SOME NON-LINEAR RECIPROCAL RELATIONS

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Abstract

The validity of the anti-symmetric reciprocal relation can be proved for non-linear constitutive equations generally if it holds in the linear approximation. The constitutive equations may be formulated so that the coefficients of the main effects are positive.

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1. Introduction

A number of practically important applications of non-equilibrium thermodynamics leads to a two-variable problem; with two thermodynamic fluxes and two forces [1 – 6]. Usually, this is the situation when studying the machines of energy transformation, e.g., heat engines [7 – 10], electric motors or generators, etc. If the reversible limit case has importance it is very convenient to choose the independent variables so that the reciprocal relation in the realm of linearity is anti-symmetry;

$$L_{21} = -L_{12} \ . \tag{1}$$

The inequalities

$$L_{11} > 0 \qquad \text{and} \qquad L_{22} > 0 \tag{2}$$

express the second law and the inequalities turn into equalities in the reversible limit. It is very useful to know that the constitutive equations can be put into the customary form [1, 2, 11–13],

$$\begin{aligned} I_1 &= L_{11}X_1 + L_{12}X_2, \\ I_2 &= L_{21}X_1 + L_{22}X_2 \ , \end{aligned} \tag{3}$$

even in the non-linear regime and the relations (1) and (2) for the L coefficients (depending on the independent variables X_1 and X_2) can be preserved. The non-linear generalization of Onsager's reciprocal relations by

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HURLEY – GARROD [14, 15], and VERHÁS [16] ensures the validity of the inequalities (2) only for an open set around the equilibrium.

Non-linear thermodynamic modelling needs some further support replacing the linear approachability of continuously differentiable functions [17]. When looking for this support the above facts (to be proved) are helpful.

2. A Lemma

The proof is based on the lemma:

> If a continuously differentiable multi-variable function $F(x_1, x_2, \ldots, x_n)$ is zero if all the independent variables are zero, it can be given in the form
>
> $$F(x_1, x_2, \ldots, x_n) = a_1 x_1 + a_2 x_2 + \ldots + a_n x_n, \tag{4}$$
>
> where $a_1, a_2, \ldots, a_n$ are continuous functions of $x_1, x_2, \ldots, x_n$. The functions $a_1, a_2, \ldots, a_n$ are not determined uniquely.

The proof of the lemma is based on Lagrange's mean value theorem. The auxiliary function

$$G(\xi) = F(\xi x_1, \xi x_2, \ldots, \xi x_n)$$

satisfies the equalities

$$G(0) = 0 \qquad \text{and} \qquad G(1) = F(x_1, x_2, \ldots, x_n),$$

from which

$$F(x_1, x_2, \ldots, x_n) = G(1) = \frac{G(1) - G(0)}{1 - 0} = \left.\frac{\mathrm{d}G}{\mathrm{d}\xi}\right|_{0<\xi<1}$$

$$= \left.\frac{\partial F}{\partial x_1}\right|_{0<\xi<1} x_1 + \left.\frac{\partial F}{\partial x_2}\right|_{0<\xi<1} x_2 + \cdots + \left.\frac{\partial F}{\partial x_n}\right|_{0<\xi<1} x_n$$

follows.

3. The Sketch of the Proof

Assume a two-variable problem for which the reciprocal relation in the linear approximation is anti-symmetric;

$$\begin{aligned} I_1 &= I_1(X_1, X_2), \\ I_2 &= I_2(X_1, X_2) \end{aligned} \tag{5}$$

with

$$\left.\frac{\partial I_1}{\partial X_2}\right|_{X_1=X_2=0} + \left.\frac{\partial I_2}{\partial X_1}\right|_{X_1=X_2=0} = 0 \ . \tag{6}$$

Applying the lemma, we can write

$$\begin{aligned} I_1 &= A(X_1,\ X_2)X_1 + B(X_1,\ X_2)X_2, \\ I_2 &= C(X_1,\ X_2)X_1 + D(X_1,\ X_2)X_2, \end{aligned} \tag{7}$$

with

$$B(0,0) + C(0,0) = 0 \ . \tag{8}$$

Applying the lemma again, we get

$$B(X_1,\ X_2) + C(X_1,\ X_2) = E(X_1,\ X_2)X_1 + F(X_1,\ X_2)X_2 \ .$$

Having eliminated C, the entropy inequality reads

$$\sigma_s = (A + EX_2)X_1^2 + (FX_1 + D)X_2^2 \geq 0 \ . \tag{9}$$

If one of the two terms (say the second) is negative the inequality

$$(A + EX_2)X_1^2 > -(FX_1 + D)X_2^2$$

holds out of equilibrium. It makes possible to choose a function H so that the expression $H(X_1,\ X_2)X_1^2X_2^2$ is between the two sides;

$$(A + EX_2)X_1^2 > HX_1^2X_2^2 > -(FX_1 + D)X_2^2 \ ,$$

from which the inequalities

$$\begin{aligned} (A + EX_2 - HX_2^2)X_1^2 &> 0 \ , \\ (FX_1 + D + HX_1^2)X_2^2 &> 0 \end{aligned} \tag{10}$$

follow. *Eqs.* (3.3) can be cast into the form

$$I_1 = (A + EX_2 - HX_2^2)X_1 + (+B - EX_1 + HX_1X_2)X_2 \ ,$$

$$I_2 = (-B + EX_1 - HX_1X_2)X_1 + (D + FX_1 + HX_1^2)X_2 \ .$$

Introducing the notations

$$\begin{aligned} L_{11} &= A + EX_2 - HX_2^2 \ , & L_{12} &= B - EX_1 + HX_1X_2 \ , \\ L_{21} &= -B + EX_1 - HX_1X_2 \ , & L_{22} &= D + FX_1 + HX_1^2 \ , \end{aligned}$$

we obtain the usual form as given in equations (3) together with the reciprocal relation (1) and the inequalities (2) for sufficiently smooth constitutive equations.

References

[1] DE GROOT, S. R. (1951): Thermodynamics of Irreversible Processes, North-Holland Publ. Co., Amsterdam.
[2] DE GROOT, S. R. – MAZUR, P. (1962): Non-equilibrium Thermodynamics, North-Holland Publ. Co., Amsterdam.
[3] GYARMATI, I. (1970): Non-Equilibrium Thermodynamics, Springer, Berlin.
[4] JOU, D. – CASAS-VASQUEZ J. – LEBON, G. (1993): Extended Irreversible Thermodynamics, Springer, New York, Berlin.
[5] MEIXNER, J. – REIK, H. G. (1959): Thermodynamik der Irreversiblen Processe *Handbuch der Physik*, Vol. III/2, pp. 413, Springer, Berlin.
[6] MÜLLER, I. (1985): Thermodynamics, Pitman Publ. Co., London.
[7] BEJAN, A. (1994): Entropy Generation through Heat and Fluid Flow, 2nd ed., J. Wiley, New York.
[8] CURZON, F. – AHLBORN, B. (1975): Efficiency of a Carnot Engine at Maximum Power Output, *Am. J. Phys.*, Vol. 43, pp. 22–24.
[9] NOVIKOV, I. (1957): Effectivyi koefficient poleznovo deystvia atomnoy energeticeskoj ustavki, *Atomnaya Energiya*, Vol. 3, pp. 409–412.
(1958): The Efficiency of Atomic Power Stations, *J. Nucl. Energy*, Vol. II. 7, pp. 125–128.
[10] DE VOSS, A. (1992): Endoreversible Thermodynamics of Solar Energy Conversion, Oxford University Press, Oxford.
[11] ONSAGER, L. (1931): Reciprocal Relations in Irreversible Processes I. *Phys. Rev.*, Vol. 37, pp. 405–426.
[12] ONSAGER, L. (1931): Reciprocal Relations in Irreversible Processes II. *Phys. Rev.*, Vol. 38, pp. 2265–2279.
[13] ONSAGER, L. – MACLUP, S. (1953): Fluctuations and Irreversible Processes. *Phys. Rev.*, Vol. 91, pp. 1505–1512.
[14] GARROD, C. – HURLEY, J. (1983): Symmetry Relations for the Conductivity Tensor. *Phys. Rev.*, Vol. A 27, pp. 1487–1490.
[15] HURLEY, J. – GARROD, C. (1982): Generalization of the Onsager Reciprocity Theorem. *Phys. Rev. Lett.*, Vol. 48, pp. 1575–1577.
[16] VERHÁS, J. (1983): An Extension of the Governing Principle of Dissipative Processes to Non-linear Constitutive Equations. *Ann. d. Phys.*, Vol. 7/40, pp. 189–193.
[17] NYÍRI, B. (1988): A Non-linear Extension of the Local Form of Gyarmati's Governing Principle of Dissipative Processes. *Acta Phys. Hung.*, Vol. 63, pp. 13–16.