A FORMALISM OF NONLINEAR NONEQUILIBRIUM THERMODYNAMICS

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The variational formalism is applied to the nonlinear law of kinetics (scalar processes). Using the Lagrangian of a system as some function of state (entropy of large departures from equilibrium) makes it possible to construct a formalism of nonlinear thermodynamics which is analogous to the linear case.

We consider a class of scalar nonlinear nonequilibrium processes subject to the system of dynamic equations

$$\dot{x}_i = \dot{x}_i(x_1, \ldots, x_n), \quad i = 1, 2, \ldots, n. \tag{1}$$

If (1) is expanded into a series and only the first-order terms in the state variables x_i are retained, then the linear law of kinetics, in the thermodynamic interpretation, corresponds to the Osnager system of equations [1].

One of the fundamental problems in nonlinear nonequilibrium thermodynamics is to find (1) in explicit form for the entire kinetic range of a process ($0 \leq t \leq \infty$).

A similar system had been postulated in [2] in the form of the time theorem. An analogous form of equations was then derived in [3], but on a physical basis using a stochastic model of a nonequilibrium process rather than by way of a priori construction.

A not less important theoretical problem is the construction of a thermodynamic formalism for nonlinear nonequilibrium processes: the introduction of nonlinear thermodynamic forces, nonlinear increases in entropy, nonlinear force equations, etc.

We will show here that, by extending the variational principle in nonlinear thermodynamics [4] to nonlinear processes with due consideration of the results in [3], it becomes possible to represent the formalism of nonlinear processes of a given type in just as simple terms as in the linear case.

We will recall that for n = 1, according to [3], (1) can be written in the form

$$\dot{x} = K\left\{\exp\left[a\frac{\partial S}{\partial x}\right] - 1\right\}, \tag{2}$$

$$K = c\exp\left[-a\frac{\partial S_2}{\partial x}\right]. \tag{3}$$

It has been assumed here that the system tends toward equilibrium in two opposing steps, inasmuch as $S = S_1 + S_2$ represents the total entropy made up of entropy S_1 in the forward process and entropy S_2 of the reverse process. The quantity S obeys the Gibbs rule.

The quantities c and a are, to the first approximation considered independent of X, i. e., are regarded as phenomenological constants.

Considering that the linear thermodynamic forces X are defined by the relation

$$X = \frac{\partial \Delta S}{\partial x} = \frac{\partial S}{\partial x}, \tag{4}$$

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we can rewrite expression (2) as

$$\dot{x} = K\{\exp[aX] - 1\}. \tag{5}$$

It is easy to ascertain that expression (5) obeys the correspondence principle: expanding (5) into a MacLaurin series and retaining only the linear terms, we obtain the same results as those based on linear thermodynamics. It is possible then to determine c and a in terms of the phenomenological coefficient L, namely:

$$ca = L. \tag{6}$$

An extension of the same stochastic model to the case n > 1 leads to a system of kinetic equations:

$$\begin{gathered}\dot{x}_i = \sum_j^n K_{ij}\{\exp[a_j X_j] - 1\},\\ K_{ij} = K_{ij}^0 \exp\left\{- a_j\left[\frac{\partial S_2}{\partial x_j} - \left(\frac{\partial S_2}{\partial x_j}\right)_{x_j=0}\right]\right\},\end{gathered} \tag{7}$$

$$K_{ij}^0 = K_{ij} \quad (\vec{x} = 0), \tag{8}$$

considering now the linear approximations, we find

$$K_{ij}^0 a_j = L_{ij}, \qquad L_{ij} = L_{ji}. \tag{9}$$

For further calculations, the system of linear kinetic equations (7) will be conveniently represented in the form

$$\begin{gathered}\dot{x}_i = \sum_j L_{ij} B_j (\exp a_j X_j - 1),\\ i = 1, 2, \ldots, n,\end{gathered} \tag{10}$$

with B_j expressed as

$$B_j(x_1, \ldots, x_n) = a_j \exp\left\{-a_j\left[\frac{\partial S_2}{\partial x_j} - \left(\frac{\partial S_2}{\partial x_j}\right)_{x_j=0}\right]\right\}. \tag{11}$$

Let us now consider (10) from the variational point of view [4].

We recall that the variational principle [4] is stated as follows:

$$\delta\mathcal{L} + \sum_i^n Q_i \delta x_i = 0 \tag{12}$$

with the Lagrange function

$$\mathcal{L} = -\Delta S(x_1, x_2, \ldots, x_n) \tag{13}$$

and the dissipation forces

$$Q_i = \frac{\partial \Phi}{\partial \dot{x}_i}, \tag{14}$$

$$\Phi = \frac{1}{2}\sum_{i,k} L_{ik}^{-1} \dot{x}_i \dot{x}_k. \tag{15}$$

Equation (12) leads to the system of kinetic equations of linear thermodynamics:

$$\dot{x}_i = \sum_k L_{ik} X_k. \tag{16}$$

In accordance with (1), we assume that the dissipation function is structurally a homogeneous second-order one. In other words, Φ^* is of the form (15) also far from equilibrium. (The asterisk * will from now on refer to nonlinear processes). For instance, as has been shown earlier in [5], chemical reactions of an arbitrary order can belong to the same class of nonlinear processes. Thus, we have for Φ^*:

$$\Phi^* = \frac{1}{2}\sum_{i,k} (L_{ik}^{-1})^* \dot{x}_i^* \dot{x}_k^*. \tag{17}$$

Since

$$\dot{x}_k^* \to x_k, \quad k = 1, 2, \ldots, n,$$
$$\Phi^* \to \Phi, \tag{18}$$

as equilibrium is approached and the matrix of phenomenological coefficients L* has been stipulated constant, hence it necessarily follows from (18) that

$$L^* = L \tag{19}$$

(the asterisk * with $\dot{x}_k^*$ will be from now on omitted).

If the nonlinear dissipation forces are defined according to the same law (14), i. e., if

$$Q_i^* = \frac{\partial \Phi^*}{\partial \dot{x}_i}, \quad i = 1, 2, \ldots, n, \tag{20}$$

then the kinetic equations (10) become a consequence of the variational principle (12) with the Lagrange function $\mathcal{L}^*$

$$\mathcal{L}^* = \int_0^{x_1} \ldots \int_0^{x_n} \sum_j B_j (\exp a_j X_j - 1)\, dx_j. \tag{21}$$

Carrying the analogy with linear processes further, and taking into account (13), we may introduce the function

$$\Delta S^* = - \int_0^{x_1} \ldots \int_0^{x_n} \Big\{ \sum_j B_j (\exp a_j X_j - 1) \Big\}\, dx_j \tag{22}$$

and define it as the entropy of large departures from equilibrium, of large fluctuations. More precisely, ΔS* is the deviation of entropy from equilibrium at large values of x_i. Such an interpretation of function (22) requires a special statistical basis. Nevertheless, as will be shown here, the introduction of ΔS* according to formula (22) appears extremely useful for constructing a formalism of nonlinear thermodynamics.

We will first examine the general properties of ΔS*.

1. Moving into the linear range, we have

$$\Delta S^* (x_1, \ldots, x_n) \to \Delta S (x_1, \ldots, x_n)$$
$$\lim_{x_1, \ldots, x_n \to 0} \Delta S^* (x_1, \ldots, x_n) = 0. \tag{23}$$

2. Unlike ΔS, function ΔS* does not obey the Gibbs rule. This feature of ΔS* applies only in the region far from equilibrium.

3. The explicit form of ΔS* or the differential equation for dS* can be found from formula (22).

For illustration, we will consider an adiabatically insulated system with r reactions of an arbitrary order. The differential version of (22) is

$$TdS^* = MR \sum_j^r \Big\{ \exp \Big[\frac{1}{R} \sum_k^p |\nu_{kj}|\, \Delta\mu_k \Big] - \exp \Big[\frac{1}{R} \sum_{m=p+1}^n |\nu'_{mj}|\, \Delta\mu_m \Big] \Big\}\, dx_j. \tag{24}$$

Here $\Delta\mu_k$ is the deviation of the chemical potential of the k-th component from equilibrium, expressed in terms of the degree of completion of the given reaction, $|\nu_{kj}|$ is the absolute value of the stoichiometric coefficient of the k-th component on the left-hand side of the j-th reaction, and $|\nu_{mj}|$ is the absolute value of the stoichiometric coefficient of the m-th component on the right-hand side of the j-th reaction.

It can be easily ascertained that at the limit, as equilibrium is approached, (24) becomes the Gibbs equation (the system is adiabatically insulated):

$$TdS = M \sum_j^r A_j dx_j. \tag{25}$$

The chemical agent A_j of the j-th reaction is

$$A_j \equiv -\sum_k^n \nu_{kj}\mu_k. \tag{26}$$

Formalism of Nonlinear Thermodynamics. We introduce nonlinear thermodynamic forces X_i^*, just as in (4),

$$X_i^* = -\frac{\partial \Delta S^*}{\partial x_i},\ i = 1,\ 2,\ \ldots,\ n. \tag{27}$$

Applying the variational principle (12) with (27), (21), (22), and (20) taken into account, we obtain the system of kinetic equations in the form

$$\dot{x}_i = \sum_k L_{ik} X_k^*. \tag{28}$$

In other words, the system of dynamic equations remains linear when represented in terms of forces. We recall that the matrix of phenomenological coefficients L_{ik} is known from linear thermodynamics and satisfies the Osnager reciprocity relations.

When applied to our case of chemical reactions, system (28) can be expressed as

$$\dot{x}_j = L_{jj} A_j^*,\quad j = 1,\ 2,\ \ldots,\ r, \tag{29}$$

where the nonlinear chemical agent A_j^* of the j-th reaction appears to play the role of nonlinear forces:

$$X_j^* \equiv A_j = R\left\{\exp\left[\frac{1}{R}\sum_k^{p} |\nu_{kj}|\,\Delta\mu_k\right] - \exp\left[\frac{1}{R}\sum_{m=p+1}^{n} |\nu'_{mj}|\,\Delta\mu_m\right]\right\}, \tag{30}$$

with which expression (29) becomes equivalent to the law of mass action.

As equilibrium is approached, $A_j^* \to A_j$. Let us now determine the nonlinear rate of entropy change σ^*:

$$\sigma^* = \frac{d\Delta S^*}{dt}.$$

Considering that $\Delta S^* = \Delta S^*(x_1, \ldots, x_n)$, we find that

$$\sigma^* = \sum_i \dot{x}_i X_i^*, \tag{32}$$

i. e., as in the linear case, the rate of entropy change is determined by the sum of products of conjugate thermal fluxes and thermodynamic forces.

We will now show that the condition

$$\sigma^* \geqslant 0 \tag{33}$$

is a criterion for the evolution of nonlinear processes in adiabatically insulated systems. Since

$$\sigma^* = 2\Phi^*, \tag{34}$$

hence condition (33) is satisfied by Φ^* in a positive-definite quadratic form, which is possible only if all the eigenvalues of matrix L are positive. This latter requirement is met, as a consequence of the Second Law of Thermodynamics

$$2\Phi = \sigma \geqslant 0. \tag{35}$$

Under steady-state conditions, when $\Delta S^* = \text{const}$, the variational principle (12) in the case of nonlinear processes becomes

$$\sum_i Q_i^*\,\delta x_i = 0. \tag{36}$$

By virtue of the arbitrariness of δx_i, we obtain the following system of equations

$$(Q_{st}^*)_i = 0,\ \ i = 1,\ 2,\ \ldots,\ n, \tag{37}$$

equivalent to the condition

$$\delta\Phi^* = 0. \tag{38}$$

Thus, under steady-state conditions, the rate of entropy change σ^* is minimum.

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