THERMODYNAMIC DESCRIPTION OF TRANSPORT PROCESSES FOR THE FLOWS IN VARIOUS REFERENCE FRAMES

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The flows in arbitrary frames of reference are shown to be implicitly linear dependent if the condition of mechanical equilibrium is fulfilled. The matrices of phenomenological coefficients need not be singular then and they can be simply inverted.

The information connected with the maximum number of independent phenomenological coefficients, which can be obtained in the convection fixed frame of reference, is reduced if the frames of reference are introduced in such a way that the flows are explicitly linear dependent. New relations for the phenomenological coefficients for such explicitly dependent flows are derived.

1. *Introduction*

We shall discuss here general problems connected with the non-equilibrium thermodynamic description of transport processes in continuous isothermal multicomponent systems.

For such systems in the case of mechanical equilibrium a linear relation between thermodynamics forces exists. The linear relations between thermodynamic flows or forces which had been examined by Hooyman and de Groot [1, 2] were additionally discussed by Fuliński and Sukiennik [3].

This problem should be analysed more extensively because it is connected with the possibility of existence of linear relations between phenomenological coefficients.

As we have already shown the maximum number of independent phenomenological coefficients exists and maximum information about transport processes in the system can be obtained if the convection fixed frame of reference is introduced [4, 5, 6, 7].

The problem of linear dependence of flows and forces will be discussed here in a new way. It will be shown that the matrices of phenomenological coefficients for the flows in the convection fixed frame of reference and for any other flows need not be singular. New relations between phenomenological coefficients for explicitly linear dependent flows will be derived.

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2. The matrices of phenomenological coefficients in the case of mechanical equilibrium

The phenomenological equations for n-component systems can be written as follows

$$J_i^A = \sum_{k=1}^{n} L_{ik}^A X_k \quad (i = 1, 2, \ldots, n) \tag{1}$$

or

$$X_i = \sum_{k=1}^{n} R_{ik}^A J_k^A \quad (i = 1, 2, \ldots, n) \tag{2}$$

where J_i^A denote vectorial flows in an arbitrary frame of reference "A", X_i — conjugated thermodynamic forces, L_{ik}^A and R_{ik}^A — phenomenological coefficients. The matrix R^A is the inverse matrix of the matrix L^A.

According to the Prigogine's theorem (in the absence of a viscous flow) the frame of reference "A" can be chosen in an arbitrary way if the following condition of mechanical equilibrium is fulfilled

$$\sum_{i=1}^{n} c_i X_i = 0 \tag{3}$$

where c_i denote concentrations. Thus the entropy production σ which can be expressed as

$$\sigma = \sum_{i=1}^{n} J_i^A X_i \tag{4}$$

does not depend on the frame of reference for the flows.

The frame of reference "a" can be chosen in such a way that the following relation results [6, 7, 8]

$$\sum_{i=1}^{n} a_i J_i^a = 0. \tag{5}$$

Such flows J_i^a are explicitly linear[1] dependent because Eq. (5) results from the very definition of the frame of reference [6].

The linear dependence between the flows J_i^A can be also discussed if Eqs (2) and (3) are taken into account. It follows then

$$\sum_{i=1}^{n} A_i J_i^A = 0 \tag{6}$$

where

$$A_i = A \sum_{k=1}^{n} c_k R_{ki}^A \quad (i = 1, 2, \ldots, n) \tag{7}$$

where A is an arbitrary constant.

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[1] The weighting factors a_i depend on the frame of reference, *e. g.* they are partial molar volumes if the volume fixed frame of reference is introduced.

Two cases can be discussed

1. $$A_i = 0 \quad (i = 1, 2, \ldots, n) \tag{8}$$

2. $$A_n \neq 0. \tag{9}$$ [2]

In the first case the flows J_i^A are linearly independent. According to the discussion given by Hooyman and de Groot [1, 2] the matrix R^A is then singular[3] then due to Eqs (7) and (8).

Fuliński and Sukiennik [3] have discussed the case[4] when the linear relation between the flows J_i^a Eq. (5) leads to a singular matrix L^a and a matrix R^a is non-singular if no linear relations between forces exist. But the matrix L^a as the inverse matrix of the non--singular matrix R^a should be non-singular too. This is in contradiction with the singularity of the matrix L^a. In such a way they have come to the conclusion that this case, which had been previously discussed by Hooyman and de Groot [1, 2], is inconsistent with the very formalism of thermodynamics of irreversible processes and that a linear relation between the thermodynamic flows implies a linear relation between the thermodynamic forces and *vice versa*.

However, it was shown by Hooyman and de Groot [1, 2] that the linear dependent flows J_i^a lead to a singular matrix L^a only if the forces are linearly independent. This case becomes inconsistent only if the inverse matrix, R^a, to the singular matrix is used. Fuliński and Sukiennik [3] have used such matrix and that is why their proof seems to be not sufficient to falsify the case discussed. But their discussion of stationary states rather confirms this falsification.

We will show here that this problem should be analized in another way which permits not only to show that this conclusion about the physical inconsistency [3] is correct but also to obtain the additional results. We shall take into account that if linearly dependent flows and forces are discussed the matrices of phenomenological coefficients no longer need to be singular. The results based on an introduction of this assumption Eq. (9) will be discussed below in the case 2.

In the second case which is consistent with the formalism of non-equilibrium thermodynamics the matrices L^A and R^A need not be singular. The flows J_i^A are then linearly dependent because of Eq. (6). We call such flows J_i^A implicitly linear dependent in order to avoid confusion with the explicitly linear dependent flows J_i^a (Eq. (5)). In the particular case when the frames of references "A" and "a" coincide with one another the implicitly dependent flows become explicitly dependent.

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[2] This means that at least one A_i is not equal to zero.

[3] The complicated method of inverting of the phenomenological equations in the case of singular matrix L^a was discussed by Helfand [9].

[4] The comparison of this discussion based on Eq. (5) with our results based on Eq. (3) is possible because the flows and forces in Eqs (1), (2), and (4) are used in the same mathematical structure.

3. The results connected with the existence of non-singular matrix R^A in the case of mechanical equilibrium

The problem of existence of a non-singular matrix connected with the second case Eq. (9), which has not been discussed so far, will be discussed here. In order to derive the relations between the phenomenological coefficients we define

$$\alpha_i^A = \frac{A_i}{\sum_{k=1}^{n} c_k A_k} \qquad (i = 1, 2, \dots, n). \tag{10}$$

From this definition it follows

$$\sum_{i=1}^{n} c_i \alpha_i^A = 1. \tag{11}$$

If $n-1$ linearly independent flows exist in the particular case of the frame of reference "a" we obtain

$$\alpha_i^a = a_i \qquad (i = 1, 2, \dots, n). \tag{12}$$

The general relations which can be readily seen from Eqs (7) and (10)

$$\frac{\sum_{k=1}^{n} c_k R_k^A}{\sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k R_{kj}^A} = \alpha_i^A \qquad (i = 1, 2, \dots, n) \tag{13}$$

simplify then to

$$\frac{\sum_{k=1}^{n} c_k R_{ki}^a}{\sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k R_{kj}^a} = a_i \qquad (i = 1, 2, \dots, n). \tag{14}$$

In a similar way we can obtain

$$\frac{\sum_{k=1}^{n} a_k L_{ki}^a}{\sum_{j=1}^{n} \sum_{k=1}^{n} a_j a_k L_{kj}^a} = c_i \qquad (i = 1, 2, \dots, n). \tag{15}$$

Thus we see that for the explicitly dependent flows J_i^a the information about transport processes in the system is partially lost because the relations (14) and (15) are then fulfilled. In general, Eqs (1) and (2) provide a maximum number of phenomenological coefficients L_{ik}^A and R_{ik}^A. The matrices L^A and R^A can be inverted because as a result of Eq. (9) each of them can be non-singular[5]. It has been shown in [6] that the convection fixed frame of reference belongs to such frames of reference "A".

[5] The existence of a singular matrix in this case is not interesting physically.

The phenomenological equations for the flows J_i^a are often used in the simplified form

$$J_i^a = \sum_{k=1}^{n-1} l_{ik}^a X_k^a \qquad (i = 1, 2, \ldots, n-1) \tag{16}$$

or

$$X_i^a = \sum_{k=1}^{n-1} r_{ik}^a J_k^a \qquad (i = 1, 2, \ldots, n-1) \tag{17}$$

where as it can be seen from [1, 2] or from [10] and Eqs (27) and (3)

$$X_i^a = X_i - \frac{a_i}{a_n} X_n \qquad (i = 1, 2, \ldots, n) \tag{18}$$

where l_{ik}^a and r_{ik}^a are phenomenological coefficients. All information connected with the phenomenological coefficients of component n is then lost.

The following relations between phenomenological coefficients from Eqs (1), (2) and (16), (17) can be derived if Eq. (23) from [6] and Eqs (1), (3), (4), (5), (16), and (18) are taken into account

$$l_{ik}^a + \sum_{j=1}^{n-1} \frac{a_j}{a_n} \frac{c_k}{c_n} l_{ij}^a = \sum_{j=1}^{n} (\delta_{ij} - c_i a_j)\left(L_{jk}^A - \frac{c_k}{c_n} L_{jn}^A\right) \qquad (i, k = 1, 2, \ldots, n-1) \tag{19}$$

and similarly

$$r_{ik}^a + \sum_{j=1}^{n-1} \frac{c_j}{c_n} \frac{a_k}{a_n} r_{ij}^a = \sum_{j=1}^{n} (\delta_{ij} - a_i c_j)\left(R_{jk}^a - \frac{a_k}{a_n} R_{jn}^a\right) \qquad (i, k = 1, 2, \ldots, n-1) \tag{20}$$

where δ_{ij} is the Kronecker δ (unity for $i = j$ and zero otherwise). It should be emphasised that the matrices l^a and L^a taken in the same frame of reference, in general, differ. The simplified form of Eq. (19) can be obtained for l^n in the n-component based frame of reference if we substitute

$$a_i = \frac{\delta_{in}}{c_n} \qquad (i = 1, 2, \ldots, n). \tag{21}$$

Such relations have been already obtained for l^n and L^a in the barycentric frame of reference [11] as well as for l^n and L^A in the convection fixed frame of reference [8, 5, 6, 7].

4. *Verification of the assumption* (9)

We shall now show here that there exist such systems for which Eq. (8) is not fulfilled and Eq. (9) is. We shall discuss diffusion in n-component systems. For some simple systems the matrices can be treated as diagonal. The phenomenological equations (1) and (2) can then be simply written

$$J_i^D = L_{ii}^D X_i \qquad (i = 1, 2, \ldots, n) \tag{22}$$

$$X_i = R_{ii}^D J_i^D \qquad (i = 1, 2, \ldots, n) \tag{23}$$

Such equations are used in Carman's theory [8] and the hydrodynamic theory [12]. Eq. (9) permits to obtain simple correspondence between such matrices

$$L_{ii}^{D} \cdot R_{ii}^{D} = 1 \qquad (i = 1, 2, \ldots, n). \tag{24}$$

However, Eq. (8) leads to false result

$$R_{ii} = 0 \qquad (i = 1, 2, \ldots, n). \tag{25}$$

Thus we see that the validity of introducing of the assumption (9) is verified for such systems.

We can also readily see that the assumption (9) is also justified in the case of diffusion in the systems in which small cross effects exist. The non-diagonal phenomenological coefficients are smaller then that the diagonal ones (*e. g.* in diffusion in binary systems [13]) and the matrices L^A and R^A are non-singular and can be inverted.

We can also justify the results obtained from this theory (namely Eq. (15)) if we consider the simplified case of self-diffusion which has been discussed by Bearman [14]. As shown in [6, 7] in this case the self-diffusion frame of reference coincides with the volume fixed frame of reference. If we take into account that

$$L_{ii}^{VD} = \frac{c_i D_i^*}{RT} \qquad (i = 1, 2, \ldots, n) \tag{26}$$

and

$$a_i = V_i \tag{27}$$

where D_i^* denote self-diffusion coefficients, V_i — partial molar volumes, R — universal gas constant and T — temperature, we obtain from Eq. (15)

$$D_i^* V_i = D_k^* V_k \qquad (i, k = 1, 2, \ldots, n) \tag{28}$$

and this is the Bearman's results [14].

5. *Discussion*

It has been shown that the linear dependence between the forces Eq. (3) need not imply the singularity of matrix R^A because of Eq. (9) and that the flows J_i^A in any arbitrary frame of reference can be treated as implicitly linear dependent. This is the result of assumption (9) and Eq. (6). The flows in the convection fixed frame of reference belong to such flows J_i^A. The maximum number of independent phenomenological coefficients exist for such frame of reference if the flows are not explicitly linear dependent. This confirms our previous results [4, 5, 6, 7][6].

The application of the assumption (9) made it possible to obtain the new ralations between the phenomenological coefficients L_{ik}^a and R_{ik}^a (Eqs [14] and (15)) for the explicitly

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[6] However, the term "linear independent flows" from the point of view of this treatment should be understood as "not explicitly linear dependent" or "implicitly linear dependent flows".

dependent flows J_i^a which fulfil Eq. (5). The number of independent phenomenological coefficients is then reduced and the information about transport processes in the system is partially lost. The Eqs (19) and (20) derived here permit to relate matrices l^a and r^a from Eqs (16) and (17), which are often used for explicitly linear dependent flows, with the matrices L^A and R^a from Eqs (1) and (2). The assumption (9) was proved in Section 4. We have proved that the other assumption, Eq. (8), is inconsistent with the thermodynamic theories discussed here. The assumption (8) which has been discussed by Hooyman and de Groot [1, 2] leads to the existence of n independent flows and $n - 1$ forces only. Such existence has been shown by Fuliński and Sukiennik [3] to be physically impossible. However, they have not discussed the possibility of the assumption (9). In this paper the assumption (9) is discussed and proved for the first time.

As a result we see that, in general, the matrices L^A and R^A need not be singular and they can be simply inverted. This permits to compare, in a very simple way the theories which use such matrices. It was not possible so far. This also permits to understand better the idea of the convection fixed frame of reference and makes it easier to compare the other thermodynamic theories with the theory, in which the flows in this frame of reference are used.

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