On the Problem of Evolution Criterion for Thermodynamical Waves

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Summary

Irreversible systems in which both dissipative and relaxation phenomena are taking place can be appropriately described by the wave approach of Onsagerian thermodynamics proposed by Gyarmati. An important consequence of this theory is that it leads to hyperbolic transfer equations and these are referred to as thermodynamical waves. In the present note we examine the possibility of existence of an evolution criterion for such thermodynamical waves. It is found that a monotonic transition of the thermodynamical waves from non-equilibrium states to stationary states is insured only when dissipative processes are dominant over relaxation phenomena.

Introduction

The classical theory of irreversible processes (Prigogine [1], Meixner and Reik [2], De-Groot and Mazur [3], Gyarmati [4]) rests on the assumption of local equilibrium. This assumption implies that although globally the system is in a state of non-equilibrium but each small element of the system remain in state of local equilibrium and the equations of thermostatics are valid in such element. In particular the local entropy has the same functional dependence on the local independent macroscopic variables as at equilibrium. This enables us to calculate the entropy production in non-equilibrium systems which in such cases is a bilinear expression of thermodynamical forces and fluxes. In kinetic terms the assumption of the local equilibrium means that the collisions effects are dominant in the system which tend to restore the thermodynamic equilibrium and as a result the local molecular distribution deviate only slightly from the equilibrium value. In fast irreversible processes or when inertial and relaxation phenomena in the continuum are strong, the system no longer remains in the state of local equilibrium and to define the non-equilibrium state of system we need new variables which vanish at equilibrium (Gyarmati [5], Verhás [6], [7], Lebon et al. [8], Lebon and Rubi [9], Jou et al. [10], Bamphi and Morro [11], Bataille and Kestin [12]).

Lebon, Rubi, Jou, Casas Vázques consider these new variables to be dissipative fluxes and they start with the generalized Gibbs equation. In the formalism of Kestin, Bataille, Verhás the departure from the state of local equilibrium is described by taking in to consideration internal variables which essentially...
account for the internal dissipation arising due to the action of internal, un-
equilibrated generalized force.

Gyarmati [5] in his “wave approach of Onsagerian thermodynamics” attempts
to enlarge the formalism of the classical irreversible thermodynamics by gener-
alizing the proposition of Machlup and Onsager. The essence of this theory is
that when imposed changes in state variables are sufficiently rapid the kinetic
energy of the currents are not negligible and they also contribute appreciably
to the entropy of system. So if “$S$” is the local entropy per unit volume, then

$$S(a_1, a_2, ..., a_f, J_1, J_2, ..., J_f) = S_{eq}(a_1, a_2, ..., a_f) + S_{kin}(J_1, J_2, ..., J_f)$$

or to be more specific

$$S = S_{eq} + S_{kin} = \sum_{i=1}^{f} a_i I_i - \frac{1}{2} \sum_{i,k=1}^{f} m_{ik} J_i \cdot J_k.$$  \hspace{1cm} (1.1)

Here $[m_{ik}]$ is the matrix of general inductivities which is positive definite$^1$, $a_i$
are generalized co-ordinates while $I_i$ are generalized conjugated thermostatic
forces (Gyarmati [4], [5], Fekete [13]). Starting from (1.2) we can calculate the
balance equation of entropy which in a convection free system would be

$$\frac{\partial S}{\partial t} + \sum_{i=1}^{f} \nabla \cdot (I_i J_i) = \sum_{i=1}^{f} J_i \cdot \left( \nabla I_i - \sum_{k=1}^{f} m_{ik} \frac{\partial J_k}{\partial t} \right)$$

$$= \sum_{i=1}^{f} J_i \cdot \bar{E}_i = \sigma \geq 0.$$ \hspace{1cm} (1.3)

Here $\bar{E}_i = \nabla I_i - \sum_{k=1}^{f} m_{ik} \frac{\partial J_k}{\partial t}$ is the new thermodynamic force incorporating
both dissipative and inertial effects. Now if a linear relation between the thermo-
dynamical force $E_i$ and the flux $J_i$ is valid then we have

$$J_i = \sum_{k=1}^{f} L_{ik} \bar{E}_k,$$  \hspace{1cm} (1.4)

where $[\tau_{ik}] = \left[ \sum_{k=1}^{f} L_{ik} m_{ik} \right]$ is the matrix of relaxation constant and in general
is a measure of time scale which is necessary to drive the system from non-local
to local equilibrium state (Nonnenmacher [14]). Eq. (1.4) is the generalization
of Cattaneo-Vernotte [15], [16] type of constitutive equations which were first
proposed to resolve the paradox of an infinite propagation velocity of the tem-
perature disturbance in a solid. However, it may be mentioned that unlike
several earlier investigations this constitutive equation is not presumed from

$^1$ (Gyarmati [5] prefers to work with a negative definite matrix $[m_{ik}]$ and the exact
relationship between the two matrices is $[m_{ik}] = -[m_{ik}^2]$).