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EXTENDED THERMODYNAMICS FOR CONTINUOUS MEDIA  
WITH INTERNAL STRUCTURE

by

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## ABSTRACT

We developed an extended thermodynamical theory for continuous media with spin. New phenomenological coefficients with definite algebraic properties are necessarily introduced and the time correlations fluctuations of the dissipative fluxes are calculated.

Key-words: Extended thermodynamics; Spin.

## 1 - INTRODUCTION

Usually in the literature<sup>(1,2)</sup> the pressure tensor of a continuous media is considered as a symmetric tensor, as consequence the orbital and intrinsic angular momentum are conserved independently. In this case, the dynamical equations of the intrinsic and orbital angular momentum are completely decoupled and don't contribute to the entropy production: Grad<sup>(3)</sup> was the first to obtain a more general equation of motion and balance of energy from which follows the possibility of an antisymmetric character of the pressure tensor. This leads, in the thermodynamical point of view, as a consequence, a new viscosity coefficient which is due to the exchange of angular momentum between the rotational hydrodynamic field and the intrinsic (or internal) angular momentum of the constituents of the continuous media. This new contribution has been developed latter by Meixner<sup>(4)</sup>, Baranowski and Romotwsky<sup>(5)</sup>. In these works the angular momentum intrinsic and orbital aren't separately conserved, a new dissipative fluxes arise from the irreversible exchange between the two angular momenta and is known by rotational viscosity.

In this context there is a new object named couple-stress tensor. Such tensor specifies the state of internal couples of the continuous media. It has been shown<sup>(3)</sup> that the irreducible parts of the couple-stress tensor are interpreted like thermodynamical fluxes that are conjugated with gradient of the field of internal angular velocity.

In our work we apply the new formulation of non-equilibrium thermodynamics, currently known as extended irreversible thermodynamics<sup>[6]</sup>, to this enlarged situation. The first section is devoted to obtain the equations of extended irreversible thermodynamics and his basic features. In the second section we apply methods of autonomous dynamical systems in order to obtain some restrictions on the new phenomenological coefficients. The last section is devoted to obtain supplementary information about the macroscopic parameters provided by fluctuation theory.

## 2 - EXTENDED IRREVERSIBLE THERMODYNAMICS

A one-component system depends locally on the equilibrium variable  $u$ , the internal energy per unit of mass,  $v$  the specif volume, the velocity  $\vec{v}$  and the dissipative fluxes  $\vec{q}$ ,  $\pi$ ,  $\pi_{ij}$ , respectively heat flux, bulk viscous pressure and the traceless symmetric shear tensor. If the one component system has intrinsic spin, we need to add the angular momentum spin tensor  $S_{ij}$  and the couple-stress tensor  $Q_{ijk}$ . In this way a more general equation of motion is obtained from which follows the possibility of the antisymmetric character of the pressure tensor described by  $\epsilon_{ijk} \pi_k^{(\omega)}$ <sup>[5]</sup>.

In the classical description of fluid mechanics, the evolution is governed by the well known balance equation of momentum, mass, energy and angular momentum  $\rho$ .

$$\rho \dot{v}_i = \frac{\partial P_{ji}}{\partial x_j} \quad (2.1)$$

$$\rho \dot{v} = \frac{\partial v_i}{\partial x_i} \quad (2.2)$$

$$\begin{aligned} \rho \dot{u} + \frac{\partial q_j}{\partial x_j} = & - (p + \pi) \frac{\partial v_i}{\partial x_i} - \dot{\pi}_{ij} \langle \nabla \cdot \dot{v} \rangle_{ij} - \pi_i^{(\omega)} \left[ \varepsilon_{ijk} \frac{\partial v_k}{\partial x_j} - \right. \\ & \left. - 2\dot{\Omega}_i \right] - Q_i \varepsilon_{ijk} \frac{\partial \Omega_k}{\partial x_j} - Q \frac{\partial \Omega_i}{\partial x_i} - \dot{Q}_{jk} \langle \nabla \cdot \dot{\Omega} \rangle_{kj} \end{aligned} \quad (2.3)$$

$$\rho \dot{S}_{ij} + \frac{\partial Q_{ijk}}{\partial x_k} = 2 \varepsilon_{ijk} \pi_k^{(\omega)} \quad (2.4)$$

In writing these equations we use the following usual decomposition of the pressure tensor  $P_{ij}^{(1)}$ :

$$P_{ij} = -p\delta_{ij} + \pi\delta_{ij} + \dot{\pi}_{ij} + \varepsilon_{ijk} \pi_k^{(\omega)} \quad (2.5)$$

where  $p$  is the thermodynamic pressure.

With the tensor  $Q_{ijk} = -Q_{jik}$  we can define the dual tensor:

$$Q_{jk} \equiv \frac{1}{2} \varepsilon_{jrs} Q_{rsk} \quad (2.6)$$

Then the dual tensor  $Q_{jk}$  can be split on his irreducibles parts as follows:

$$Q_{jk} = \delta_{jk} Q + \dot{Q}_{jk} + \varepsilon_{jki} Q_i \quad (2.7)$$

where the symbol  $\cdot$  means:

$$\dot{L}_{jk} = \frac{1}{2} (L_{jk} + L_{kj}) - \frac{\delta_{jk}}{3} L_{ii} . \quad (2.8)$$

The intrinsic angular velocity is represented by  $\Omega_{ij}$  or its dual  $\Omega_i$ , where:

$$\Omega_i = \frac{1}{2} \epsilon_{ijk} \Omega_{jk} . \quad (2.9)$$

In the model in consideration, the intrinsic angular velocity is related to the spin vector  $S_i = \frac{1}{2} \epsilon_{ijk} S_{jk}$  by:

$$S_i = I_{ij} \Omega_j \quad (2.10)$$

where  $I_{ij}$  is the density of momentum of inertia.

The classical description of fluid mechanics is not self-contained since the evolution equations (2.1), (2.2), (2.3) and (2.4) involve new unknowns parameters as  $p$ ,  $\vec{q}$ ,  $\pi$ ,  $\vec{\pi}_{ij}$ ,  $\pi_k^{(\omega)}$  and  $Q_{ijk}$  in terms of the basic variables and their spatial gradients<sup>[4,5]</sup>. Our purpose is to propose a theory which goes beyond the classical description. This is done by considering the dissipative fluxes  $q_i$ ,  $\pi$ ,  $\pi_{ij}$ ,  $\pi_k^{(\omega)}$  and  $Q_{ijk}$ , appearing in the balance equations (2.1), ..., (2.4) as independent variables. It is expected that the results of classical theory will be recovered as a limiting case. In this formulation we need to find evolution equations for the dissipative fluxes. We do not adopt the local-equilibrium assumption, so the entropy of the system depends locally on the classical variables  $u$  and  $v$  and also on the dissipative fluxes.

In this way, the following expression is valid:

$$\begin{aligned}
 ds = & \frac{\partial s}{\partial u} du + \frac{\partial s}{\partial v} dv + \frac{\partial s}{\partial q_i} dq_i + \frac{\partial s}{\partial \pi} d\pi + \frac{\partial s}{\partial \dot{n}_{ij}} d\dot{n}_{ij} + \\
 & + \frac{\partial s}{\partial \pi_i^{(\omega)}} d\pi_i^{(\omega)} + \frac{\partial s}{\partial Q} dQ + \frac{\partial s}{\partial Q_i} dQ_i + \frac{\partial s}{\partial \dot{Q}_{ij}} d\dot{Q}_{ij} .
 \end{aligned} \tag{2.11}$$

We define a non-equilibrium absolute temperature  $T$  and a non-equilibrium thermodynamic pressure  $p$  by:

$$\frac{\partial s}{\partial u} = T^{-1} (u, v, q_i, \pi, \dot{n}_{ij}, \pi_i^{(\omega)}, Q, Q_i, \dot{Q}_{ij}) \tag{2.12a}$$

$$\frac{\partial s}{\partial v} = T^{-1} p (u, v, q_i, \pi, \dot{n}_{ij}, \pi_i^{(\omega)}, Q, Q_i, \dot{Q}_{ij}) . \tag{2.12b}$$

The remaining partial derivatives are denoted as:

$$\frac{\partial s}{\partial q_i} = T^{-1} v (\alpha_1 q_i + \bar{\alpha}_1 Q_i) \tag{2.12c}$$

$$\frac{\partial s}{\partial \pi} = T^{-1} v \alpha_0 \pi \tag{2.12d}$$

$$\frac{\partial s}{\partial \pi_i^{(\omega)}} = T^{-1} v \alpha_3 \pi_i^{(\omega)} \tag{2.12e}$$

$$\frac{\partial s}{\partial \dot{n}_{ij}} = T^{-1} v \alpha_2 \dot{n}_{ij} \tag{2.12f}$$

$$\frac{\partial s}{\partial Q} = T^{-1} \nu \alpha_i Q \quad (2.12g)$$

$$\frac{\partial s}{\partial Q_i} = T^{-1} \nu (\alpha_0 Q_i + \bar{\alpha}_0 q_i) \quad (2.12h)$$

$$\frac{\partial s}{\partial \dot{Q}_{ij}} = T^{-1} \nu \alpha_s \dot{Q}_{ij} \quad (2.12i)$$

We restrict ourselves to linear terms, the  $\alpha_i$  ( $i = 0, 1, \dots, 6$ ) are coefficients that must be identified in terms of physical parameters as will be done later.

The introduction of equations (2.12) into (2.11) yields the generalized Gibbs equation. In order to exhibit the entropy production, we need an expression for the entropy flux, writing in linear approximation by:

$$\vec{j}_s = \beta \vec{q} \quad (2.13)$$

where  $\beta$  is a parameter that will be given later.

The most general form of the entropy balance equation is

$$\rho \dot{s} + \nabla \cdot \vec{j}_s = \sigma \quad (2.14)$$

Considering the equations (2.11), (2.12) and (2.13), we have the following expression for the entropy production:



$$\begin{aligned} \sigma_s = & \left[ \beta_s - \frac{1}{T} \right] \vec{\nabla} \cdot \vec{q} + \pi^s X + \vec{q} \cdot \vec{X} + \dot{\pi}_{ij}^s X_{ij} + Q^s X + \\ & + \dot{\pi}^{(a)} \cdot \vec{X} + \dot{Q}_{ij}^s X_{ij} + \dot{Q} \cdot \vec{X} \geq 0 . \end{aligned} \quad (2.15)$$

The thermodynamics forces  $^s X$ , ...,  $^s \vec{X}$ , appearing in (2.15) are:

$$^s X = - \frac{1}{T} \left[ \frac{\partial V_i}{\partial X_i} + \alpha_s \dot{\pi} \right] \quad (2.16a)$$

$$^s X_i = \frac{\partial \beta_s}{\partial x_i} + \frac{\alpha_s}{T} \dot{q}_i + \frac{\alpha_s}{T} \dot{Q}_i \quad (2.16b)$$

$$^s X_{ij} = - \frac{(\nabla \cdot \vec{\nabla})_{ij}}{T} + \frac{\alpha_s}{T} (\dot{\pi}_{ij}) \quad (2.16c)$$

$$^s X = - \frac{\nabla \cdot \vec{\nabla}}{T} + \frac{\alpha_s}{T} \dot{Q} \quad (2.16d)$$

$$^s X_i = - \frac{(\nabla \times \vec{\nabla})_i - 2\Omega_i}{T} + \frac{\alpha_s}{T} \dot{\pi}_i \quad (2.16e)$$

$$^s X_{ij} = - \frac{(\nabla \cdot \vec{\nabla})_{ij}}{T} + \frac{\alpha_s}{T} (\dot{Q}_{ij}) \quad (2.16f)$$

$$^s X_i = - \frac{(\nabla \times \vec{\nabla})_i}{T} + \frac{\alpha_s}{T} \dot{q}_i + \frac{\alpha_s}{T} \dot{Q}_i \quad (2.16g)$$

In order to obtain the evolutions equations (new phenomenological equations) for fluxes we need to express the  $X$ 's as functions of the fluxes, thus up to first order we have:

$${}^0X = a_{\infty} \pi \quad (2.17a)$$

$${}^1X_i = a_{10} q_i + a_{16} Q_i \quad (2.17b)$$

$${}^2X_{ij} = a_{20} \pi_{ij} \quad (2.17c)$$

$${}^3X = a_{30} X \quad (2.17d)$$

$${}^4X_i = a_{40} \pi_i^{(\omega)} \quad (2.17e)$$

$${}^5X_{jk} = a_{50} \dot{Q}_{jk} \quad (2.17f)$$

$${}^6X_i = a_{60} Q_i + a_{61} q_i \quad (2.17g)$$

Substituting these expressions in (2.15) and assuming  $\beta_0 = \frac{1}{T}$ , we obtain:

$$\begin{aligned} \sigma_s = & a_{\infty} \pi^2 + a_{10} q_i q_i + a_{20} \pi_{ij} \pi_{ij} + a_{30} Q^2 + a_{40} \pi_i \pi_i + \\ & + a_{50} \dot{Q}_{jk} \dot{Q}_{jk} + a_{60} Q_i Q_i + (a_{61} + a_{16}) Q_i q_i \geq 0. \end{aligned} \quad (2.18)$$

The restrictions imposed by the second law on these coefficients are:

$$\left. \begin{aligned} a_{\infty} > 0; a_{20} \geq 0; a_{30} \geq 0; a_{40} \geq 0; a_{50} \geq 0; \\ a_{10} a_{60} \geq \frac{1}{4} (a_{16} + a_{61})^2 \end{aligned} \right\} \quad (2.19)$$

Finally, from equations (2.16) and (2.17) we obtain

the following evolution equations:

$$\frac{\alpha_0}{T} \dot{\pi} = a_{00} \pi + \frac{\nabla \cdot \dot{\vec{\psi}}}{T} \quad (2.20)$$

$$\frac{\alpha_2}{T} (\dot{\pi}_{ij})' = a_{20} \dot{\pi}_{ij} + \frac{(\nabla \cdot \dot{\vec{\psi}})_{ij}}{T} \quad (2.21)$$

$$\frac{\alpha_3}{T} \dot{Q} = a_{30} Q + \frac{\dot{\vec{\psi}} \cdot \dot{\vec{\Omega}}}{T} \quad (2.22)$$

$$\frac{\alpha_4}{T} \dot{\pi}^{(\omega)} = a_{40} \dot{\pi}^{(\omega)} + \frac{(\nabla \times \dot{\vec{\psi}} - 2\dot{\vec{\Omega}})}{T} \quad (2.23)$$

$$\frac{\alpha_5}{T} (\dot{Q}_{jk})' = a_{50} \dot{Q}_{jk} + \frac{(\nabla \cdot \dot{\vec{\Omega}})_{jk}}{T} \quad (2.24)$$

$$\begin{pmatrix} \dot{q}_i \\ \dot{Q}_i \end{pmatrix} = \mathbb{M} \begin{pmatrix} q_i \\ Q_i \end{pmatrix} + \mathbb{N}_i \quad (2.25)$$

where

$$\mathbb{M} = T (\bar{\alpha}_1 \bar{\alpha}_\sigma - \alpha_1 \alpha_\sigma)^{-1} \begin{pmatrix} a_{\sigma 1} \bar{\alpha}_\sigma - a_{10} \alpha_\sigma & a_{\sigma 0} \bar{\alpha}_\sigma - a_{11} \alpha_\sigma \\ a_{10} \bar{\alpha}_1 - a_{\sigma 1} \alpha_1 & a_{11} \bar{\alpha}_1 - a_{\sigma 0} \alpha_1 \end{pmatrix} \quad (2.26)$$

$$\mathbb{N}_i = T (\bar{\alpha}_1 \bar{\alpha}_\sigma - \alpha_1 \alpha_\sigma)^{-1} \begin{pmatrix} \frac{\bar{\alpha}_\sigma}{T} (\nabla \times \dot{\vec{\Omega}})_i + \alpha_\sigma \frac{\partial T^{-1}}{\partial x_i} \\ \frac{\alpha_1}{T} (\nabla \times \dot{\vec{\Omega}})_i + \bar{\alpha}_1 \frac{\partial T^{-1}}{\partial x_i} \end{pmatrix} \quad (2.27)$$

We have introduced many coefficients, which can be

identified in physical terms as<sup>(a)</sup>:

$$\begin{aligned}
 a_{\infty} &= \frac{1}{\zeta T} & ; & \quad \alpha_0 = -\tau_0 a_{\infty} T \\
 a_{20} &= \frac{1}{\eta T} & ; & \quad \alpha_2 = -\tau_2 a_{20} T \\
 a_{30} &= \frac{1}{k T} & ; & \quad \alpha_3 = -\tau_3 a_{30} T \\
 a_{40} &= \frac{1}{\eta_r T} & ; & \quad \alpha_4 = -\tau_4 a_{40} T \\
 a_{50} &= \frac{1}{\xi T} & ; & \quad \alpha_5 = -\tau_5 a_{50} T
 \end{aligned}
 \tag{2.28}$$

where  $\zeta$ ,  $\eta$  and  $\eta_r$  are bulk, shear and rotational viscosity coefficients respectively. The other coefficients  $k$  and  $\xi$  are associated to the dissipative fluxes  $Q$  and  $\hat{Q}_{ij}$ , respectively.  $\tau_0$ ,  $\tau_2$ , ...,  $\tau_5$  are the relaxation times related to the respective fluxes. The coefficients of equations (2.25) and (2.27) are more complex due of the cross terms:

$$\alpha_1 = -\tau_{10} a_{10} T ; \quad \alpha_6 = -\tau_{60} a_{60} T ; \quad \bar{\alpha}_1 = -\tau_{11} a_{11} T ; \quad \bar{\alpha}_6 = -\tau_{61} a_{61} T
 \tag{2.29}$$

where

$$\begin{aligned}
 a_{10} &= \frac{\xi T^{-2}}{\chi\zeta - \mu_{10} \mu_{01}} & a_{00} &= \frac{\chi T^{-2}}{\chi\zeta - \mu_{10} \mu_{01}} \\
 a_{10} &= \frac{\mu_{10} T^{-2}}{\chi\zeta - \mu_{10} \mu_{01}} & a_{10} &= \frac{\mu_{01} T^{-2}}{\chi\zeta - \mu_{10} \mu_{01}}
 \end{aligned}
 \tag{2.30}$$

Those expressions come from the well known equations of classical thermodynamics<sup>(5)</sup>:

$$q_i = -\chi \frac{\partial T}{\partial x_i} + \mu_{10} (\nabla x_i)_i \tag{2.31a}$$

$$Q_i = -\zeta (\nabla x_i)_i + \mu_{01} \frac{\partial T}{\partial x_i} \tag{2.31b}$$

In these equations  $\chi$  and  $\zeta$  are the heat conduction coefficient and the similar associated to the flux  $Q_i$ , respectively;  $\mu_{10}$ ,  $\mu_{01}$  are coefficients linked to the cross effects between both phenomena. The relaxation times  $\bar{\tau}_1$  and  $\bar{\tau}_0$  are linked to the cross effects too. Finally, we have a relation that has to be obeyed by the coefficients  $a_{10}$ ,  $a_{00}$ ,  $a_{11}$  and  $a_{10}$ .

$$a_{10} a_{00} \geq \frac{1}{4} (a_{11} + a_{01})^2 \tag{2.32}$$

### 3 - SOME APPLICATIONS OF THE NEW PHENOMENOLOGICAL EQUATIONS

The first relation between the phenomenological coefficients is deduced when we take the reciprocal Onsager's relations<sup>(11)</sup>. In our particular case we have two phenomena of

same tensorial character, so we write:

$$a_{ii} = a_{\alpha\alpha} = a. \quad (3.1)$$

Consequently the relaxation times  $\bar{\tau}_i$  and  $\bar{\tau}_\sigma$  linked to the cross effects between both phenomena are the same:

$$\bar{\tau}_i = \bar{\tau}_\sigma = \tau. \quad (3.2)$$

Let's consider a situation where dissipation is due to  $\vec{q}$  and  $\vec{Q}$  only, and temperature  $T$  and field of spin velocity,  $\vec{\Omega}_7$  are made constants. In this way, the thermodynamical forces vanish and consequently the system tends to a state of thermodynamical equilibrium characterized by  $\vec{q} = \vec{Q} = 0$ .

Taking in mind the system of equations (2.25) and the theory of autonomous dynamical systems<sup>(7)</sup> in this situation, we can conclude some informations about the new phenomenological coefficients. So, making  $\vec{\nabla}T = \nabla\chi = 0$  in (2.25), we have:

$$\begin{pmatrix} \dot{q}_i \\ \dot{Q}_i \end{pmatrix} = M \begin{pmatrix} q_i \\ Q_i \end{pmatrix} \quad (3.3)$$

In order to simplify the analysis, let's consider that all phenomenological coefficients are approximately constants. It's easy to realize that the system (3.3) has one critical point (in sense of dynamical system theory) characterized by  $\vec{q} = \vec{Q} = 0$ . Such point must be stable, in sense that all curves of plane phase goes to this point (fig. 1). Two conditions must

be satisfied for such behaviour:

$$\det M = \frac{T^2 (a_{00} a_{10} - a_{01} a_{11})}{\alpha_1 \alpha_0 - \bar{\alpha}_1 \bar{\alpha}_0} > 0, \quad (3.4)$$

and

$$\text{tr } M = \frac{-(\tau_1 + \tau_0) a_{10} a_{00} + (a_{01}^2 \bar{\tau}_0 + a_{11}^2 \bar{\tau}_1)}{T^{-2} (\alpha_1 \alpha_0 - \bar{\alpha}_1 \bar{\alpha}_0)} < 0 \quad (3.5)$$

where  $\det M$  and  $\text{tr } M$  are, respectively, the determinant and trace of matrix  $M$ . In this way, the following relations can be easily deduced:

$$\tau_1 \tau_0 > \frac{a^2}{a_{10} a_{00}} \tau^2 \quad (3.6)$$

$$\tau_1 + \tau_0 > \frac{2a^2 \tau}{a_{10} a_{00}} \quad (3.7)$$

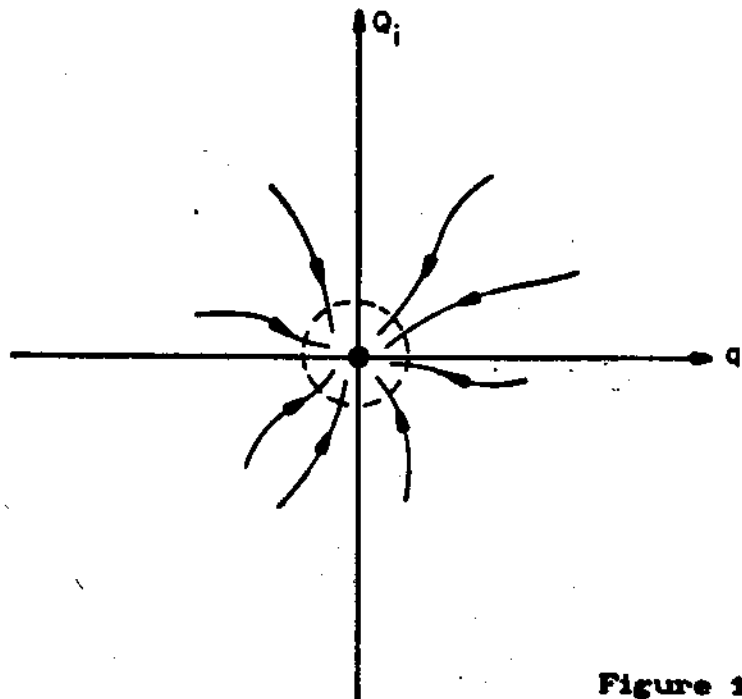


Figure 1

It's clear from these equations the compromise between the relaxation times. A new situation can be considered where the thermodynamical forces are making time independent and keeping again the constancy of the phenomenological coefficients. As consequence  $\vec{N}$  (eq. 2.27) is time independent also. On these conditions the system of equations (2.25) has a critical point characterized by  $\vec{q} = \vec{q}_0$  and  $\vec{Q} = \vec{Q}_0$ , where  $\vec{q}_0$  and  $\vec{Q}_0$  are determined doing  $\vec{q} = 0$  and  $\vec{Q} = 0$  in (2.25). The behaviour of the curves on phase plane will be the same that in the previously analysed case.  $P_0$  (fig. 2) will specify a non-equilibrium stationary thermodynamic state, where all physical terms are time independent. In this way we conclude that the non-equilibrium stationary state is stable.

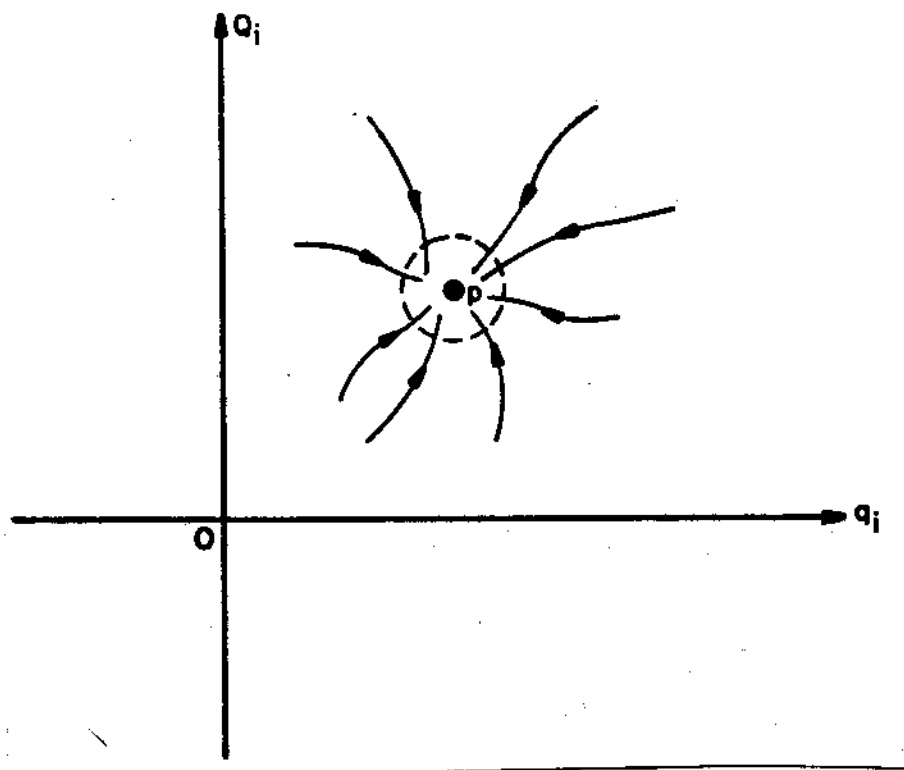


Figure 2



- Fluctuations of dissipative fluxes near the non-equilibrium stationary state -

The second moments of the fluctuations of the dissipative fluxes  $\vec{q}$  and  $\vec{Q}$  near the stationary state  $P_0$  can be calculated following the well known Einstein approximation modified to apply to non-equilibrium fluctuation<sup>(8)</sup>. The probability of a fluctuation is:

$$P_r \sim \exp \left[ \frac{\delta^2 s}{k} \right] \quad (3.8)$$

where  $k$  is the Boltzmann constant and  $\delta^2 s$  is the second differential of specific entropy, starting from the non-equilibrium state  $P_0$ . Next we have to expand the entropy around its value at the state of reference. Since for the state  $P_0$  the entropy has a maximum value and neglecting higher-order terms<sup>(8)</sup>, we obtain:

$$\delta^2 s = - 2a_{10} \tau_1 \delta\vec{q} \cdot \delta\vec{q} - 2\tau_0 a_{\infty} \delta\vec{Q} \cdot \delta\vec{Q} - 2\tau a \delta\vec{q} \cdot \delta\vec{Q} . \quad (3.9)$$

Substituting (3.9) in (3.8), leads to:

$$P_r(\delta q_i, \delta Q_j) \sim \exp \left[ - \frac{a_{10}}{k} \tau_1 \delta\vec{q} \cdot \delta\vec{q} - \frac{\tau_0 a_{\infty}}{k} \delta\vec{Q} \cdot \delta\vec{Q} - \frac{\tau a}{k} \delta\vec{q} \cdot \delta\vec{Q} \right] \quad (3.10)$$

This expression leads for the second momentum of the fluctuations of the dissipative fluxes to the formula:

$$\langle \delta q_i(\vec{r}, t) \delta q_j(\vec{r}, t) \rangle = \frac{k}{a_{10} \tau_1} \delta_{ij} \quad (3.11)$$

$$\langle \delta Q_i(\vec{r}, t) \delta Q_j(\vec{r}, t) \rangle = \frac{k}{a_{10} \tau_a} \delta_{ij} \quad (3.12)$$

$$\langle \delta q_i(\vec{r}, t) \delta q_j(\vec{r}, t) \rangle = \frac{k}{\tau_a} \delta_{ij} \quad (3.13)$$

As we can see directly the second moments of the fluctuations determine the phenomenological coefficients. Such point of view has been exploited in the Green-Kubo relations for the dissipative coefficients<sup>(9)</sup>.

We specialize here to consider the time dependence of the correlation functions of the fluctuations of the dissipative fluxes  $q_i$  and  $Q_i$ . We assume that the time decay of  $\delta T$  and  $\delta(\vec{V} \cdot \vec{x})$  are much longer than the characteristic time of decay of random independent fluctuations  $\delta q_i$  and  $\delta Q_i$ <sup>(8)</sup>. So, the term evolution of the fluctuation are obtained from the system of equations (2.25) and write as:

$$\begin{bmatrix} \dot{\delta q}_i \\ \dot{\delta Q}_i \end{bmatrix} = M \begin{bmatrix} \delta q_i \\ \delta Q_i \end{bmatrix} \quad (3.14)$$

As a consequence of these equations, the time correlation of the fluctuations of the dissipative fluxes in a stationary state is given by:

$$\begin{aligned} \langle \delta q_i(\vec{r}, t) \delta q_j(\vec{r}, t+t') \rangle &= \frac{b_1 c_2 e^{k_1 t'} - b_2 c_1 e^{k_2 t'}}{b_1 c_2 - b_2 c_1} \frac{k \delta_{ij}}{a_{10} \tau_1} + \\ &+ \frac{b_2 b_1 \left[ e^{k_2 t'} - e^{k_1 t'} \right]}{b_1 c_2 - b_2 c_1} \frac{k \delta_{ij}}{a \tau} \quad (3.15) \end{aligned}$$

$$\begin{aligned}
\langle \delta Q_i(\vec{r}, t) \delta Q_j(\vec{r}, t+t') \rangle &= \frac{b_{12} c_2 e^{k_2 t'} - b_{21} c_1 e^{k_1 t'}}{b_{12} c_2 - b_{21} c_1} \frac{k \delta_{ij}}{a \omega \tau} + \\
&+ \frac{c_1 c_2 \left[ e^{k_1 t'} - e^{k_2 t'} \right]}{b_{12} c_2 - b_{21} c_1} \frac{k \delta_{ij}}{a \tau}, \quad (3.16)
\end{aligned}$$

$$\begin{aligned}
\langle \delta q_i(\vec{r}, t) \delta Q_j(\vec{r}, t+t') \rangle &= \frac{c_1 c_2 \left[ e^{k_1 t'} - e^{k_2 t'} \right]}{b_{12} c_2 - b_{21} c_1} \frac{k \delta_{ij}}{a \omega \tau} + \\
&+ \frac{b_{12} c_2 e^{k_2 t'} - b_{21} c_1 e^{k_1 t'}}{b_{12} c_2 - b_{21} c_1} \frac{k \delta_{ij}}{a \tau}, \quad (3.17)
\end{aligned}$$

$$\begin{aligned}
\langle \delta Q_i(\vec{r}, t) \delta q_j(\vec{r}, t+t') \rangle &= \frac{b_{12} b_2 \left[ e^{k_2 t'} - e^{k_1 t'} \right]}{b_{12} c_2 - b_{21} c_1} \frac{k \delta_{ij}}{a \omega \tau} + \\
&+ \frac{b_{12} c_2 e^{k_1 t'} - b_{21} c_1 e^{k_2 t'}}{b_{12} c_2 - b_{21} c_1} \frac{k \delta_{ij}}{a \tau}, \quad (3.18)
\end{aligned}$$

where  $b_1, c_1$  and  $b_2, c_2$  are, respectively, the components of the eigenvectors of matrix  $M$  associated to the eigenvalues  $k_1$  and  $k_2$ . It can be shown that  $k_1$  and  $k_2$  are negatives, so the fluctuations go to zero as  $t'$  goes to infinity.

#### 4 - CONCLUSIONS

In the classical theory,  $Q, Q_i$  and  $\hat{Q}_{ij}$  are not

considered as independent variables, but they are given in terms of equilibrium variables by means of constitutive equations. Here they are considered as independent dynamic variables and their respective fluctuations are described by the non-equilibrium entropy (2.11) via Einstein relation (3.8). The dissipative flux  $Q_i$  has the same tensorial character of the heat flux  $q_i$ , then cross-effects terms appear in the respective phenomenological equations. New phenomenological coefficients have been introduced and it was possible to obtain some restrictions to these coefficients.

In the case where the dissipation is due to  $q_i$  and  $Q_i$  only, we computed the fluctuations of these fluxes near to a non-equilibrium stationary state. As usual, the fluctuations are expressed in terms of phenomenological coefficients associated to  $q_i$  and  $Q_i$ . At last, the time correlation of the fluctuations of the dissipative fluxes  $q_i$  and  $Q_i$  in this stationary system were obtained.

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