ON THE INTERMEDIATE REPRESENTATION IN THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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The properties of the intermediate representation for thermodynamics of irreversible processes are described. In this representation, m forces X_k and $n-m$ fluxes J_i are chosen as the n independent variables. The symmetry properties, physical meaning and transformational properties of this representation are examined. It is found *i.a.* that the matrix M of phenomenological coefficients is not entirely symmetrical, but consists of four submatrices, two of them being symmetric and two antisymmetric. It is also shown that the transformation of Coleman and Truesdell [5] is a special case of the intermediate representation.

1. Introduction

In phenomenological linear non-equilibrium thermodynamics [1,2], $n(i = 1, ..., n)$ irreversible processes are described in terms of $2n$ variables: n fluxes J_i and n forces X_i. Of these, only n variables are treated as independent, the remaining n ones being regarded as linear functions of the former. The choice of the n independent variables is rather arbitrary from the formal phenomenological point of view and the most frequent procedure is to write the flows J_i as functions of the forces X_i

$$J_i = \bar{\Sigma}_k L_{ik} X_k, \qquad |J\rangle = L|X\rangle; \tag{1.1}$$

$|\rangle$ denotes a one-column matrix. Sometimes, too, the choice is made the other way round, thus

$$\mathrm{X}_k = \bar{\Sigma}_i R_{ki} J_i, \quad |\mathrm{X}\rangle = R|J\rangle. \tag{1.2}$$

The elements L_{ik} of the admittance matrix L, and R_{ik} of the resistance matrix R are refered to as the phenomenological coefficients. We shall term the first case the admittance or L-representation and the second — the resistance or R-representation. If no relation exists of the type

$$\bar{\Sigma}_i a_i J_i = 0, \qquad \langle a|J\rangle = 0,$$

or

$$\bar{\Sigma}_i b_i \mathrm{X}_i = 0, \qquad \langle b|X\rangle = 0, \tag{1.3}$$

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($<|$ being the transpose of $|>$ *i.e.* a one-row matrix), with at least one non-zero a_i or b_i *i.e.* if all the fluxes and all the forces are linearly independent, the matrices L and R are connected, as is seen immediately from (1.1) and (1.2), by the relation

$$L = R^{-1}, \qquad R = L^{-1}, \tag{1.4}$$

which gives the direct connection between both representations.

In the case when L and R are singular (*i.e.* when at least one relation of the form (1.3) exists), it is also possible to find the relations between both representations (see [3]). In this paper we shall restrict ourselves to the case of independent fluxes and forces.

Now, if the J_i are time derivatives of the thermodynamical parameters, and if the forces X_i are chosen in such a manner that

$$\sigma = \sum_{i=1}^{n} J_i X_i = \langle J|X\rangle, \tag{1.5}$$

σ being the entropy production (and if no relation of the type (3) exists), the well-known Onsager theorem states that

$$L_{ik} = L_{ki}, \quad R_{ik} = R_{ki}; \qquad L = L^T, \quad R = R^T. \tag{1.6}$$

The use of the L- or R-representation depends on the physical situation in the case considered. As already mentioned, the L-representation is more commonly used. However, a third case is also possible, namely, we can treat as independent only some, say, m forces and thus n-m fluxes. This case can be written down as follows:

Let us select as independent variables m forces X_k $(k = 1,\dots,m)$ and n-m fluxes $J_k(k = m+1,\dots, n)$. The remaining fluxes J_i $(i = 1,\dots, m)$ and forces X_i $(i = m+1,\dots, n)$ will be dealt with as linear functions of the first n ones. Then denoting the independent variables by Y_i and the dependent ones by $Z_i(i = 1,\dots, n)$ we can write the phenomenological equations as follows:

$$Z_i = \Sigma_k M_{ik} Y_k, \qquad |Z> = M|Y>, \tag{1.7}$$

with
$$Z_i = \begin{cases} J_i & \text{for} \quad i = 1,\dots, m \\ X_i & \text{for} \quad i = m+1,\dots, n \end{cases}$$

$$Y_i = \begin{cases} X_i & \text{for} \quad i = 1,\dots, m \\ J_i & \text{for} \quad i = m+1,\dots, n \end{cases}$$

i.e.,
$$<Z| = ||J_1 \cdots J_m X_{m+1} \cdots X_n||$$
$$<Y| = ||X_1 \cdots X_m J_{m+1} \cdots J_n||.$$

It is obvious that this does not affect the form (1.5) of the entropy production

$$\langle Z|Y\rangle = \langle J|X\rangle = \sigma. \tag{1.8}$$

There are many physical situations which require such a choice: in fact, this is the choice made *e.g.* in the description of thermoelectric or thermomagnetic phenomena, where for various phenomena various J and X are regarded as independent (see, *e.g.*, [2], Ch. 13,

[4], Ch. 17). Now, no formal description of this intermediate, or mixed, or — as we shall call it — M-representation has been proposed as yet. The purpose of this paper is to give such a formal description of the M-representation; as we shall see below, its properties are not trivially related to those of the L-representation, as is the case of the R-representation (in the case of independent fluxes and forces) where, in view of Eqs (1.4) all the properties of the matrix L (as *e.g.* its symmetry properties) are immediately transmitted to the matrix R.

2. *Symmetry properties*

Let us now search for the relations between the matrix M and the matrices L and R. For this purpose let us first decompose the matrices L,R, M, each into four submatrices, as follows:

$$L = \left\| \begin{array}{c:c} L^{mm} & L^{m\mu} \\ \hdashline L^{\mu m} & L^{\mu\mu} \end{array} \right\|, \quad R = \left\| \begin{array}{c:c} R^{mm} & R^{m\mu} \\ \hdashline R^{\mu m} & R^{\mu\mu} \end{array} \right\|, \quad M = \left\| \begin{array}{c:c} M^{mm} & M^{m\mu} \\ \hdashline M^{\mu m} & M^{\mu\mu} \end{array} \right\|, \tag{2.1}$$

where the elements of the submatrices are

$$L^{mm}{}_{ik} \equiv L_{ik} \quad \text{with} \quad i, k = 1,\ldots, m$$

$$L^{m\mu}{}_{ik} = L_{ik} \quad \text{with} \quad i = 1,\ldots, m; \quad k = m+1,\ldots, n; \; etc.$$

and where μ stands for n-m. This decomposition follows from our choice of the independent variables and is rather obvious. (It should be remembered that matrices $L^{m\mu}$ etc. are not, in general, square matrices.)

The three schemes (1.1), (1.2) and (1.7) of phenomenological equations can now be written as follows:

$$\begin{aligned} |J>^{m} &= L^{mm}\,|X>^{m} + L^{m\mu}\,|X>^{\mu} \\ |J>^{\mu} &= L^{\mu m}\,|X>^{m} + L^{\mu\mu}\,|X>^{\mu} \end{aligned} \tag{2.2}$$

$$\begin{aligned} |X>^{m} &= R^{mm}\,|J>^{m} + R^{m\mu}\,|J>^{\mu} \\ |X>^{\mu} &= R^{\mu m}\,|J>^{m} + R^{\mu\mu}\,|J>^{\mu} \end{aligned} \tag{2.3}$$

$$\begin{aligned} |Z>^{m} &= M^{mm}\,|Y>^{m} + M^{m\mu}\,|Y>^{\mu} \\ |Z>^{\mu} &= M^{\mu m}\,|Y>^{m} + M^{\mu\mu}\,|Y>^{\mu} \end{aligned} \tag{2.4}$$

with

$$|J>^{m} = |Z>^{m} = \|\, J_1 \cdots J_m \|^T,$$

$$|J>^{\mu} = |Y>^{\mu} = \|J_{m+1} \cdots J_n\|^T, \quad etc.$$

Eqs (2.4) in more clear form are

$$\begin{aligned} |J>^{m} &= M^{mm}|X>^{m} + M^{m\mu}|J>^{\mu}, \\ |X>^{\mu} &= M^{\mu m}|X>^{m} + M^{\mu\mu}|J>^{\mu}. \end{aligned} \tag{2.4a}$$

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Now, solving (22) with respect to $|Z>$ (*i.e.*, $|J>^m$, $|X>^\mu$), we have

$$|J>^m = [L^{mm} - L^{m\mu}(L^{\mu\mu})^{-1} L^{\mu m}]|X>^m + L^{m\mu}(L^{\mu\mu})^{-1} |J>^\mu,$$
$$|X>^m = - (L^{\mu\mu})^{-1} L^{\mu m} |X>^m + (L^{\mu\mu})^{-1} |J>^\mu, \tag{2.5}$$

and similarly from (2.3)

$$|J>^m = (R^{mm})^{-1} |X>^m - (R^{mm})^{-1} R^{m\mu} |J>^\mu,$$
$$|X>^\mu = R^{\mu m} (R^{mm})^{-1} |X>^m + [R^{\mu\mu} - R^{\mu m} (R^{mm})^{-1} R^{m\mu}] |J>^\mu. \tag{2.6}$$

Comparing (2.5), (2.6) and (2.4a) we obtain the required relations between M and L, R

$$M^{mm} = L^{mm} - L^{m\mu} (L^{\mu\mu})^{-1} L^{\mu m} = (R^{mm})^{-1},$$
$$M^{m\mu} = L^{m\mu} (L^{\mu\mu})^{-1} = - (R^{mm})^{-1} R^{m\mu},$$
$$M^{\mu m} = - (L^{\mu\mu})^{-1} L^{\mu m} = R^{\mu m} (R^{mm})^{-1},$$
$$M^{\mu\mu} = (L^{\mu\mu})^{-1} = R^{\mu\mu} - R^{\mu m} (R^{mm})^{-1} R^{m\mu}. \tag{2.7}$$

The symmetry properties (1.6) of matrix L yield for its submatrices

$$L^{mm} = (L^{mm})^T,\ L^{m\mu} = (L^{\mu m})^T,\ L^{\mu\mu} = (L^{\mu\mu})^T,$$
$$(L^{mm})^{-1} = [(L^{mm})^{-1}]^T,\ (L^{\mu\mu})^{-1} = [(L^{\mu\mu})^{-1}]^T, \tag{2.8}$$

and similarly for submatrices R. Eqs (2.7) and (2.8) give the following symmmetry properties for the matrix M:

$$M^{mm} = (M^{mm})^T,\ M^{\mu\mu} = (M^{\mu\mu})^T,$$
$$M^{m\mu} = - (M^{\mu m})^T, \tag{2.9}$$

i.e. the whole matrix M is, despite the matrices L and R, not symmetric. It consists of two symmetric square submatrices (of orders $m\times m$, $(n\text{-}m)\times(n\text{-}m)$, respectively) and of two mutually antisymmetric rectangular matrices (of orders $m\times(n\text{-}m)$, $(n\text{-}m)\times m$, respectively).

For an illustration, let us consider the simplest case of two independent processes. We have, in turn,

$$\sigma = J_1X_1+J_2X_2, \tag{2.10}$$

$$J_1 = L_{11}X_1+L_{12}X_2,$$
$$J_2 = L_{12}X_1+L_{22}X_2, \tag{2.11}$$

$$X_1 = R_{11}J_1+R_{12}J_2,$$
$$X_2 = R_{12}J_1+R_{22}J_2, \tag{2.12}$$

where the symmetry relations $L_{12} = L_{21}$, $R_{12} = R_{21}$, were used. In the M-representation the phenomenological equations are

$$J_1 = M_{11}X_1+M_{12}J_2,$$
$$J_2 = M_{21}X_1+M_{21}J_2, \tag{2.13}$$

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and we easily find from the above that

$$M_{11} = \frac{L_{11}}{1-L_{12}R_{12}} = L_{11}-\frac{L_{12}^2}{L_{22}} = \frac{1}{R_{11}},$$

$$M_{12} = \frac{L_{12}R_{22}}{1-L_{12}R_{12}} = \frac{L_{12}}{L_{22}} = -\frac{R_{12}}{R_{11}},$$

$$M_{21} = \frac{L_{11}R_{12}}{1-L_{12}R_{12}} = -\frac{L_{12}}{L_{22}} = \frac{R_{12}}{R_{11}},$$

$$M_{22} = \frac{R_{22}}{1-L_{12}R_{12}} = \frac{1}{L_{22}} = R_{22}-\frac{R_{12}^2}{R_{11}}, \tag{2.14}$$

and thus $M_{12} = -M_{21}$, and the phenomenological equations can be written

$$J_1 = M_{11}X_{11}+M_{12}J_2, \tag{2.15}$$

$$X_2 = -M_{12}X_1+M_{22}J_2.$$

3. *Physical meaning of the M-matrix*

It is easy to see from the relations (2.7) that the submatrix M^{mm} partakes of the physical character of the admittance (conductivity) matrix, the submatrix $M^{\mu\mu}$ — of that of the resistance matrix whereas submatrices $M^{m\mu}$ and $M^{\mu m}$ have no definite physical character, as being the products of factors of the resistance and admittance type.

Let us examine more precisely the meaning of the components of the M-matrix, especially of the diagonal ones. First let us take up once more the example at the end of the preceding section.

Let us remark that both the coefficient L_{11} and the coefficient $M_{11} = L_{11}-L_{12}^2 L_{22}$ have the meaning of a conductivity in process 1, though in different conditions: L_{11} gives the value of the conductivity (of the process 1) in the absence of the field of process 2 (*i.e.* when $X_2 = 0$) while M_{11} gives that value in the absence of the flow of process 2 ($J_2 = 0$)

$$L_{11} = \left(\frac{J_1}{X_1}\right)_{X_2=0}, \qquad M_{11} = \left(\frac{J_1}{X_1}\right)_{J_2=0}. \tag{3.1}$$

Similarly. R_{22} and M_{22} determine two resistivities of the process 2 in two different conditions

$$R_{22} = \left(\frac{X_2}{J_2}\right)_{J_1=0}, \qquad M_{22} = \left(\frac{X_2}{J_2}\right)_{X_1=0}. \tag{3.2}$$

The above interpretation can be easily extended to the case of many simultaneous processes: both L_{ii} and M_{ii}^{mm} determine the conductivities of the process i; or: both R_{ii} and $M_{ii}^{\mu\mu}$ determine the resistivities of the process i, respective of conditions imposed on the system. L_{ii} is the conductivity of the process i in the absence of all the forces except X_i; M_{ii}^{mm} — in the absence of the $m-1$ forces $X_{j\neq 1}$ and of the μ (remaining) flows. R_{ii} is the resistance of the process i in the absence of all flows except J_i and $M_{ii}^{\mu\mu}$ — in the absence of the (μ—1) flows $J_{j\neq 1}$ and the m remaining forces

$$L_{ii} = \left(\frac{J_i}{X_i}\right)_{X_j=0} \qquad (i, j = 1, \ldots, n;\ i\neq j)$$

$$M_{ii}^{mm} = \left(\frac{J_i}{X_i}\right)_{X_j=0,\, J_k=0} \qquad (i, j = 1, \ldots, m;\ i\neq j;\ k = m+1, \ldots, n)$$

$$M_{ii}^{\mu\mu} = \left(\frac{X_i}{J_i}\right)_{J_j=0,\, X_k=0} \qquad (i, j = m+1, \ldots, n;\ i\neq j;\ k = 1, \ldots, m) \tag{3.3}$$

$$R_{ii} = \left(\frac{X_i}{J_i}\right)_{J_j=0} \qquad (i, j = 1, \ldots, n;\ i\neq j).$$

In a similar manner we can interpret the cross-coefficients M_{ij} for $i\neq j$. Namely, M_{ij}^{mm} determines the magnitude of the flow J_i given rise to by the unit force X_j, in the absence of the other forces and flows, respectively (see below, Formulas (3.4)), while L_{ij} determines the same effect in the absence of all forces except X_j. $M_{ii}^{\mu\mu}$ determines the magnitude of the flow J_i arising from the unit flow J_j, in the absence of the other forces and flows, according to the indices m and μ. $M_{ij}^{\mu m}$ determines the magnitude of the force (field) X_i due to the unit force X_j, and finally $M_{ij}^{\mu\mu}$ — the same, as caused by the unit flow J_j, in the absence of the respective other forces and flows, while R_{ij} also determines the last effect, although when all other forces can differ from zero but all flows except J_j are zero

$$M_{ij}^{mm} = \left(\frac{J_i}{X_j}\right)_{X_k=0,\, J_l=0} \qquad (i, j, k = 1, \ldots, m; j\neq k; l = m+1, \ldots, n) \tag{3.4a}$$

$$M_{ij}^{m\mu} = \left(\frac{J_i}{J_j}\right)_{X_k=0,\, J_l=0} \qquad (i, k = 1, \ldots, m; j, l = m+1, \ldots, n; j\neq l) \tag{3.4b}$$

$$M_{ij}^{\mu m} = \left(\frac{X_i}{X_j}\right)_{J_k=0,\, X_l=0} \qquad (j, k = m+1, \ldots, n; j, l = 1, \ldots, m; j\neq l) \tag{3.4c}$$

$$M_{ij}^{\mu\mu} = \left(\frac{X_i}{J_j}\right)_{J_k=0,\, X_l=0} \qquad (i, j, k = m+1, \ldots, n; j\neq k; l = 1, \ldots, m) \tag{3.4d}$$

$$L_{ij} = \left(\frac{J_i}{X_j}\right)_{X_k=0} \qquad (i, j, k = 1, \ldots, n; j\neq k) \tag{3.4e}$$

$$R_{ij} = \left(\frac{X_i}{J_j}\right)_{J_k=0} \qquad (i, j, k = 1, \ldots, n; j\neq k). \tag{3.4f}$$

For example, from Eqs (2.13) we have

$$M_{12} = \left(\frac{J_1}{J_2}\right)_{X_1=0}, \qquad M_{21} = \left(\frac{X_2}{X_1}\right)_{J_2=0}. \tag{3.5}$$

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The symmetry relations (2.9) yield also that

$$\left(\frac{J_i}{X_j}\right)_{X_{k\neq j}=0,\, J_l=0} = \left(\frac{J_j}{X_i}\right)_{X_{k\neq j}=0,\, J_l=0} \qquad (i, j, k = 1, \ldots, m;\ i\neq j;\ l = m+1, \ldots, n) \tag{3.6a}$$

$$\left(\frac{X_i}{J_j}\right)_{J_{k\neq j}=0,\, X_l=0} = \left(\frac{X_j}{J_i}\right)_{J_{k\neq j}=0,\, X_l=0} \qquad (i, j, k = m+1, \ldots, n;\ i\neq j;\ l = 1, \ldots, m) \tag{3.6b}$$

and

$$\left(\frac{J_i}{J_j}\right)_{J_{k\neq j}=0,\, X_l=0} = -\left(\frac{X_j}{X_i}\right)_{X_{l\neq j}=0,\, J_k=0} \qquad (i, l = 1, \ldots, m;\ j, k = m+1, \ldots, n). \tag{3.6c}$$

This last relation expresses the fact that some of the coupled cross-effects are interrelated not by the simple symmetry relations, but by the antisymmetric ones. For example, from (3.5) and (2.14) we have

$$\left(\frac{J_1}{J_2}\right)_{X_1=0} = -\left(\frac{X_2}{X_1}\right)_{J_2=0} \qquad (n = 2). \tag{3.7}$$

4. *Transformation properties*

We can distinguish here two different kinds of linear transformations of flows and forces. First, we can consider what we term homogeneous transformations, written as follows:

$$|J^*> = a|J>, \quad |X^*> = b|X>, \tag{4.1}$$

with at least one element of the matrix a and b different from zero. The new (transformed) flows J_i^* now are linear functions of the old flows J_i and the new forces X_i^* are linear functions of the old forces X_i.

The second kind of linear transformation can be referred to as inhomogeneous and can be written in terms of our variables Y_i, Z_i as follows:

$$|Y^*> = a|Y>, \qquad |Z^*> = b|Z>. \tag{4.2}$$

In this case, obviously, the new flows J_i^* are linear functions of both the old flows J_i and the old forces X_i, and similarly the new forces X_i^*.

It is easily proved that in order to preserve the invariance of entropy production,

$$\sigma = \langle J|X\rangle = \langle J^*|X^*\rangle,$$

or

$$\sigma = \langle Z|Y\rangle = \langle Z^*|Y^*\rangle, \tag{4.3}$$

in either case, (4.1) and (4.2), the following relation has to be fulfilled:

$$b = (a^{-1})^T \tag{4.4}$$

(if a^{-1} exists).

The phenomenological equations in the L- and M-representation are written in both cases in the form

$$|J^*> = L^*|X^*>, \qquad |Z^*> = M^*|Y^*>, \tag{4.5}$$

and we shall search for the properties of the transformed phenomenological matrix M.

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Let us first examine the first case (4.1). We could indeed find the relations between the matrices M and M^* and derive from these the symmetry properties of the transformed matrix M^*, but in this case the simpler way is the following:

It can be easily proved (see *e.g.* [2]) that the transformed matrix L^* has the same symmetry properties as the matrix L. Since the transformed matrix M^* is connected with the transformed matrix L^* by the same relations as the matrix M with the matrix L *i.e.* by Eqs (2.7), and since the submatrices of L^* have the properties (2.8), the matrix M^* has the same symmetry properties as the matrix M. We can thus formulate the following theorem:

A linear homogeneous transformations of flows and forces, such that the entropy production remains unchanged, does not affect the symmetry properties of any of the phenomenological matrices, L, R, or M.

Let us now examine the second case (4.2). From (4.2), (4.5) and (4.4) we have

$$M^* = bMb^T = (a^{-1})^T M(a^{-1}), \tag{4.6}$$

but this relation does not provide any information about the symmetry properties of M^*. Indeed, we have

$$(M^*)^T = bM^Tb^T \tag{4.7}$$

and, because $M^T \neq \pm M$, we known only that $(M^*)^T \neq M^*$. We now divide the matrices a, b, M^* into submatrices, according to the subdivision of the matrix M (see (2.1)). It is readily verified that the submatrices of M^* are given by

$$\begin{aligned}
M^{*mm} &= (b^{mm}M^{mm}+b^{m\mu}M^{\mu m})(b^{mm})^T+(b^{mm}M^{m\mu}+b^{m\mu}M^{\mu\mu})(b^{m\mu})^T\\
M^{*m\mu} &= (b^{mm}M^{mm}+b^{m\mu}M^{\mu m})(b^{\mu m})^T+(b^{mm}M^{m\mu}+b^{m\mu}M^{\mu\mu})(b^{\mu\mu})^T,\\
M^{*\mu m} &= (b^{\mu m}M^{mm}+b^{\mu\mu}M^{\mu m})(b^{mm})^T+(b^{\mu m}M^{m\mu}+b^{\mu\mu}M^{\mu\mu})(b^{m\mu})^T,\\
M^{*\mu\mu} &= (b^{\mu m}M^{mm}+b^{\mu\mu}M^{\mu m}(b^{\mu m})^T+(b^{\mu m}M^{m\mu}+b^{\mu\mu}M^{\mu\mu}(b^{\mu\mu})^T.
\end{aligned} \tag{48}$$

Eqs (4.8) show that the submatrices of M^* do not possess the same symmetry properties as the submatrices of M, so that the matrix M^* as a whole has no symmetry at all. The same result is obtained for the matrices L^* and R^* (we do not write explicitly the corresponding formulas as they are rather complicated in this case). We can now formulate the following (second) theorem:

A linear homogeneous transformation of the variables Y, Z (i.e. inhomogeneous with respect to the flows J and forces X), such that the entropy production remains unchanged, destroys completely the symmetry properties of all phenomenological matrices, L, R, and M.

It is easy to see that the above theorem can be extended: *The linear transformation inhomogeneous in both Y, Z, and J, X, also leads in general to asymmetrical transformed matrices L*, R* and M*,*

Let us mention that a few years ago Coleman and Truesdell [5] proposed a special linear inhomogeneous transformation of flows and forces (somewhat later generalized by Nettleton [6]), which yielded an asymmetrical transformed matrix L^*. This transformation was

$$|J^*> = |J> + W|X>, \qquad |X^*> = |X>, \tag{4.9}$$

with

$$W = -W^T. \tag{4.10}$$

It is readily proved that (4.9) with the condition (4.10) leads to

$$L^* = \pm L^{*T} \qquad (L = L^T). \tag{4.11}$$

Thus (4.9) represents a special case of the above theorem.

Let us remark that our transformation (4.2) does not mix the independent and dependent variables, contrary to the transformation (4.9).

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