THE HOLONOMY OF PFAFFIAN FORMS IN THE THERMOKINETIC POTENTIAL AND THE SYMMETRY PROPERTIES OF PHENOMENOLOGICAL COEFFICIENTS

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The existence of an integration multiplyer for Pfaffian forms of the thermokinetic potential leads to certain symmetry properties of phenomenological coefficients in the nonlinear domain of thermokinetics.

Li [1] proposed the macroscopic separability of nonequilibrium steady processes on the basis of a generalization of the classical Thomson hypothesis to the effect that simultaneous reversible and irreversible processes are independent of each other. The hypothesis of macroscopic separability is based on the assumption that any macroscopic process can be expanded and, in unique fashion, into a series of independent processes with regard to which the system may find itself in a state of partial equilibrium, i.e., when the rate of the indicated forward process is equal to the rate of the reverse process.

Proceeding from the formal expansion of the flows J_ν and the corresponding thermokinetic forces X_ν near the equilibrium state

$$J_\nu = \sum_\eta \beta_{\nu\eta} X_\eta + \frac{1}{2} \sum_\rho \sum_\sigma \beta_{\nu\rho\sigma} X_\rho X_\sigma + \ldots, \tag{1}$$

$$X_\nu = \sum_\eta \alpha_{\nu\eta} J_\eta + \frac{1}{2} \sum_\rho \sum_\sigma \alpha_{\nu\rho\sigma} J_\rho J_\sigma + \ldots \tag{2}$$

and using the one-to-one correspondence between the set of thermal forces and the set of flows governing the steady state, and also assuming the hypothesis of macroscopic separability, which is equivalent to adopting

$$\alpha_{\nu\eta} = \beta_{\nu\eta} = 0 \text{ when } \nu \neq \eta, \tag{3}$$

as well as

$$\alpha_{\nu\rho\sigma} = \beta_{\nu\rho\sigma} = 0 \tag{4}$$

in all cases with the exception of $\nu = \rho$ or $\nu = \sigma$, we can achieve the expansion of the arbitrary flow J_λ with respect to the arbitrary set of forces

$$J_\lambda = \sum_\eta L_{\lambda\eta} X_\eta + \frac{1}{2} \sum_\eta \sum_\sigma L_{\lambda\eta\sigma} X_\eta X_\sigma + \ldots, \tag{5}$$

where the phenomenological coefficients $L_{\lambda\eta}$ and $L_{\lambda\eta\sigma}$ are associated with the phenomenological coefficients $\alpha_{\nu\eta}$, $\beta_{\nu\eta}$, $\alpha_{\nu\rho\sigma}$, and $\beta_{\nu\rho\sigma}$ of expansions (1) and (2) by the relations

$$L_{\lambda\eta} = \sum_\nu \beta_{\nu\nu} k_{\lambda\nu} k_{\eta\nu}, \tag{6}$$

$$L_{\lambda\eta\sigma} = -\sum_\nu \beta_{\nu\nu\nu} k_{\lambda\nu} k_{\sigma\nu} k_{\eta\nu} + \sum_\nu \sum_\delta \beta_{\nu\nu\delta} k_{\lambda\nu} k_{\eta\nu} k_{\sigma\delta} + \sum_\nu \sum_\delta \beta_{\nu\delta\nu} k_{\lambda\nu} k_{\sigma\nu} k_{\eta\delta}, \tag{7}$$

where $\|k_{\lambda\nu}\|$ is the matrix for the transformation of the independent flows J_ν^+ into the arbitrary values of

$$J_\lambda = \sum_\nu k_{\lambda\nu} J_\nu^+,$$

where J_ν^+, according to (3) and (4) has the following form (accurate to terms of order X^3)

$$J_\nu^+ = \beta_{\nu\nu} X_\nu + \frac{1}{2} \sum_\eta \beta_{\nu\nu\eta} X_\nu X_\eta + \frac{1}{2} \sum_\eta \beta_{\nu\eta\nu} X_\eta X_\nu - \frac{1}{2} \beta_{\nu\nu\nu} X_\nu^2. \tag{8}$$

The following symmetry relations follow directly from the structure of (6) and (7):

$$L_{\lambda\eta} = L_{\eta\lambda}, \tag{9}$$

$$L_{\lambda\eta\sigma} = L_{\lambda\sigma\eta}. \tag{10}$$

The Onsager relationships and the symmetry with respect to the second and third subscripts in the third-order coefficients are a consequence of the hypothesis of macroscopic separability and the existence of independent irreversible processes.

For the existence of the steady-state function — the thermokinetic potential $F(\{X\})$ — it is necessary and sufficient for the corresponding Pfaffian form, determined from the expression

$$dF = \sum_i^M J_i dX_i, \tag{11}$$

to be integrable, i.e., we must have the integration relationships

$$\frac{\partial J_i}{\partial X_k} = \frac{\partial J_k}{\partial X_i} \tag{12}$$

for any pair of subscripts (i, k) (max(i, k) corresponds to the number M in (11)).

The use of (12) with regard to (11) in conjunction with (1) immediately brings forth the requirement of complete symmetry for all phenomenological coefficients with respect to all the subscripts, i.e., condition (12) is sufficiently strong in its own right that to resort to an additional hypothesis such as the hypothesis of macroscopic separability is devoid of sense. It is therefore desirable, to the extent possible, to weaken condition (12) so as to achieve the consequences of conditions (3) and (4) and some additional hypothesis which does not extend to the requirement that there exist independent reversible processes.

As such a requirement we will use the assumption of holonomy, as expressed by form (11), i.e., unlike (12) we will assume that for form (11) there exists an integrating factor $\mu(\{X\})$ not equal to unity (the contention expressed in (12) reduces precisely to the condition that $\mu(\{X\}) = 1$). We then must have the following holonomy relationship for any triplet of subscripts (i, j, k):

$$\sum_{\substack{j \\ i \triangle k}} J_j \left(\frac{\partial J_i}{\partial X_k} - \frac{\partial J_k}{\partial X_i} \right) = 0, \tag{13}$$

where the sign $\sum_{\substack{j \\ i \triangle k}}$ denotes summation of the three following expressions with cyclical substitution of the subscripts $i \to j \to k \to i$. In the interest of simplicity, we will limit ourselves to the case of three arbitrary flows, although the general case can also be treated in this manner.

In the case of three flows there is a single holonomy condition:

$$\sum_{\substack{2 \\ 1 \wedge 3}} J_1 \left(\frac{\partial J_2}{\partial X_3} - \frac{\partial J_3}{\partial X_2} \right) = 0; \tag{14}$$

for the general form of flow expansion we have

$$J_i = \sum_j^3 L_{ij} X_j + \frac{1}{2} \sum_j^3 \sum_k^3 L_{ijk} X_j X_k + \cdots. \tag{15}$$

Substituting (15) into (14) and restricting ourselves to terms no higher than the second order, we obtain

$$\left(L_{11}X_1 + L_{12}X_2 + L_{13}X_3 + \frac{1}{2}L_{111}X_1^2 + \frac{1}{2}L_{122}X_2^2 + \frac{1}{2}L_{133}X_3^2 + L_{112}X_1X_2 + L_{113}X_1X_3 + L_{123}X_2X_3\right)$$

$$\times(L_{23} + L_{231}X_1 + L_{232}X_2 + L_{233}X_3 - L_{32} - L_{321}X_1 - L_{322}X_2 - L_{323}X_3)$$

$$+\left(L_{21}X_1 + L_{22}X_2 + L_{23}X_3 + \frac{1}{2}L_{211}X_1^2 + \frac{1}{2}L_{222}X_2^2 + \frac{1}{2}L_{233}X_3^2 + L_{212}X_1X_2 + L_{213}X_1X_3 + L_{223}X_2X_3\right)$$

$$\times(L_{31} + L_{311}X_1 + L_{312}X_2 + L_{313}X_3 - L_{13} - L_{131}X_1 - L_{132}X_2 - L_{133}X_3)$$

$$+\left(L_{31}X_1 + L_{32}X_2 + L_{33}X_3 + \frac{1}{2}L_{311}X_1^2 + \frac{1}{2}L_{322}X_2^2 + \frac{1}{2}L_{333}X_3^2 + L_{312}X_1X_2 + L_{313}X_1X_3 + L_{323}X_2X_3\right)$$

$$\times(L_{12} + L_{121}X_1 + L_{122}X_2 + L_{123}X_3 - L_{21} - L_{211}X_1 - L_{212}X_2 - L_{213}X_3) = 0. \tag{16}$$

We can then take into consideration the symmetry relationships which follow from the principle of macroscopic separability, and we can then separately equate to zero the coefficients for identical combinations of arbitrary thermal forces. These operations lead to the following system of uniform equations relating the coefficients of second and third order:

$$L_{11}[L_{231} - L_{321}] + L_{12}[L_{311} - L_{131}] + L_{13}[L_{121} - L_{211}] = 0;$$

$$L_{12}[L_{232} - L_{322}] + L_{22}[L_{312} - L_{132}] + L_{23}[L_{122} - L_{212}] = 0;$$

$$L_{13}[L_{233} - L_{323}] + L_{23}[L_{313} - L_{133}] + L_{33}[L_{123} - L_{213}] = 0;$$

$$L_{11}[L_{232} - L_{322}] + L_{12}[L_{213} - L_{123}] + L_{22}[L_{211} - L_{131}] + L_{13}[L_{122} - L_{212}] + L_{23}[L_{121} - L_{211}] = 0; \tag{17}$$

$$L_{11}[L_{233} - L_{323}] + L_{13}[L_{132} - L_{312}] + L_{12}[L_{313} - L_{133}] + L_{23}[L_{311} - L_{131}] + L_{33}[L_{121} - L_{211}] = 0;$$

$$L_{12}[L_{233} - L_{323}] + L_{13}[L_{232} - L_{322}] + L_{22}[L_{313} - L_{133}] + L_{23}[L_{321} - L_{231}] + L_{33}[L_{122} - L_{212}] = 0.$$

This system of six equations can be treated as determinant for the six second-order coefficients which remained after we have taken into consideration the Onsager symmetry relations: L_{11}, L_{12}, L_{13}, L_{22}, L_{23}, and L_{33}. The condition of a nontrivial solution for this system of equations with respect to the second-order coefficients, i.e., the physical requirement of free choice for these coefficients and the requirement that they not all be equal to zero simultaneously is expressed in terms of the properties of the determinant of this system, which must clearly vanish. For convenience, we introduce the notation

$$\begin{aligned}
A &= L_{231} - L_{321}, & B &= L_{232} - L_{322}, \\
C &= L_{233} - L_{323}, & M &= L_{311} - L_{131}, \\
E &= L_{213} - L_{123}, & K &= L_{313} - L_{133}, \\
T &= L_{121} - L_{211}, & H &= L_{122} - L_{212}, \\
P &= L_{132} - L_{312}.
\end{aligned} \tag{18}$$

With this notation the determinant of system (17) has the form

$$\begin{vmatrix}
A & M & T & 0 & 0 & 0 \\
0 & B & 0 & -P & H & 0 \\
0 & 0 & C & 0 & K & -E \\
B & E & H & M & T & 0 \\
C & K & P & 0 & M & T \\
0 & C & B & K & -A & H
\end{vmatrix} \tag{19}$$

We rearrange the columns as follows: column 2 changes places with column 4, 3 with 6, and then 5 with 6; this brings the determinant to the form

$$\begin{vmatrix}
A & 0 & 0 & M & T & 0 \\
0 & -P & 0 & B & 0 & H \\
0 & 0 & -E & 0 & C & K \\
B & M & 0 & E & H & T \\
C & 0 & T & K & P & M \\
0 & K & H & C & B & -A
\end{vmatrix}$$

A single relationship exists between the elements of this determinant, which follows from the symmetry of (10), and we obtain

$$A = P + E. \tag{20}$$

The final form of the determinant is thus

$$
\begin{vmatrix}
P+E & 0 & 0 & M & T & 0 \\
0 & -P & 0 & B & 0 & H \\
0 & 0 & -E & 0 & C & K \\
B & M & 0 & E & H & T \\
C & 0 & T & K & P & M \\
0 & K & H & C & B & -P-E
\end{vmatrix}
\tag{21}
$$

If we require that each of the second-order coefficients is independent, this will indicate that the rank of a given determinant must be equal to zero and, thus, all elements of the determinant are equal to zero. This requirement is equivalent to complete symmetry for the third-order coefficients, as we can see from (18). Consequently, the complete symmetry of the second- and third-order coefficients follows as a consequence of macroscopic separability, the holonomy of form (15), and the independence of the six second-order coefficients: L_{11}, L_{12}, L_{13}, L_{23}, L_{22}, and L_{33}.

However, the requirement that the second-order coefficients be independent is not necessary, since in the nonlinear domain these relationships between irreversible phenomena can be realized so that this requirement is violated. For example, an interesting special case is the vanishing of the determinant under conditions that the rank of the determinant shown in (21) is four and $P = E = 0$. In this case the independent second-order coefficients will number only three: L_{11}, L_{22}, and L_{33}, while the determinant reduces to a determinant of third order:

$$
\begin{vmatrix}
0 & 0 & 0 & M & T & 0 \\
0 & 0 & 0 & B & 0 & H \\
0 & 0 & 0 & 0 & C & K \\
B & M & 0 & 0 & H & T \\
C & 0 & T & K & 0 & M \\
0 & K & H & C & B & 0
\end{vmatrix}
=
\begin{vmatrix}
M & T & 0 \\
B & 0 & H \\
0 & C & K
\end{vmatrix}
\times
\begin{vmatrix}
B & M & 0 \\
C & 0 & T \\
0 & K & H
\end{vmatrix}
= (BTK + MHC)^2.
\tag{22}
$$

Thus, in the case $P = E = 0$ the remaining coefficients satisfy the relationship

$$BTK = -MHC. \tag{23}$$

The special realization of this case involves the selection of three independent processes. Then, according to (3), (4), and (18), we have $A = P = E = 0$, while $B = L_{232}$, $T = L_{121}$, $K = L_{313}$, $M = -L_{131}$, $H = -L_{212}$, $C = -L_{323}$. Relation (23) gives us the relationship between these coefficients:

$$L_{232}L_{121}L_{313} = L_{131}L_{212}L_{323}. \tag{24}$$

This special case is apparently more accessible to experimental verification.

Similar relationships may be achieved in the assumption of other values for the rank of the determinant, e.g., in the case of rank five we have the relationship $HK = CT$, etc. The selection of the rank naturally relates to the competence of the very nature of the phenomenon and is solved by experimentation. The only thing that can be stated reliably, a priori, is the fact that within the framework of the hypothesis of macroscopic separability and for processes with a holonomic form (11) between coefficients of the third order there exists at least one relationship in the form of determinant (21) equal to zero.

LITERATURE CITED

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