Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

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From microscopic to macroscopic reversibility

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **66** (1979), n.6, p. 540–547.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1979_8_66_6_540_0>

Fisica matematica. — *From microscopic to macroscopic reversibility* (*). Nota di ANGELO MORRO, presentata (**) dal Socio D. GRAFFI.

RIASSUNTO. — Partendo dalla reversibilità microscopica, nella forma delle relazioni di Onsager–Casimir per la matrice di autocorrelazione, si perviene ad un preciso enunciato di reversibilità macroscopica. Il procedimento seguito applica in un modo non usuale un'idea dovuta a Callen e Greene e già utilizzata nella dimostrazione del teorema di dissipazione delle fluttuazioni. Come risultato intermedio si mostra che valgono relazioni di reciprocità per funzioni di rilassamento purchè le variabili corrispondenti risultino coniugate all'equilibrio.

1. INTRODUCTION

This note deals with the search of a connection between microscopic and macroscopic reversibilities. Such a possible connection, besides being interesting on its own, is needed for warranting the use of reciprocity relations in Continuum Thermodynamics. Indeed, since the famous works by Onsager [1] in 1931, the reciprocity relations have been considered extensively in the framework of constitutive equations simply by appealing to microscopic reversibility.

In a paper by Day [2], appeared in 1971, reciprocity relations are exhibited without having recourse to microscopic reversibility. Precisely, Day considered an anisotropic linear viscoelastic material and showed that the stress-strain relaxation function $\mathbf{G}(t)$ is symmetric for every t in $0 \leq t \leq \infty$ if and only if the work done on every closed path starting from the virgin state is invariant under time-reversal. The importance of Day's paper is that it yields a characteristic condition for the symmetry of $\mathbf{G}$ while it is well known that this result cannot be obtained through compatibility with thermodynamics. In fact, as shown by Coleman [3] in his theory of thermodynamics for materials with memory, the work done by the stress is non-negative on every isothermal strain path which starts from an equilibrium state of constant strain. As a consequence of this restriction Day [4] proved that the instantaneous elastic modulus $\mathbf{G}(0)$ and the equilibrium elastic modulus $\mathbf{G}(\infty)$ must both be symmetric but [5] $\mathbf{G}(t)$ need not be symmetric for every t in $0 < t < \infty$.

Subsequently Gurtin [6], in connection with thermo-viscoelasticity, introduced a principle of macroscopic reversibility through the invariance of the entropy production under time-reversal. The same invariance assump-

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(*) This work was supported by the "Gruppo Nazionale per la Fisica Matematica" of C.N.R.

(**) Nella seduta del 14 giugno 1979.

tion has been investigated by Borghesani and myself in some papers concerning linear [7] and non-linear [8] thermo-galvano-magnetic effects and thermo-viscoelasticity [9].

Such a macroscopic reversibility appeared to be independent of microscopic reversibility. Recently, however, an important bridge has been built by Meixner [10] who achieves two principles of macroscopic reversibility from microscopic reversibility by translating the problem into the frequency domain. Here a further little bridge is built borrowing from a method of Callen and Greene used for deriving the fluctuation dissipation theorem [11]. The resulting procedure turns out to be more direct than the analogous ones in the frequency domain. The main result is that reciprocity relations for the aftereffect matrices hold provided forces and fluxes (i.e. responses) are conjugate variables at equilibrium. Moreover it is shown that the invariance of the work under time-reversal considered by Day [2] is a straightforward consequence of microscopic reversibility.

2. AN OUTLINE OF MICROSCOPIC REVERSIBILITY

The time evolution of a body is examined through a corresponding microcanonical ensemble M whose elements are termed systems. The ensemble M is associated with an open subset Γ (sample space) of a finite dimensional vector space and a probability measure μ defined on Γ by a probability density $f \in C^1(\Gamma, \mathbf{R}^+)$. So, letting $\boldsymbol{x} \in \Gamma$ stand for the specific value of the state variables, for every open subset $\Xi \subset \Gamma$ we have

$$\mu(\Xi) = \int_{\Xi} f(\boldsymbol{x})\, \mathrm{d}x$$

$\mathrm{d}x$ being the volume element in Ξ. The mean value $\langle \boldsymbol{x} \rangle = \boldsymbol{x}_0$ of $\boldsymbol{x} \in \Gamma$ is defined by

$$\boldsymbol{x}_0 = \int_{\Gamma} \boldsymbol{x} f(\boldsymbol{x})\, \mathrm{d}x .$$

Introduce now the distribution function w of the fluctuation $\xi = \boldsymbol{x} - \boldsymbol{x}_0$, related to f by

$$w(\xi) = f(\boldsymbol{x}_0 + \xi),$$

subject to the requirement

$$w = 0 \quad \text{on} \quad \partial\Omega \tag{2.1}$$

being $\Omega = \Gamma - \boldsymbol{x}_0$. Then we can define the ensemble average $\langle \phi\, \psi \rangle$ of any two functions $\phi, \psi \in C^1(\Omega)$ in the form

$$\langle \phi\, \psi \rangle = \int_{\Omega} \phi(\xi)\, \psi(\xi)\, w(\xi)\, \mathrm{d}\xi . \tag{2.2}$$

As a function of time, the fluctuation of a system in M is given by a stationary stochastic process $\xi \in C^2(\mathbf{R}, \Omega)$; the symbol $\langle \tau ; \xi' \mid \xi \rangle$ denotes the value of the fluctuation ξ of a system at time τ after the fluctuation of the same system had the value ξ'. Accordingly the autocorrelation matrix $\varrho(\tau) = \langle \xi(t)\, \xi(t+\tau) \rangle$ can be written as

$$\varrho(\tau) = \int_{\Omega} \xi' \langle \tau ; \xi' \mid \xi \rangle\, w(\xi)\, d\xi' . \tag{2.3}$$

For later reference, introduce now an assumption whose plausibility is widely accepted in the physical literature—see, e.g., [12], Chs. 1,12.

The distribution function w *is related to the specific entropy function* $\eta \in C^2(\Gamma, \mathbf{R})$ *by*

$$w(\xi) = \text{const. } \exp(\eta(\boldsymbol{x}_0 + \xi)/k)$$

k being the Boltzmann constant.

As a consequence, on defining the generalised forces σ by $\sigma = \partial\eta/\partial\boldsymbol{x}$ we have

$$\sigma = k \frac{\partial \ln w}{\partial \xi}$$

and hence, in view of (2.1), an integration by parts yields

$$\langle \xi \sigma \rangle = k \int_{\Omega} \xi \frac{\partial \ln w}{\partial \xi}\, w\, d\xi = -kI_{\Omega} . \tag{2.4}$$

Given a fixed time t, time-reversal relative to t means the time change $t + \tau \rightarrow t - \tau$, $\tau \in \mathbf{R}$. The corresponding change of the even variables ξ_α is $\xi_\alpha(t+\tau) \rightarrow \xi_\alpha(t-\tau)$ while that of the odd variables ξ_β is $\xi_\beta(t+\tau) \rightarrow -\xi_\beta(t-\tau)$. This is summarised by the transformation

$$\xi(t+\tau) \rightarrow \tilde{\xi}(t+\tau) = \varepsilon\, \xi(t-\tau) \tag{2.5}$$

ε being the diagonal matrix whose elements are 1 or -1 according as the corresponding variable is even or odd; for example, if ξ_i is odd then $\varepsilon_{ii} = -1$. The fundamental result of Onsager and Casimir's theory is that, in view of the invariance of the microscopic equations of motion under time-reversal, the autocorrelation matrix is required to satisfy the condition

$$\langle \xi(t)\, \xi(t+\tau) \rangle = \varepsilon \langle \xi(t+\tau)\, \xi(t) \rangle\, \varepsilon . \tag{2.6}$$

As a final remark, it is worth noticing that in the present paper no appeal is made to time averages and hence no assumption is needed about whether the ensemble M is ergodic—see, e.g., [13] Ch. 1.

3. TOWARD MACROSCOPIC REVERSIBILITY

As a first step along the road to macroscopic reversibility we need a link between the microscopic and the macroscopic behaviour of a body. Such a link is assumed here in a form due to Callen and Greene [11].

Upon identifying the state variables $\boldsymbol{x} \in \Gamma$ with the response of the body, we imagine that the distribution of fluctuations at time t in M is prepared via suitable contraints—forces—on each system. Moreover these contraints are to be such that each system is in a state of equilibrium. At the time t the constraints are lifted and we determine the expectation value $\langle \tau ; \boldsymbol{\xi}' \mid \boldsymbol{\xi} \rangle$ by assuming that the beaviour of a system is given by the (macroscopic) constitutive equation.

To make this point precise denote by σ the forces and assume the validity of $\sigma = \partial\eta/\partial\boldsymbol{x}$ at equilibrium, that is when $\boldsymbol{x}$ and σ are constant in time. Suppose now that the response is given by a linear functional so that we can write

$$\boldsymbol{\xi}(t) = \mathbf{J}_0 \boldsymbol{s}(t) + \int_0^\infty \mathbf{J}(\zeta)\, \boldsymbol{s}(t-\zeta)\, d\zeta \tag{3.1}$$

being $\boldsymbol{s} = \sigma - \sigma_0$, $\sigma_0 = (\partial\eta/\partial\boldsymbol{x})(\boldsymbol{x}_0)$. Each system undergoes a constant constraint, $\boldsymbol{s} = \boldsymbol{s}'$ say, up to time t and afterwards $\boldsymbol{s} = 0$. Accordingly we have

$$\boldsymbol{\xi}(t+\tau) = \boldsymbol{j}(\tau)\, \boldsymbol{s}'$$

where

$$\boldsymbol{j}(\tau) = \int_\tau^\infty \mathbf{J}(\zeta)\, d\zeta .$$

Letting $\boldsymbol{\xi}' = (\mathbf{J}_0 + \boldsymbol{j}(0))\, \boldsymbol{s}'$, (2.6) implies that

$$\int_\Omega \{\boldsymbol{\xi}' (\boldsymbol{j}(\tau)\, \boldsymbol{s}')\}\, w(\boldsymbol{\xi}')\, d\xi' = \int_\Omega \varepsilon \{(\boldsymbol{j}(\tau)\, \boldsymbol{s}')\, \boldsymbol{\xi}'\}\, \varepsilon\, w(\boldsymbol{\xi}')\, d\xi' . \tag{3.2}$$

Since $\boldsymbol{s}' = \partial\eta/\partial\boldsymbol{\xi}' - \sigma_0$ and $\langle \boldsymbol{\xi}' \sigma_0 \rangle = 0$, (3.2) yields

$$\boldsymbol{j}(\tau) = \varepsilon\, \boldsymbol{j}^{\mathrm{T}}(\tau)\, \varepsilon , \qquad \tau \in \mathbf{R}^+ ; \tag{3.3}$$

differentiation with respect to τ delivers the result

$$\mathbf{J}(\tau) = \varepsilon\, \mathbf{J}^{\mathrm{T}}(\tau)\, \varepsilon , \qquad \tau \in \mathbf{R}^+ .$$

An interesting consequence of (3.3) may be derived as follows. Consider the tensor function $\mathbf{K}$, on $\mathbf{R}^+$, defined by

$$\dot{\mathbf{K}}(\zeta) = \mathbf{J}(\zeta) \quad , \quad \mathbf{K}(0) = 0 .$$

In view of (3.3) it follows at once that

$$\mathbf{K}(\tau) = \varepsilon\,\mathbf{K}^{\mathrm{T}}(\tau)\,\varepsilon\,, \qquad \tau \in \mathbf{R}^{+}\,. \tag{3.4}$$

Then the response $\boldsymbol{x}$ may be expressed in the form

$$\boldsymbol{x}(t) = \mathbf{J}_0\,\sigma(t) - \mathbf{K}(\infty)\,\sigma(-\infty) + \int_0^\infty \mathbf{K}(\zeta)\,\sigma(t-\zeta)\,\mathrm{d}\zeta\,. \tag{3.5}$$

In connection with the case of constant histories we see that (3.5) is meaningful only if $\mathbf{J}_0$ and $\mathbf{K}(\infty)$ exhibit the same behaviour under time-reversal, that is

$$\mathbf{J}_0 = \varepsilon\,\mathbf{J}_0^{\mathrm{T}}\,\varepsilon\,. \tag{3.6}$$

Restricting now our attention to finite processes, that is to say $\sigma(-\infty) = \sigma(\infty) = 0$, we have

$$\Delta\{\sigma(\cdot)\} = \int_{-\infty}^{\infty} \sigma(t)\cdot\dot{\boldsymbol{x}}(t)\,\mathrm{d}t = -\int_{-\infty}^{\infty} \dot{\sigma}(t)\cdot\boldsymbol{x}(t)\,\mathrm{d}t\,.$$

Examine now the properties of Δ against time-reversal. Assuming that σ behaves like $\boldsymbol{x}$ under time-reversal, namely

$$\tilde{\sigma}(\zeta) = \varepsilon\,\sigma(-\zeta)\,,$$

a straightforward calculation yields

$$\Delta\{\sigma(\cdot)\} - \Delta\{\tilde{\sigma}(\cdot)\} =$$

$$= \int_{-\infty}^{\infty} \dot{\sigma}(t)\cdot(\varepsilon\,\mathbf{J}_0^{\mathrm{T}}\,\varepsilon - \mathbf{J}_0)\,\sigma(t)\,\mathrm{d}t + \int_{-\infty}^{\infty}\int_0^{\infty} \dot{\sigma}(t)\cdot(\varepsilon\,\mathbf{K}^{\mathrm{T}}(\tau))\,\varepsilon - \mathbf{K}(\tau))\,\sigma(t-\tau)\,\mathrm{d}\tau\,\mathrm{d}t\,.$$

As a consequence of (3.4), (3.6) the right hand side vanishes identically. So we can state the following

THEOREM. *If $\boldsymbol{x}$ and σ are conjugate variables at equilibrium and the response functional is linear,*

$$\boldsymbol{x}(t) = \mathbf{J}_0\,\sigma(t) + \int_0^\infty \mathbf{J}(\tau)\,\sigma(t-\tau)\,\mathrm{d}\tau\,,$$

microscopic reversibility implies the condition

$$\mathbf{J}(\tau) = \varepsilon\,\mathbf{J}^{\mathrm{T}}(\tau)\,\varepsilon\,, \qquad \tau \in \mathbf{R}^{+}\,.$$

Moreover, if the processes $\sigma(\cdot)$ *are finite, the microscopic reversibility implies the invariance of*

$$\Delta = \int_{-\infty}^{\infty} \sigma(t) \cdot \dot{x}(t) \, \mathrm{d}t$$

under time-reversal,

$$\sigma(\cdot) \to \tilde{\sigma}(\cdot) \quad , \quad \tilde{\sigma}(\zeta) = \varepsilon \sigma(-\zeta) \quad , \quad \zeta \in \mathbf{R} .$$

4. APPLICATIONS TO CONTINUUM THERMODYNAMICS

The procedure of the previous section shows that the essential assumption is the conjugacy property of σ and x at equilibrium. This property is now examined through the example of the linearised theory of viscoelasticity.

According to various theories of thermodynamics—see, e.g., [14]—the stress tensor **T** and the infinitesimal strain tensor **E** are related by

$$\frac{1}{\rho\theta} \mathbf{T} = - \frac{\partial \eta}{\partial \mathbf{E}} \text{ , at equilibrium,}$$

ρ being the mass density and θ the temperature. So, usually **T** and **E** are not conjugate variables, but, in the linearised isothermal viscoelasticity — $\rho = \rho_0$, $\theta = \theta_0$—they are conjugate in that the relation

$$x(t) \equiv \mathbf{E}(t) = \int_0^{\infty} \hat{\mathbf{J}}(\tau) \frac{\dot{\mathbf{T}}}{\rho_0 \theta_0} (t - \tau) \, \mathrm{d}\tau = \int_0^{\infty} \hat{\mathbf{J}}(\tau) \, \dot{\sigma}(t - \tau) \, \mathrm{d}\tau$$

where $\sigma \equiv - \mathbf{T}/\rho_0 \theta_0$ and $\hat{\mathbf{J}}(\tau) = - \mathbf{J}(\tau)$, $\hat{\mathbf{J}}(0) = - \mathbf{J}_0$, relates conjugate variables. Moreover $\hat{\mathbf{J}}/\rho_0 \theta_0$ plays the role of creep compliance. Then, according to the previous theorem, microscopic reversibility implies the symmetry of the creep compliance and the invariance of the work

$$w = \int_{-\infty}^{\infty} \mathbf{T}(t) \cdot \dot{\mathbf{E}}(t) \, \mathrm{d}t$$

in connection with finite processes.

Analogous considerations lead to the symmetry of the relaxation function.

More in general, further results within the continuum thermodynamics follow whenever the conjugacy property is available. Of course the existence of conjugacy properties may depend on the particular model adopted for the body. For example, a proper theory of thermo-viscous fluids with hidden variables [15] allows us to derive the heat flux from the entropy function while this result does not occur in other theories.

5. COMMENTS

The above derivation, strongly based on the conjugacy property, leads to the invariance of the work under time-reversal in the case of linearised isothermal viscoelasticity. So, the characteristic conditions of Day's theorem are consequences of microscopic reversibility. At this stage nothing can be said about the invariance of the entropy production under time-reversal [6–9].

Some remarks are in order about the present procedure. First, note that we have identified the microscopic entropy η with the macroscopic entropy. Sometimes, instead, the macroscopic entropy—or Gibbsian entropy—is defined as the average value of η—see, e.g., [16], § 2.4. However such a difference is merely formal because we have used the conjugacy property only at equilibrium that is to say as if all systems had the same entropy.

A second remark concerns the present procedure versus procedures within the frequency domain based on Callen and Greene's paper itself. It seems to the author that the analysis through Fourier's components is more cumbersome. Moreover Callen and Greene's procedure, once $\xi(t+\tau)$ is evaluated for $\tau > 0$, needs the knowledge of $\xi(t+\tau)$ also for $\tau < 0$. To this purpose it is assumed that $\xi(t+\tau)$ is an even function of τ. Besides being not motivated, this assumption appears not to be consistent with the process imagined for obtaining the reciprocity relations.

Acknowledgments.

I am thankful to Dr. W. A. Day for valuable discussions and suggestions.

REFERENCES

[1] L. ONSAGER (1931) – *Reciprocal relations in irreversible processes I, II*, « Phys. Rev. », *37*, 405–426; *38*, 2265–2279.

[2] W. A. DAY (1971) – *Time-reversal and the symmetry of the relaxation function of a linear viscoelastic material*, « Arch. Rational Mech. Anal. », *40*, 155–159.

[3] B. D. COLEMAN (1964) – *Thermodynamics of materials with fading memory*, « Arch. Rational Mech. Anal. », *17*, 1–46.

[4] W. A. DAY (1968) – *Thermodynamics based on a work axiom*, « Arch. Rational Mech. Anal. », *31*, 1–34.

[5] W. A. DAY (1971) – *Restrictions on relaxation functions in linear viscoelasticity*, « Quart. J. Mech. Appl. Math. », *24*, 487–497.

[6] M. E. GURTIN (1972) – *Time-reversal and symmetry in the thermodynamics of materials with memory*, « Arch. Rational Mech. Anal. », *44*, 387–399.

[7] R. BORGHESANI and A. MORRO (1974) – *Time-reversal invariance and thermodynamics of electromagnetic fields in materials with memory*, « Ann. Mat. Pura Appl. » 99, 65–80.

[8] R. BORGHESANI and A. MORRO (1977) – *Relaxation functions and time-reversal invariance in thermal and electric conduction*, « Ann. Mat. Pura Appl. », *114*, 271–288.

[9] A. MORRO (1979) – *Thermoviscoelasticity and invariance of the entropy production under time-reversal*, « Ann. Mat. Pura Appl. », *119*, 115–137.

[10] J. MEIXNER (1975) – *Macroscopic and microscopic reversibility*, « Rep. Math. Phys. », *7*, 37–57.

[11] H. B. CALLEN and R. F. GREENE (1952) – *On a theorem of irreversible thermodynamics I, II*, « Phys. Rev. », *86*, 702–710; *88*, 1387–1391.

[12] L. D. LANDAU and E.M. LIFSHITZ (1959) – *Statistical Physics*, Pergamon, London.

[13] G. GALLAVOTTI (1976) – *Problemi ergodici in meccanica classica*, ed. by S. Graffi, Quaderni GNFM–CNR, Bologna.

[14] W. A. DAY (1972) – *The thermodynamics of simple materials with fading memory*, Springer Verlag, Berlin.

[15] A. MORRO (1979) – *Wave propagation in thermo-viscous materials with hidden variables*, « Arch. Mech. », to appear.

[16] D. N. ZUBAREV (1974) – *Nonequilibrium statistical thermodynamics*, Consultants Bureau, New York.