STATIONARY STATES WITH MINIMUM ENTROPY PRODUCTION AND NON CONSTANT PHENOMENOLOGICAL COEFFICIENTS

J. J. DELGADO DOMINGOS

Núcleo de Estudos de Engenharia Mecânica
Departamento de Engenharia Mecânica
Instituto Superior Técnico
Lisboa

ABSTRACT — Neglecting second order terms on the dependence of the phenomenological coefficients on the local intensive parameters, a generalization of Prigogine's theorem of minimum entropy production is presented, assuming local validity of Onsager's reciprocal relations.

1. A well know theorem of I. Prigogine [1], [2] shows that for thermodynamic systems in mechanical equilibrium the stationary states have the property of minimum entropy production when:

— The generalized fluxes J_i are linear functions of the generalized forces X_k, the phenomenological coeficients L_{ik} being constants

$$J_i = \sum_k L_{ik} X_k$$

— The Onsanger's reciprocical relations have the form

$$L_{ik} = L_{ki}$$

The minimum entropy production is an important physical property but its interest is severely restricted by the condition of constant phenomenological coefficients, because the L_{ik} are functions of X_k, their constancy being only acceptable when the system as a whole is not far from equilibrium.

2. To deal with the realistic situation of non constant phenomenological coefficients, Glansdorff and Prigogine [2] considered later a more general theorem where it is proved that:

$$\frac{\partial_{\times} P}{\partial t} = \int_v \sum_i J_i \frac{\partial X_i}{\partial t} dv \leqslant 0$$

However, no conclusion could be reached about the relative value of

$$\frac{\partial J_P}{\partial t} = \int_v \sum_i \frac{\partial J_i}{\partial t} X_i \, dv$$

Praventing therefore a generalization regarding the sign of the total entropy production:

$$\frac{\partial P}{\partial t} = \frac{\partial_\times P}{\partial t} + \frac{\partial J_P}{\partial t}$$

The purpose of the present note is to show that in the stationary states the entropy production is indeed a minimum, provided that second order terms (on the dependence of L_{ik} in F_k, local intensive variables) are neglected, which is wholly acceptable within the present scope of non — equilibrium theories.

3.1 — In non equilibrium-thermodynamics, it is always assumed, as a first order approximation, that there is a local equilibrium and this assumption seems to have become a basic postulate even for higher order approximations through the introduction of hidden coordinates.

If we assume local equilibrium, the local values of L_{ik} have also a well defined value. For the stationary state, the generalized forces and fluxes are no longer time-dependent, though a function of space coordenates if the thermodynamic system is not in equilibrium.

This means that in the stationary states the L_{ik} depend only on the space coordinates and, neglecting second order terms, they stay at their local values for small perturbations on X_k around the stationary state.

Therefore, around the stationary state, where $F_k = F_k^o$ we have the local relation

$$J_i = \sum_k L_{ik} (F_k^o) X_k$$

from which follows

$$\frac{\partial J_i}{\partial t} = \sum_k L_{ik}(F_k^o) \frac{\partial X_k}{\partial t}$$

$$X_i \frac{\partial J_i}{\partial t} = \sum_k L_{ik}(F_k^o)\ X_i \frac{\partial X_k}{\partial t}$$

$$\sum_i X_i \frac{\partial J_i}{\partial t} = \sum_k L_{ik}(F_k^o)\, X_i \frac{\partial X_k}{\partial t}$$

$$= \sum_k J_k \frac{\partial X_k}{\partial t}$$

$$= \sum_i J_i \frac{\partial X_i}{\partial t}$$

where it has been assumed that the Onsanger's relations hold good:

$$L_{ik}(F_k^o) = L_{ki}(F_k^o)$$

Integration on the whole system gives

$$\int_v \sum_i X_i \frac{\partial J_i}{\partial t}\, \partial v = \int_v \sum_i J_i \frac{\partial X_i}{\partial t}\, d v$$

or

$$\frac{\partial J_P}{\partial t} = \frac{\partial_\times P}{\partial t}$$

But Glansdorff and Prigogine have already proved [2] that

$$\frac{\partial_\times P}{\partial t} \leqslant 0$$

It follows, for the stationary state, that even in this case of non constant phenomenological coefficients it is

$$\frac{\partial P}{\partial t} \leqslant 0$$

3.2 — The previous derivation shows that it is sufficient local equilibrium, not overall equilibrium for the system as implied for exemple by De Groot and Mazur [2, p. 46]. Indeed, for arbitrarily large systems, we can have arbitrarily large variations of X_k and the whole system remaining far from equilibrium, while local equilibrium prevails throughout. This condition of local equilibrium must be stressed because it is, as referred, one of the basic assumptions of modern non-equilibrium theories.

4. — More recently, Glansdorff and Prigogine introduced the concept of a local potential as a generalization of their relation $\frac{\partial_{\times} P}{\partial t}$ for systems not in mechanical equilibrium or with non-constant phenomenological coefficients, aiming at a formulation of a general evolutions critorion in macroscopic physics. In this sense, non-stationary states are considered as well. This formulation is not unique and, as have been shown elsewhere [5], suffers from several drawbacks to be considered a general formulation; moreover, some demonstrations which have been promised have not yet been published and a few doubts arise if they ever will be. This fact impaires its value as a tool for the solution of practical problems by variational methods.

Whit the basic, and physically intuitive, derivation of the present note, the same results of the general evolution criterion can be more easily achieved as has already been shown on a different context [5].

5. — The present contribution can be summarized as follows — assuming the physical validity of Prigogine's theorem of minimum entropy production for stationary states, a generaliszation for non constant phenomenological coeffients, neglecting second order terms on the dependence of the phenomelogical coefficients on the generalized forces, is proposed.

The results of the «general evolution criterion of macroscopic physics» due to Glansdorff and Prigogine can be more easily obtained with the present type of approach if some of the objections on that work are removed.

REFERENCES

(1) Prigogine, I. — «Thermodynamique des Phénomènes Irreversibles», *Deseer* Liége, 1947.

(2) De Groot, S. R. — *Non-Equililibrium Thermodynamics Nort-Holland*, 1962.

(3) Domingos, J. J. D. — «As equações fundamentais em mecânica dos fluídos e transmissão do calor». *Rev Port. Quím.* 8, 88, 1966.

(4) Domingos, J. J. D. — «O mínimo de produção de entropia no escoamento uniforme dum fluído newtoniano». *Técnica*, 29, 61, 1966.

(5) Glansdorff, P. et Prigogine, I. — «On a general evolution criterion in Macroscopic Physics». *Physica*, 30, 251, 1964.

(6) Domingos, J. J. D. — «Métodos variacionais em mecânica dos fluídos e transmissão do calor». *Técnica*, 30, 1, 1967.