\nabla \varphi_n}{T} - \frac{M_{0nQ}}{M_{0nn}} T \nabla T \right) \tag{42}
\]
\[
\frac{I_p}{-e} = j_p = -\frac{\sigma_p}{e^2} \left( T \frac{\nabla \varphi_p}{T} - \frac{M_{0pQ}}{M_{0pp}} T \nabla T \right) \tag{43}
\]
which should be compared with the well known thermoelectric current equations\textsuperscript{15}
\[
\frac{I_n}{-e} = -\frac{\sigma_n}{e^2} \left( \nabla \varphi_n + \frac{Q_n}{T} \nabla T \right) \tag{44}
\]
\[
\frac{I_p}{-e} = -\frac{\sigma_p}{e^2} \left( \nabla \varphi_p + \frac{Q_p}{T} \nabla T \right) \tag{45}
\]
where \(Q_n\) and \(Q_p\) stand for the excess of kinetic energy with respect to the mean energy of electrons and a holes, respectively. The following correspondance are found
\[
Q_n = -\left( M_{0nQ}/M_{0QQ} + \varphi_n \right) \quad \text{and} \quad Q_p = -\left( M_{0pQ}/M_{0QQ} + \varphi_p \right).
\]
Based on these results, the heat flux equation can be reduced to the simple form
\[
J_Q = -\lambda \nabla T + (Q_n + \varphi_n) j_n + (Q_p + \varphi_p) j_p \tag{46}
\]
where we used \(\lambda = 1/M_{0QQ} T^2\). Finally, the following relations are found
\[
M_{0nn} = \left( e^2/\sigma_n T \right) + (1/\lambda) \left[ (Q_n + \varphi_n)/T \right]^2 \tag{47}
\]
\[
M_{0pp} = \left( e^2/\sigma_p T \right) + (1/\lambda) \left[ (Q_p + \varphi_p)/T \right]^2 \tag{48}
\]
\[
-M_{0nQ} = \left( Q_n + \varphi_n \right)/\lambda T^2 \tag{49}
\]
\[
-M_{0pQ} = \left( Q_p + \varphi_p \right)/\lambda T^2 \tag{50}
\]
\[
M_{0np} = \left( Q_n + \varphi_n \right) \left( Q_p + \varphi_p \right)/\lambda T^2 \tag{51}
\]
As for the local rate of electron-hole generation recombination process, we obtain \(v = M_{0nn}^{-1} \Gamma / T\) or, by putting \(M_{0nn}^{-1} = L_{0nn} T_0\), \(v = L_{0nn} \Gamma \) (at SNES).

**External forces**

The thermodynamics of SNES involve non isolated system because of the necessity of continuously feeding the stationary processes. The external parameters fixing the SNES are not included in the theory which only establishes the relations among physical quantities of the system dealt with. In several case this could generate difficulties if internal fluxes to be varied are bound with
the external ones. This problem can be figured out by means of proper additional constraining equations. However, we may also conveniently re-define the thermodynamic potentials to include explicitly the external fluxes. To this purpose, we use a different entropy balance equation in which negative terms are added to the entropy production. These additional terms account for the action of external forces continuously displacing the system from equilibrium. This is tantamount to say that we are considering the rate of the whole system entropy change, which is expected to vanish at SNES (the system entropy remain constant). The nature of additional terms discriminate the internal fluxes (which appear in the kinetic term of potential $\psi$) from the internal forces. In this connection, it is to be taken into account that derivatives with respect to forces $X_\alpha$ conjugated to external fluxes $J_\alpha$ should satisfy

$$\frac{\partial \psi}{\partial X_\alpha} = -\frac{J_\alpha}{T}$$

(52)

Thus, we will consider as internal fluxes the ones which links to fixed $J_\alpha$. Note that presence of external terms does not change the conclusions about the potential $\psi$ which depends on the internal properties of the system. We have only a shift of the stationary point in the $\psi, J, X$ map. Of course, this topic merges with the boundary problem discussed in section 5.

**The Maxwell theorem of circuits**

To explain the above point, let us consider a network of resistances and voltage sources $\mathcal{F}_\alpha$ (thus a discrete system), for example ideal batteries. All the chemical processes taking place inside a battery are to be considered as external to the circuit (open system). The whole entropy of battery increases due to spontaneous processes, but it release a negative entropy $-I_\alpha \mathcal{F}_\alpha / T$ to the circuit due to the work of charge separation. The current $I_\alpha$ crossing the voltage source depend on the circuit features. Thus, all the circuit currents are to be considered as forces in the potential $\psi$. Instead, the corresponding affinities are to be considered as fluxes to be linked with fixed $\mathcal{F}_\alpha$. On this ground, potential $\psi$ should be written as

$$\psi = \sum_i \frac{I_i \Gamma_i}{T} - \sum_\alpha \frac{J_\alpha \mathcal{F}_\alpha}{T} - \sum_i \frac{1}{2} M_{0i} \Gamma_i^2$$

(53)

SNES is to be searched for with additional current constraints, that is,

$$\Omega = \sum_i \frac{I_i \Gamma_i}{T} - \sum_\alpha \frac{J_\alpha \mathcal{F}_\alpha}{T} - \sum_i \frac{1}{2} M_{0i} \Gamma_i^2 + \sum_\beta \lambda_\beta f_\beta(I_{\{i\}}, I_{\{\alpha\}})$$

(54)

Alternatively, if we deal with current sources $\mathcal{J}_\alpha$ (now the fixed external fluxes), SNES is to be searched for by means of

$$\psi = \sum_i \frac{I_i \Gamma_i}{T} - \sum_\alpha \frac{\mathcal{J}_\alpha \mathcal{F}_\alpha}{T} - \sum_i \frac{1}{2} M_{0i} I_i^2$$

(55)
and

\[ \Omega_I = \sum_i \frac{I_i \Gamma_i}{T} - \sum_\alpha \frac{\vartheta_\alpha \Gamma_\alpha}{T} - \sum_i \frac{1}{2} L_{0i} I_i^2 + \sum_\beta \eta_\beta g_\beta(\Gamma_{\{i\}}, \Gamma_{\{\alpha\}}) \]  

(56)

where \( g_\beta(\Gamma_{\{i\}}, \Gamma_{\{\alpha\}}) \) are the affinity constraints.

As example, let us consider the simple circuit formed by a battery \( \mathcal{E} \) and two parallel resistances, \( R_1 \) and \( R_2 \), connected to a resistance \( R_3 \). Current constraints are \( I = I_1 + I_2 = I_3 \). Thus,

\[ \Omega_\Gamma = \sum_i \frac{I_i \Gamma_i}{T} - \frac{I \mathcal{E}}{T} - \sum_i \frac{1}{2} M_{0i} \Gamma_i^2 + \lambda_a (I - I_2 - I_3) + \lambda_b (I - I_3) \]  

(57)

From \( \partial \Omega_\Gamma / \partial \Gamma_i = 0 \), \( \partial \Omega_\Gamma / \partial I_1 = 0 \) and \( \partial \Omega_\Gamma / \partial I = 0 \) it follows \( \Gamma_i = I_i / (T M_{0i}) \), \( \Gamma_1 = \Gamma_2 = T \lambda_a \), \( \Gamma_3 = T \lambda_b \) and \( \mathcal{E} = \Gamma_1 + \Gamma_3 = \Gamma_2 + \Gamma_3 \), respectively. As for potential \( \psi \) (for variations of \( \psi \) along \( \delta I_i = M_{0i} \delta \Gamma_i \) paths) we have

\[ \tilde{\psi} = \sum_i \frac{1}{2} R_i I_i^2 - \frac{I \mathcal{E}}{T} \]  

(58)

where \( R_i = (T M_{0i})^{-1} \). Equation (58) (or its generalization) by addition of current constraints call for the Maxwell theorem of circuits\(^{16}\).

### Photo-excitations in semiconductors and recombination resistances.

Now let us consider the electron-hole recombinations in semiconductors under steady injection of carrier in conduction and valence bands. For simplicity, we will deal with the case of uniform photo-excitation and temperature. According to these settings we are assuming the infinite thermal conductivity of the lattice to which the heat produced by energy conversion (which accounts for the external entropy production) is released. Blackbody field is taken into account in rate equations. Of course, the uniformity conditions make the foregoing considerations suitable for the system near equilibrium. Potential \( \psi \) becomes

\[ \psi = \frac{\nu \Gamma}{T} - \frac{\Phi \Gamma}{T} - \frac{1}{2} M_{0\nu \nu} \nu^2 \]  

(59)

where \( \Phi \) stands for the rate of (externally induced) carrier generation. The sign minus account for the negative contribution to the entropy induced in the system by the external force. Really, it is not relevant how the system is moved from equilibrium since we are dealing with a fixed rate \( \Phi \). At the steady state we obtain the expected equation \( \nu = L_{0\nu \nu} \Gamma_0 = \Phi \). As for \( \tilde{\psi} \) (for variations of \( \psi \) along \( \delta \nu = L_{0\nu \nu} \delta \Gamma \) path) it holds

\[ \tilde{\psi} = \frac{1}{2} \frac{L_{0\nu \nu} \Gamma_0^2}{T} - \frac{\Phi \Gamma}{T} \]  

(60)
Finally, it is easily recognizable that eq. (59) is similar to eq. (55). Thus we can conclude that at SNES (near equilibrium) a Maxwell theorem can be called for the recombination rate distribution in a semiconductor analogously to the distribution of currents in a electric circuit; now resistances are to be replaced by recombination resistances related to the inverse of recombination probabilities.

V. FINAL REMARKS AND CONCLUSIONS.

We still remark that the variational equation (27) stands on the condition of having fixed state variables at the system boundary. We can remove this condition by considering a surface integral such that

\[ \int \sum_k J_{0k} \cdot \delta \mathbf{X}_k dV - \oint_{\text{Surf}} \sum_k \left[ \delta \left( \frac{\varphi_k}{T} \right) \right] J_{0k} \cdot d\mathbf{A} = 0 \quad (61) \]

Consequently eq. (27) is to be replaced by

\[ \delta \left( \Psi - \oint_{\text{Surf}} \sum_k \frac{\varphi_k}{T} J_{0k} \cdot d\mathbf{A} \right) = 0 \quad (62) \]

We need not modify anything in the conclusion of the previous section concerning the extremum properties of the functional \( \Psi \). Indeed, eq. (61) holds at any variation order so that the second variation of the modified functional coincides with \( \delta^{(2)} \Psi \).

In the case \( \text{grad} \, \mathbf{v} \neq 0 \) we must include the viscoelastic term in the entropy production. In this connection we point out that \( \mathbf{v} \) cannot be considered as a functional variable. This is because the variational criterion (27) is closely related to the entropy conservation law and does not account for momentum conservation. Thus, the functional (33), as it stands, cannot be used in the field of hydrodynamics. We need not go further in this matter which is beyond the scope of this paper.

We have shown that in continuous systems satisfying LTE conditions, the (extended) MREP and (local) LDE principles are connected by means of a suitable functional. In the case of a single state variable, the density of the functional describes a saddle-shaped surface in the force-flux domain. The saddle point represents the stationary state. The MREP path is the one where the phenomenological coefficient maintains its reference state (SNES) value. Instead, the LDE path is the one where the force is kept fixed. In particular, along the MREP path the functional behaves as a Glansdorff-Prigogine local potential.

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