Time Reversal Behaviour and Reciprocity Theorem of Transport-Relaxation-Equations

L. Waldmann

Institut für Theoretische Physik der Universität Erlangen-Nürnberg, Erlangen

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The coefficient matrices in the transport-relaxation-equations (moment equations of generalized thermo-hydrodynamics) depend on the polynomials used in the expansion of the underlying kinetic equation. The known behaviour under time reversal of these polynomials, Eq. (7), entails symmetries of the fore-mentioned coefficient matrices, Eqs. (12) and (16). From these symmetries a reciprocity theorem for two stationary solutions of the transport-relaxation-equations is derived, Eqs. (21 a und b): the divergence of a certain vector field, bilinear in the two solutions, vanishes. The relaxation matrix does not appear in this form. The theorem is useful for investigating the proliferation of the Onsager symmetries from the basic differential equations into the linear algebraic relations between the few global quantities governing "discontinuous systems". A simple example in heat conduction is worked out. A more complicated case and the role of a magnetic field are briefly considered. Equivalent with (21 a) is the kinetic reciprocity theorem (40).

From the linearized kinetic equation for a dilute polyatomic gas [1, 2] one obtains *transport-relaxation-equations* [3, 4] (or: equations of linear generalized thermo-hydrodynamics) of the structure

$$\frac{\partial a_i}{\partial t} + \sum_k c_{\nu ik} \frac{\partial a_k}{\partial x_\nu} + \sum_k \omega_{ik}\, a_k = 0\,. \tag{1}$$

Among the moments $a_i(t, \boldsymbol{x})$ are, apart from certain normalization factors, the density, the translational and internal temperatures, the velocity, the heat flux, the pressure tensor, the average local tensor polarization of the molecules, etc. The three coefficient matrices $c_{\nu ik}$ ($\nu = 1, 2, 3$ numbers the Cartesian coordinates; summation rule!) arise from the streaming term of the kinetic equation and are given by brackets taken with the equilibrium distribution:

$$c_{\nu ik} = \langle \varphi_i\, c_\nu\, \varphi_k \rangle_0 = c_{\nu ki}\,. \tag{2}$$

They are symmetrical in the Latin subscripts. The φ's depend on the linear, the angular momentum etc. of a molecule; they are the orthonormalized polynomials used in the expansion of the distribution function; the a's are the coefficients in this expansion. The symmetry of the relaxation matrix

$$\omega_{ik} = \langle \varphi_i\, \omega(\varphi_k) \rangle_0 \tag{3}$$

is more sophisticated and will be dealt with immediately. The symbol $\omega(\ldots)$ denotes the linearized binary collision operator of the kinetic equation. In any case, ω_{ik} is a positive-semidefinite matrix.

Let us first assume that the basis polynomials φ are chosen as eigenfunctions of the "*time reversal*" *operation*. The time (or motion) reversed polynomial φ_T is defined by

$$\varphi_T(\boldsymbol{p}, \vec{\mathrm{j}}, \ldots) = \varphi(-\boldsymbol{p}, \overleftarrow{\mathrm{j}}, \ldots)\,. \tag{4}$$

Here $\boldsymbol{p}$ denotes the linear, $\vec{\mathrm{j}}$ the angular molecular momentum and the arrow pointing to the left means reversed order of non-commuting factors in all products. The φ's are eigenfunctions of the time reversal operation if one has

$$\varphi_{iT} = \Theta_i\, \varphi_i \quad \text{with} \quad \Theta_i = \pm 1 \quad \text{or} \quad \Theta_i^2 = 1\,. \tag{5}$$

But for the intended general considerations it is preferable to choose arbitrary linear orthogonal combinations of such eigenfunctions as a basis. Instead of (5) one will then have a linear connection of the kind

$$\varphi_{iT} = \sum_{i'} \Theta_{ii'}\, \varphi_{i'} \tag{6}$$

as the time reversal behaviour of the φ's. In a *short hand matrix writing*, this is expressed by

$$\varphi_T = \Theta \cdot \varphi\,. \tag{7}$$

The dot indicates the scalar product in the space of the φ's. The "*time reversal matrix*" Θ of the φ's is symmetrical (identical with its transposed) because it has a diagonal eigenvalue representation, and on iteration it gives the identity:

$$\Theta = \widetilde{\Theta}\,; \quad \Theta \cdot \Theta = 1\,. \tag{8}$$

In the same matrix notation the *transport-relaxation-equations* take on the concise form

$$\frac{\partial a}{\partial t} + c_\nu \cdot \frac{\partial a}{\partial x_\nu} + \omega \cdot a = 0\,. \tag{9}$$

Reprint requests to Prof. Dr. L. Waldmann, Institut für Theoretische Physik der Universität, Glückstr. 6, *D-8520 Erlangen.*

The time reversal behaviour (6) or (7) of the φ's now entails certain symmetries of the coefficient matrices c_ν and ω. With the c_ν's, the situation is very simple. Employing the identity

$$\langle \varphi_i \, c_\nu \, \varphi_k \rangle_0 \equiv \langle \varphi_{kT} \, c_{\nu T} \, \varphi_{iT} \rangle_0 \quad \text{with} \quad c_{\nu T} = -c_\nu \tag{10}$$

and the time reversal behaviour (6), one obtains from definition (2)

$$c_{\nu ik} = -\sum_{k'} \sum_{i'} \Theta_{kk'} \, c_{\nu k' i'} \, \Theta_{i' i} \tag{11}$$

or in short hand writing

$$c_\nu = -\widetilde{\Theta \cdot c_\nu \cdot \Theta} = -\Theta \cdot c_\nu \cdot \Theta \, ,$$

because of $\tilde{\Theta} = \Theta$ and $\tilde{c}_\nu = c_\nu$. An alternative form of the *c_ν-symmetry is*

$$\Theta \cdot c_\nu = -c_\nu \cdot \Theta \, . \tag{12}$$

A little more has to be said about the ω-matrix. For the ω_{ik}, defined in (3), one has the identity

$$\langle \varphi_i \, \omega(\varphi_k) \rangle_0 \equiv \langle \varphi_{kT} \, \omega_T(\varphi_{iT}) \rangle_0 \, , \tag{13}$$

where $\omega_T(\dots)$ is the time reversed linearized collision operator of the kinetic equation, with the original binary S-matrix replaced by S_T and with reversed order of factors in comparison to $\omega(\dots)$. But if the binary molecular dynamics is invariant under time reversal – which is supposed to be exactly true in nature –, both operators coincide:

$$\omega_T(\dots) = \omega(\dots) \, . \tag{14}$$

The identity (13) then becomes the equality

$$\langle \varphi_i \, \omega(\varphi_k) \rangle_0 = \langle \varphi_{kT} \, \omega(\varphi_{iT}) \rangle_0 \, .$$

Employing this and behaviour (6) in the definition (3), one obtains the *Onsager symmetry relations*

$$\omega_{ik} = \sum_{k'} \sum_{i'} \Theta_{kk'} \, \omega_{k' i'} \, \Theta_{i' i} \, , \tag{15}$$

or in short hand

$$\omega = \widetilde{\Theta \cdot \omega \cdot \Theta} = \Theta \cdot \tilde{\omega} \cdot \Theta \, .$$

An alternative form of this *ω-symmetry is*

$$\Theta \cdot \omega = \tilde{\omega} \cdot \Theta \, . \tag{16}$$

The symmetries (12) and (16) are closely related: in (12) occurs the minus sign, because the molecular velocity vector is odd under time reversal whereas the collision operator is invariant; and instead of c_ν on the right side of (12) there was originally $\tilde{c}_\nu \, (= c_\nu)$, in concordance with (16).

The transport-relaxation-equations (1) or (9) have been obtained from dilute gas kinetics. However, one will expect the same structure to be valid for the generalized linear thermo-hydrodynamics of a dense gas or liquid. In these cases the c_ν-matrices no more come from the streaming term of the kinetic equation only, but partly also from the nonlocal collision term. It seems plausible that the symmetry (12) still holds.

The symmetries (12) and (16) lead to a *reciprocity theorem for two stationary solutions* of the transport-relaxation equations. Let us call these solutions $a^{(1)}$, $a^{(2)}$. Then one has after (9)

$$\begin{aligned} c_\nu \cdot \frac{\partial a^{(1)}}{\partial x_\nu} + \omega \cdot a^{(1)} &= 0 \, , \\ c_\nu \cdot \frac{\partial a^{(2)}}{\partial x_\nu} + \omega \cdot a^{(2)} &= 0 \, . \end{aligned} \tag{17}$$

Let us multiply the first equation by $\widetilde{a^{(2)}} \cdot \Theta \cdot$, the second by $-\widetilde{a^{(1)}} \cdot \Theta \cdot$ and add both equations. The tilded "vector" $\tilde{a}$ denotes the "line vector" associated with the "column vector" a, giving a "scalar" on scalar multiplication $\tilde{a} \cdot a$. By the said combination procedure the ω-terms of (17) add to

$$\widetilde{a^{(2)}} \cdot \Theta \cdot \omega \cdot a^{(1)} - \widetilde{a^{(1)}} \cdot \Theta \cdot \omega \cdot a^{(2)} \, . \tag{18}$$

Now, the second term is first rewritten identically and then the ω-symmetry (16) is applied:

$$\widetilde{a^{(1)}} \cdot \Theta \cdot \omega \cdot a^{(2)} \equiv \widetilde{a^{(2)}} \cdot \tilde{\omega} \cdot \tilde{\Theta} \cdot a^{(1)} = \widetilde{a^{(2)}} \cdot \Theta \cdot \omega \cdot a^{(1)} \, . \tag{19}$$

Therefore, both ω-terms in (18) cancel and the c-terms of (17) give, by the fore-mentioned combination procedure,

$$\widetilde{a^{(2)}} \cdot \Theta \cdot c_\nu \cdot \frac{\partial a^{(1)}}{\partial x_\nu} - \widetilde{a^{(1)}} \cdot \Theta \cdot c_\nu \cdot \frac{\partial a^{(2)}}{\partial x_\nu} = 0 \, . \tag{20}$$

Again, the second term is first rewritten identically and then the c-symmetry (12) is applied:

$$\begin{aligned} \widetilde{a^{(1)}} \cdot \Theta \cdot c_\nu \cdot \frac{\partial a^{(2)}}{\partial x_\nu} &\equiv \frac{\partial \widetilde{a^{(2)}}}{\partial x_\nu} \cdot \tilde{c}_\nu \cdot \tilde{\Theta} \cdot a^{(1)} \\ &= -\frac{\partial \widetilde{a^{(2)}}}{\partial x_\nu} \cdot \Theta \cdot c_\nu \cdot a^{(1)} \, . \end{aligned}$$

Inserting this into (20) leads to the *reciprocity theorem*

$$\frac{\partial}{\partial x_\nu} \left(\widetilde{a^{(2)}} \cdot \Theta \cdot c_\nu \cdot a^{(1)} \right) = 0 \, . \tag{21 a}$$

This says that with any two stationary solutions of the transport-relaxation-equations a divergenceless three-dimensional vector field is linked, in a bilinear way. With $a^{(1)} = a^{(2)}$, Eq. (21 a) is void, because of $\tilde{a} \cdot \Theta \cdot c_\nu \cdot a \equiv 0$. In the derivation, the coefficient matrices c_ν have been assumed to be $\boldsymbol{x}$-independent. This assumption had not to be made with the ω-matrix; it may be $\boldsymbol{x}$-dependent.

From (21 a), by Gauß's theorem, one can immediately deduce the vanishing of the associated surface integral

$$\int_\sigma \widetilde{a^{(2)}} \cdot \Theta \cdot c \cdot a^{(1)} \, \mathrm{d}\sigma = 0 , \tag{21 b}$$

where the scalar coefficient matrix

$$c = c_\nu \, n_\nu \tag{22}$$

depends on the outer unit normal n_ν of the closed surface σ. Realizing that (21 b) is valid for any surface, one may say that the integral form (21 b) and the differential form (21 a) are equivalent.

The reciprocity theorem is useful in investigating the *proliferation of the Onsager symmetries* present in the fundamental differential equations, into the linear algebraic relations between global quantities (continuum versus "discontinuous systems[5]"). This will now be exemplified in a simple case: *heat conduction in a non-uniform, anisotropic medium.*

There are four variables $\{a\}$, apart from normalization factors, in this case: the temperature and the three components of the heat flux, $\{T, q_\mu\}$. The transport-relaxation-equations are

$$\begin{aligned} \varrho c \frac{\partial T}{\partial t} + \frac{\partial q_\mu}{\partial x_\mu} &= 0 , \\ \frac{\partial q_\mu}{\partial t} + \frac{5}{2} \frac{k p_0}{m} \frac{\partial T}{\partial x_\mu} + \omega_{\mu\mu'}(\boldsymbol{x}) \, q_{\mu'} &= 0 . \end{aligned} \tag{23}$$

The first equation, with the heat capacity ϱc per volume, expresses energy conservation. The factor in the middle term of the second equation, with Boltzmann's constant k, equilibrium pressure p_0 and atomic mass m, is valid for a dilute monatomic gas, for which in reality the relaxation matrix is isotropic and constant. Now, the stationary equations for two solutions are written down, as in Eqs. (17), and the multiplications which were applied to Eqs. (17) are indicated distinctly:

$$\begin{aligned} + T^{(2)} \cdot \Big| \; & \frac{\partial q_\mu^{(1)}}{\partial x_\mu} &= 0 , \\ - q_\mu^{(2)} \cdot \Big| \; & \frac{\partial T^{(1)}}{\partial x_\mu} + \lambda^{-1}{}_{\mu\mu'}(\boldsymbol{x}) \, q_{\mu'}^{(1)} &= 0 , \\ - T^{(1)} \cdot \Big| \; & \frac{\partial q_\mu^{(2)}}{\partial x_\mu} &= 0 , \\ + q_\mu^{(1)} \cdot \Big| \; & \frac{\partial T^{(2)}}{\partial x_\mu} + \lambda^{-1}{}_{\mu\mu'}(\boldsymbol{x}) \, q_{\mu'}^{(2)} &= 0 . \end{aligned} \tag{24}$$

The Θ-factors are contained in the sign ± at the left end. The heat resistivity tensor

$$\boldsymbol{\lambda}^{-1} = \frac{2 \, m}{5 \, k \, p_0} \, \boldsymbol{\omega}$$

is symmetric according to Onsager

$$\lambda^{-1}{}_{\mu\mu'}(\boldsymbol{x}) = \lambda^{-1}{}_{\mu'\mu}(\boldsymbol{x}) . \tag{25}$$

By addition of the four Eqs. (24) one obtains the reciprocity theorem in differential form, see (21 a),

$$\frac{\partial}{\partial x_\mu} \left(T^{(2)} \, q_\mu^{(1)} - q_\mu^{(2)} \, T^{(1)} \right) = 0 \tag{26}$$

or in integral form, see (21 b),

$$\int_\sigma \left(T^{(2)} \, q^{(1)} - q^{(2)} \, T^{(1)} \right) \mathrm{d}\sigma = 0 \tag{27}$$

where $q = q_\mu \, n_\mu$ is the normal heat flux at the surface σ. A stationary solution of the heat conduction problem is uniquely determined by the T-values at the boundary σ*. Therefore, the normal heat flux at σ must be a linear functional of those T-values:

$$q(\boldsymbol{x} \in \sigma) = \int_\sigma L(\boldsymbol{x}, \boldsymbol{x}') \, T(\boldsymbol{x}') \, \mathrm{d}\sigma' . \tag{28}$$

The kernel $L(\ldots)$, coordinated with the given envelope σ, depends also on the heat conductivity $\boldsymbol{\lambda}(\boldsymbol{x})$ everywhere inside σ. To know $L(\ldots)$ amounts to having completely solved the differential equation problem. Utilizing (28) in the reciprocity theorem (27) one obtains

$$\begin{aligned} 0 &= \iint [T^{(2)}(\boldsymbol{x}) \, L(\boldsymbol{x}, \boldsymbol{x}') \, T^{(1)}(\boldsymbol{x}') \\ &\qquad - L(\boldsymbol{x}, \boldsymbol{x}') \, T^{(2)}(\boldsymbol{x}') \, T^{(1)}(\boldsymbol{x})] \, \mathrm{d}\sigma \, \mathrm{d}\sigma' \\ &\equiv \iint T^{(2)}(\boldsymbol{x}) \, [L(\boldsymbol{x}, \boldsymbol{x}') \\ &\qquad - L(\boldsymbol{x}', \boldsymbol{x})] \, T^{(1)}(\boldsymbol{x}') \, \mathrm{d}\sigma \, \mathrm{d}\sigma' . \end{aligned}$$

As this is true for arbitrary boundary values $T^{(1)}$, $T^{(2)}$ at σ, the *kernel* must be *symmetric*

$$L(\boldsymbol{x} . \boldsymbol{x}') = L(\boldsymbol{x}', \boldsymbol{x}) , \tag{29}$$

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* In the stationary case, the problem (23) coincides with the simple Fourier constitutive law $q_\mu = -\lambda_{\mu\mu'} \, \partial T / \partial x_{\mu'}$.

regardless of any asymmetry of σ and of any asymmetric $\boldsymbol{x}$-dependence of λ. This is a first proliferation of the fundamental Onsager symmetry (25) into a global statement.

Now let us choose special boundary values

$$T(\boldsymbol{x} \in \sigma) = x_{\mu'} T_{\mu'}\,, \tag{30}$$

where $T_{\mu'}$ are the three components of a given vector ("temperature gradient"). Hence, the boundary values are prescribed linearly in $\boldsymbol{x}$; this of course does not imply that T were linear in $\boldsymbol{x}$ anywhere off σ. After (28) the normal heat flux at σ is

$$q(\boldsymbol{x} \in \sigma) = \int_\sigma L(\boldsymbol{x}, \boldsymbol{x}')\, x'_{\mu'}\, \mathrm{d}\sigma'\, T_{\mu'}\,. \tag{31}$$

In order to make use of the symmetry (29) one has obviously to multiply (31) by x_μ and integrate:

$$\begin{aligned} W_\mu &\equiv \int x_\mu\, q\, \mathrm{d}\sigma \\ &= \iint x_\mu\, L(\boldsymbol{x}, \boldsymbol{x}')\, x'_{\mu'}\, \mathrm{d}\sigma\, \mathrm{d}\sigma'\, T_{\mu'} \equiv L_{\mu\mu'}\, T_{\mu'}\,. \end{aligned} \tag{32}$$

After (29) the 3×3 matrix appearing in (32) is symmetric

$$L_{\mu\mu'} = L_{\mu'\mu}\,. \tag{33}$$

This is the second (and last) proliferation of the fundamental symmetry (25). The quantity W_μ on the left side of (32) can be transformed by Gauß's theorem into a volume integral

$$\begin{aligned} W_\mu &\equiv \int_\sigma x_\mu\, q_\nu\, n_\nu\, \mathrm{d}\sigma = \int_\tau \frac{\partial}{\partial x_\nu} (x_\mu\, q_\nu)\, \mathrm{d}\tau \\ &= \int_\tau \delta_{\mu\nu}\, q_\nu\, \mathrm{d}\tau = \int_\tau q_\mu\, \mathrm{d}\tau\,, \end{aligned} \tag{34}$$

it shall be termed "heat flux integral". So, the result of our consideration is that the heat flux integral is the extensive vector quantity which is associated with the intensive vector quality T_μ in the sense of Onsager, or in other words: that both are linearly connected by a symmetric matrix. Again, $L_{\mu\mu'}$ is symmetric for any asymmetric (screw like) shape of the surface σ and any asymmetric $\boldsymbol{x}$-dependence of the heat conductivity tensor $\lambda_{\mu\mu'}(\boldsymbol{x})$; only the symmetry (25) of the latter had to be stipulated. – So far this example.

The reciprocity theorem in the general forms (21 a or b) enables one to treat more complicated cases in an equally lucid way, e. g. full ordinary thermo-hydrodynamics for a streaming medium or the *mildly generalized hydrodynamics* of Ref. [4], part A. In the notation used in that paper the reciprocity (21 b) becomes

$$\begin{aligned} \int [&T_0 (p + k'')^{(2)}\, v^{(1)} + \widetilde{T}^{(2)}\, q^{(1)} + T_0\, \boldsymbol{k}^{\tan(2)} \cdot \tilde{\boldsymbol{v}}^{\tan(1)} \\ &- T_0 (p + k'')^{(1)}\, v^{(2)} - \widetilde{T}^{(1)}\, q^{(2)} \\ &- T_0\, \boldsymbol{k}^{\tan(1)} \cdot \tilde{\boldsymbol{v}}^{\tan(2)}]\, \mathrm{d}\sigma = 0\,. \end{aligned} \tag{35}$$

With this relation at hand one can ascertain the symmetry properties of the mass and heat fluxes through a porous, statistically homogeneous material.

Another point, only indicated here, is the contribution of the *intra-molecular Hamiltonian* and of an *applied magnetic field* in the transport-relaxation-equations. The internal Hamiltonian, with inclusion of the magnetic energy, leads to an additional term $H \cdot a$ on the left side of Equation (9). The antisymmetric matrix $H(\boldsymbol{h}) = -\widetilde{H}(\boldsymbol{h})$, dependent on the unit vector $\boldsymbol{h}$ of direction of the magnetic field, has the time reversal property

$$\Theta \cdot H(\boldsymbol{h}) = \widetilde{H}(-\boldsymbol{h}) \cdot \Theta\,. \tag{36}$$

The matrix H can be combined with the relaxation matrix ω to the matrix

$$\Omega(\boldsymbol{h}) = \omega + H(\boldsymbol{h}) \tag{37}$$

with the unified property

$$\Theta \cdot \Omega(\boldsymbol{h}) = \widetilde{\Omega}(-\boldsymbol{h}) \cdot \Theta\,. \tag{38}$$

(That ω is taken independent of $\boldsymbol{h}$ is somewhat restrictive.) The considerations leading to (21 a) can now be repeated and give the reciprocity theorem in the presence of an external magnetic field:

$$\frac{\partial}{\partial x_\nu} [\widetilde{a^{(2)}}(-\boldsymbol{h}) \cdot \Theta \cdot c_\nu \cdot a^{(1)}(\boldsymbol{h})] = 0\,. \tag{39}$$

This means that the two solutions to be combined bilinearly must refer to magnetic fields equal in strength, opposite in sign, a feature which, in a somewhat different context, is entirely familiar from non-equilibrium thermodynamics [6].

In conclusion a remark is made on the *reciprocity theorem for the linearized Boltzmann equation itself*, or for the quantum mechanical version of it [1, 2]. Starting, in analogy with Eqs. (17), from the stationarity conditions for two one-particle distributions $f^{(1)}(\boldsymbol{x}, \boldsymbol{p}, \vec{\mathrm{j}}, \ldots)$ and $f^{(2)}(\boldsymbol{x}, \boldsymbol{p}, \vec{\mathrm{j}}, \ldots)$, multiplying both equations with $f^{(2)}(\boldsymbol{x}, -\boldsymbol{p}, -\overleftarrow{\mathrm{j}}, \ldots) = f_{\mathrm{T}}{}^{(2)}(\boldsymbol{x}, \boldsymbol{p}, \vec{\mathrm{j}}, \ldots)$ and $-f^{(1)}(\boldsymbol{x}, -\boldsymbol{p}, -\overleftarrow{\mathrm{j}}, \ldots)$ respectively from the left, adding, integrating and tracing, one gets the *kinetic reciprocity theorem*

$$\begin{aligned} \frac{\partial}{\partial x_\nu} [&\mathrm{Tr} \int \mathrm{d}^3 p \\ &\cdot f^{(2)}(\boldsymbol{x}, -\boldsymbol{p}, -\overleftarrow{\mathrm{j}}, \ldots)\, c_\nu\, f^{(1)}(\boldsymbol{x}, \boldsymbol{p}, \vec{\mathrm{j}}, \ldots)] = 0\,. \end{aligned} \tag{40}$$

The trace Tr has to be taken over all internal molecular states generated by the molecular angular momentum $\boldsymbol{j}$, etc. The collision operator of the kinetic equation drops out in the combination procedure just described, thanks to its time reversal invariance. Again, by expanding the distributions f in terms of polynomials φ with coefficients a and by recalling that the brackets in Eq. (2) abbreviate the prescription $\mathrm{Tr} \int d^3p\, f_0 \ldots$, one observes that the "kinetic" reciprocity theorem (40) and the foregoing formulation (21 a) are equivalent.

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