

HEAT CONDUCTION WITH RELAXATIONS

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Introduction

The main concept of the thermodynamic theory of relaxations is to introduce—besides the well-known external variables of state—the existence of so-called internal variables of state [1, 2, 3, 6]. The internal state variables are to give an over-all description of microscopic processes having influence on the macroscopic properties of the system investigated. The theory does not require an exact knowledge of the mechanisms of the molecular processes, a few main features of them are enough to apply the formalism of non-equilibrium thermodynamics as far as it is needed for getting an exact picture of the macroscopic processes influenced by relaxations. So this theory has a wider range of validity than the statistical mechanical theories.

In this paper the heat conduction influenced by relaxation phenomena is investigated. The principle of local states is supposed and so the fields of local state variables are used. Moreover the existence of local specific entropy, which is a unique function of local state variables, is presumed [1, 2, 3; 5, 17].

1. Relaxations in closed systems

Let us consider a body, the equilibrium states of which are described by the internal energy, but out of equilibrium more variables are needed. The specific entropy s is given as a function of the specific internal energy u and a number of the internal variables:

$$s = s(u, \xi_1, \xi_2, \dots, \xi_K) \quad (1)$$

During processes in a homogeneous closed system the internal energy does not change, only the internal co-ordinates vary. When the system has reached the equilibrium its entropy is a maximum and the internal variables take their equilibrium values. A suitable choice of the internal parameters yields a simple form for (1) [6, 8]:

$$s = s_0(u) - \frac{1}{2} \sum_{j=1}^K \xi_j^2. \quad (2)$$

From (2) the actual form of the entropy production is

$$\varrho \dot{s} = \sigma_s = -\varrho \sum_{j=1}^K \xi_j \dot{\xi}_j. \quad (3)$$

The linear Onsager laws are the differential equations describing the relaxation phenomena. Since no effect of inertia is intended to be considered, the Onsager reciprocal relations hold [2, 6, 7], and no Casimir's relations occur. For this reason, the differential equations mentioned can be given in a diagonalized form (see e.g. in [8]):

$$\varrho \dot{\xi}_j = -L_j \xi_j. \quad (4)$$

The processes can only be considered as simultaneous relaxations if inertiae are omitted.

2. The homothermic relaxations

a) The first type of homothermic relaxations

The processes during which a unique thermodynamic temperature exists and the relations

$$\frac{\partial s}{\partial u} = \vartheta = \frac{1}{T} \quad \text{and} \quad \vec{J}_s = \vartheta \vec{J}_q \quad (5)$$

hold belong the first type of homothermic relaxations. The balance equations for the internal energy and for the entropy have the customary forms:

$$\varrho \dot{u} + \text{div } \vec{J}_q = 0 \quad (6)$$

and

$$\varrho \dot{s} + \text{div } \vec{J}_s = \sigma_s \geq 0. \quad (7)$$

Combining (5), (6), (7) and (2) we get the actual form of the entropy production:

$$\sigma_s = \vec{J}_q \text{ grad } \vartheta - \varrho \sum_{j=1}^K \xi_j \dot{\xi}_j. \quad (8)$$

The linear laws, which have to lead to (4) when heat conduction is absent, are

$$\vec{J}_q = L_{qq} \text{ grad } \vartheta - \sum_{j=1}^K L_{qj} \xi_j \quad (9)$$

$$\varrho \dot{\xi}_j = L_{qj} \text{ grad } \vartheta - L_j \xi_j. \quad (10)$$

In the case of an isotropic body the coefficients L_{qj} are non-zero if and only if the internal variables ξ_j are vectors [6, 7]. For this reason, in the case of the first type of homothermic relaxations, only the vectorial internal variables are important, the equations for all the others are homogeneous, their solutions do not depend on any boundary condition. The internal co-ordinates with no vector character tend to zero during the processes, and they will not be generated any more.

In the simplest case, the body needs a single internal variable, $K = 1$. The constitutive equation for the heat current density arises by eliminating ξ_1 from (9) and (10):

$$\varrho \dot{\vec{J}}_q + L_1 \vec{J}_q = \varrho L_{qq} \text{grad } \vartheta + (L_1 L_{qq} - L_{q1}^2) \text{grad } \vartheta' \quad (11)$$

Introducing (11) into (6) we get the equation of heat conduction:

$$-\varrho^2 \ddot{u} - L_1 \varrho \dot{u} = \varrho L_{qq} \Delta \dot{\vartheta} + (L_1 L_{qq} - L_{q1}^2) \Delta \vartheta. \quad (12)$$

b) *The second type of homothermic relaxations*

The processes during which the entropy current is proportional to the heat current, but the factor of proportion differs from the derivative of the entropy with respect to the internal energy belong to the second type of homothermic relaxations. Instead of (5) we have

$$\frac{\partial s}{\partial u} = \vartheta^e = \frac{1}{T^e} \quad \text{and} \quad \vec{J}_s = \vartheta \vec{J}_q \quad (13)$$

where T^e is the thermodynamic temperature of the body in an equilibrium state with the same internal energy and ϑ is the reciprocal value of the so-called Meixner temperature [5, 11, 4]. The balance equations for the internal energy and the entropy — (6) and (7) respectively — do not change. Combining (2), (6), (7) and (13) we get the actual form of entropy production:

$$\sigma_s = \vec{J}_q \text{grad } \vartheta + (\vartheta - \vartheta^e) \text{div } \vec{J}_q - \varrho \sum_{j=1}^K \xi_j \dot{\xi}_j. \quad (14)$$

Since the factor $(\vartheta - \vartheta^e)$ occurring here must equal zero in the state of local equilibrium, it is well approximated by

$$\vartheta - \vartheta^e = - \sum_{j=1}^K \gamma_j \xi_j \quad (15)$$

not too far from a local equilibrium state. For an isotropic body, only the scalar

internal parameters appear in (15), so scalars are taken care of alone. The equation (15) permits to simplify (14) to

$$\sigma_s = \vec{J}_q \text{grad } \vartheta - \sum_{j=1}^K \xi_j (\varrho \dot{\xi}_j + \gamma_j \text{div } \vec{J}_q). \quad (16)$$

The Onsager laws are given in the forms of

$$\vec{J}_q = L_{qq} \text{grad } \vartheta = L_{qq} \text{grad } \left(\vartheta^e - \sum_{j=1}^K \gamma_j \xi_j \right) \quad (17)$$

and

$$\varrho \dot{\xi}_j + \gamma_j \text{div } \vec{J}_q = -L_j \xi_j. \quad (18)$$

These equations are analogous to those of heat conduction in a chemically reacting body, moreover give a good description of heat conduction in colloidal systems.

3. Heterothermic relaxations

There is a close connection between the heat current and the entropy current in the case of the heterothermic relaxations too, but it is more involved than in (13). The heat conduction is supposed to be a result of a number of different processes,

$$\vec{J}_q = \sum_{n=1}^N \vec{J}_n \quad (19)$$

and each part of the heat flux joins an entropy flux in the usual way. This is the situation in plasmas where electrons as well as ions take part in the heat conduction at different temperatures, moreover in difform systems and in some kind of mixtures [15, 16]. The balance equation of the entropy turns into

$$\varrho \dot{s} + \text{div} \left(\sum_{n=1}^N \vartheta_n \vec{J}_n \right) = \sigma_s \geq 0. \quad (20)$$

Substituting (2) and (6) into (20) yields σ_s ,

$$\sigma_s = \sum_{n=1}^N \vec{J}_n \text{grad } \vartheta_n + \sum_{n=1}^N (\vartheta_n - \vartheta^e) \text{div } \vec{J}_n - \varrho \sum_{j=1}^K \xi_j \dot{\xi}_j. \quad (21)$$

The factors $(\vartheta_n - \vartheta^e)$ occurring here can be given in forms similar to (15):

$$\vartheta_n - \vartheta^e = - \sum_{j=1}^K \gamma_{nj} \xi_j. \quad (22)$$

These relations simplify (21) to

$$\sigma_s = \sum_{n=1}^N \vec{J}_n \text{grad } \vartheta_n - \sum_{j=1}^K \xi_j \left(\varrho \dot{\xi}_j + \sum_{n=1}^N \gamma_{nj} \text{div } \vec{J}_n \right). \quad (23)$$

The Onsager-laws have the forms of

$$\vec{J}_n = \sum_{k=1}^N L_{nk} \text{grad } \vartheta_k \quad (24)$$

and

$$\varrho \dot{\xi}_j + \sum_{n=1}^N \gamma_{nj} \text{div } \vec{J}_n = -L_j \xi_j. \quad (25)$$

Eq. (25) are similar to the balance equations, they describe the transports of internal degrees of freedom. Eqs (24) and (25), together with (6) and (22), form a system of partial differential equations that can be solved when the proper initial and boundary conditions are known.

4. Remarks on the effects of inertia

Till now no effects of inertia have been considered, so all the internal variables were even with respect to time reversal. From a theoretical point of view, no circumstance prevents the occurrence of odd internal parameters. An analysis of (15) and (22) shows that no odd internal parameter can occur in them, and so the inertia of processes can play no central role either in the heterothermic relaxations or in the second type of homothermic relaxations. Hence the first type of homothermic relaxations with vectorial internal variables has been left to investigate. For the sake of simplicity the case of an only internal parameter will be restricted to which is odd with respect to time reversal. The argumentation in item 2a is still valid but the Onsager reciprocal relation turns to Casimir's one. Eqs (5), (6), (7) and (8) with $K = 1$ hold and the linear laws become

$$\vec{J}_q = L_{qq} \text{grad } \vartheta - L_{q1} \vec{\xi}_1 \quad (26)$$

$$\varrho \dot{\xi}_1 = -L_{q1} \text{grad } \vartheta - L_1 \vec{\xi}_1 \quad (27)$$

if the body is isotropic. Eliminating $\vec{\xi}_1$ we get the constitutive equation for the heat current density:

$$\varrho \dot{\vec{J}}_q + L_1 \vec{J}_q = \varrho L_{qq} \text{grad } \vartheta + (L_1 L_{qq} + L_{q1}^2) \text{grad } \vartheta. \quad (28)$$

This equation is very like (11), but the sign of L_{q1}^2 in the last term is different, still this difference is significant enough. Namely, as a consequence of

entropy production being positive definite, the coefficients both in (11) and in (28) are positive. Hence L_{qq} in (11) can only be zero if the body is unable to conduct heat because the disappearance of L_{qq} involves the disappearance of the coefficient of $\text{grad } \vartheta$ as well. The case in (28) is quite different. Here L_{qq} may equal zero, while L_{q1} has a finite value. In this way (28) reduces to

$$\rho \dot{\vec{J}}_q + L_1 \vec{J}_q = L_{q1}^2 \text{grad } \vartheta \quad (29)$$

which leads to an equation of heat conduction of the form

$$-\rho^2 \ddot{u} - \rho L_1 \dot{u} = L_{q1}^2 \Delta \vartheta. \quad (30)$$

This equation is analogous to that proposed by CATTANEO [18] and VERNOTTE [19], and does not lead to an infinite velocity of temperature propagation. An analysis of the equations of heat conduction obtained shows that odd internal parameters are needed for avoiding the infinite velocity of temperature propagation.

Summary

This paper is concerned with the phenomenon of heat conduction influenced by relaxation. The processes are classified within the framework of Onsagerian thermodynamics. The argumentation includes a generalization with respect to temperature and bodies with several temperatures are dealt with. Finally, some effects of inertia are discussed.

References

1. KÄSTNER, S.: Zur Theorie der Relaxation I—II—III. *Ann. Phys.* (7) **1**, 377 (1958); (7) **2**, 146 (1958); (7) **3**, 82 (1959)
2. MEIXNER, J.—REIK, H. G.: *Thermodynamik der irreversiblen Prozesse*, in: *Encyclopedia of Physics*. Vol III/2, p. 413. Springer Verlag, Berlin 1959
3. MÜSER, H. E.—PETERSSON, J.: *Thermodynamic Theory of Relaxation Phenomena*. *Fortschritte der Physik* **19**, 559 (1971)
4. BATAILLE, I.—KESTIN, J.: L'interprétation physique de la thermodynamique rationnelle. *Journal de Mécanique* **14**, 365 (1975). General Forms of the Dissipation Inequality. *J. Non-Equilib. Thermodyn.* **1** (1976) 25
5. MEIXNER, J.: On the Foundation of Thermodynamics of Processes, in: *A Critical Review of Thermodynamics*, p. 37. Mono Book Corp. Baltimore 1970
The Entropy Problem in Thermodynamics of Processes. *Rheol. Acta.* **12**, 465 (1973)
6. DE GROOT, S. R.—MAZUR, P.: *Non-equilibrium Thermodynamics*. North-Holland Publ. Co. Amsterdam 1962
7. GYARMATI, I.: *Non-equilibrium Thermodynamics*. Springer, Verlag, Berlin Heidelberg, New York 1970.
8. GANTMACHER, F. R.: *Theory of Matrices*. Vol. I. Chelsea Publ. Co. New York 1959
9. FARKAS, H.: On the Phenomenological Theory of Heat Conduction. *Int. J. Engng. Sci.* **13**, 1035—1053 (1975)
10. FARKAS, H.—NOSZTICZIUS, Z.: On the Non-linear Generalization of the Gyarmati Principle and Theorem. *Ann. der Phys.* **7/27**, 341—348 (1971)
11. MEIXNER, J.: On the Linear Theory of Heat Conduction. *Arch. Rat. Mech. Anal.* **29**, 108—130 (1970)
12. MÜLLER, I.: Die Kältefunktion, eine universelle Funktion in der Thermodynamik viskoser wärmeleitender Flüssigkeiten. *Arch. Rat. Mech. Anal.* **40**, 1—36 (1971)

13. VINCZE, Gy.: Heat Conduction in Solids, Reports 1973 of the Agricultural University, Gödöllő
14. TEMKIN, A. G.: Discrete Formulation of Heat Conduction and Diffusion Equations. *Int. J. Heat Mass Transfer.* **19**, 785—789 (1976)
15. BOWEN, R. M.—CARCIA, D. J.: On the Thermodynamics of Mixtures with Several Temperatures, *Int. J. Engng. Sci.* **8**, 63—83 (1970)
16. BATAILLE, J.—KESTIN, J.: Thermodynamics of Mixtures. *J. Non-Equilibrium Thermodyn.* **2**, 49—65 (1977)
17. WILMANSKI, K.: On Thermodynamics and Functions of States of Nonisolated Systems. *Arch. Rat. Mech. Anal.* **45**, 251—281 (1972)
18. CATTANEO, C.: *Atti del seminario matematico e fisico dell'a Università di Modena* **3** (1948)
19. VERNOTTE, P.: Les paradoxes de la théorie de l'équation de la chaleur. *Comptes Rend.* **246**, 3154 (1958)
20. GYARMATI, I.: On the Wave Approach of Thermodynamics and some Problems of Non-Linear Theories. *J. Non-Equilib. Thermodyn.* **2**, 233—260 (1977)

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