

A Variational Principle of Steady-State Transport Processes

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A variational principle of steady-state transport processes has been derived from a basic inequality in the macroscopic theory of nonequilibrium thermodynamics. The extremum property of a variational integral Φ is established from the stability of steady state, and the existence of Φ is discussed from the integrability of a Pfaffian differential equation. The extremum principle presented here may be called the principle of minimum thermokinetic potential and may be regarded as the generalization of the principle of minimum entropy production for the case of nonlinear fluxes. For illustration, a simple heat-conduction problem has been given as an example.

I. Introduction

IN 1954, Glansdorff and Prigogine had derived a general evolution criterion applicable to the whole range of macroscopic physics.¹ Specifically, they have shown the validity of the following fundamental inequality:

$$\int_V dV \mathbf{J}_i \cdot d\mathbf{X}_i \leq 0 \quad (1)$$

for a natural dissipative process in a continuous medium with time-independent boundary conditions. Here \mathbf{J}_i is the vectorial flux of a conservative variable a_i and $d\mathbf{X}_i$ is the time variation of the corresponding thermodynamic force \mathbf{X}_i ,² and the repeated subscripts i imply the summation consists of all the independent fluxes and forces within the system and at the boundary.

The inequality essentially states that the irreversible changes of a system along a time evolutionary path must be such that the thermodynamic forces \mathbf{X}_i decrease by virtue of the fluxes \mathbf{J}_i induced by them and may be regarded as the stability requirement of all irreversible processes. In fact, it can be shown³ that it is a direct consequence of the second law inequality being applied to a local volume element in a nonequilibrium system, assuming that the local state is stable.

In an analogous manner one defines the entropy function in the theory of equilibrium thermodynamics⁴; the relationship in (1) may be used to define a state functional F when the following is a total differential:

$$dF = \int_V dV \mathbf{J}_i \cdot d\mathbf{X}_i \quad (2)$$

Obviously, when F exists, it defines an entropylike functional, and may be expected to play a role similar to that of the entropy function S in the theory of equilibrium thermodynamics.

Much has been written⁵ on the physical interpretations and the mathematical implications of this inequality since Glansdorff and Prigogine first published their paper in 1954. Among these, one of the most fruitful results is the use of the inequality to formulate a variational principle for steady-state transport processes. However, in most of the previous works, the existence of a variational principle was drawn directly from the monotone behavior of F and no derivation was given to show that the variation of F in the neighborhood of steady states is, in fact, positive definite. In other words, the validity of the inequality

$$\int_V dV \mathbf{J}_i \cdot \delta\mathbf{X}_i \geq 0 \quad (3)$$

has not been shown explicitly.

In what follows, we shall attempt to construct Glansdorff and Prigogine's inequality directly from the basic postulate

of irreversible thermodynamics, namely the principle of local stable equilibrium. The inequality will then be used to derive a variational principle of steady-state transport processes. The existence of the potential will also be examined from the viewpoint of the integrability of a Pfaffian differential equation. As an example, a simple heat-conduction problem has been given to illustrate the implication of the inequality.

II. Stability of Steady State

For the derivation of the universal evolutionary criterion, it is only necessary to postulate the validity of the principle of local stable equilibrium. In other words, the thermodynamic functions for a small local element in a nonequilibrium system will be represented by the same functions of the state variables as those of the corresponding equilibrium system. Thus, for a typical nonequilibrium system, one may write the fundamental relation associated with a local entropy S , per unit volume, as

$$dS = P_i da_i \quad (4)$$

where a_i are the conservative variables per unit volume, and P_i are the corresponding thermodynamic functions

$$P_i = \partial S / \partial a_i = S_{,i} \quad (5)$$

Consequently, in a local volume element of a nonequilibrium system, the entropy maximum principle implies that for local equilibrium

$$dS = 0 \quad (6)$$

and for stability

$$d^2S \leq 0 \quad (7)$$

or, stated equivalently, the matrix $S_{,ij}$ is negative semidefinite.

Now consider a nonequilibrium system described by the following set of partial differential equations:

$$\partial a_i / \partial t + \nabla \cdot \mathbf{J}_i = 0, \quad i = 1, 2, \dots, n \quad (8)$$

By virtue of (5) and (8), the rate of entropy production \dot{S}_V in a continuous system of volume V can be written as

$$\dot{S}_V = \int_V dV \mathbf{J}_i \cdot \mathbf{X}_i \quad (9)$$

where \mathbf{J}_i is the vectorial flux of a conservative quantity a_i and \mathbf{X}_i is the generalized force defined by

$$\mathbf{X}_i = \nabla S_{,i} \quad (10)$$

Within the scope of the foregoing assumptions, one can show that the inequality

$$\int_V dV \mathbf{J}_i \cdot d\mathbf{X}_i \leq 0 \quad (11)$$

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is valid for a natural dissipative process with time stationary boundary conditions.

This is done first by substituting the time variation of \mathbf{X}_i into (10), and then rewriting the expression by means of the divergence theorem;

$$\int_V dV \mathbf{J}_i \cdot d(\nabla S_{,i}) = \int_V dV \mathbf{J}_i \cdot \nabla S_{,ij} da_j = - \int_V dV \nabla \nabla \cdot \mathbf{J}_i S_{,ij} da_j + \int_A dA \mathbf{n} \cdot \mathbf{J}_i S_{,ij} da_j \quad (12)$$

It is evident that for stationary boundary conditions, namely $da_j = 0$ on the boundary surface A , the contribution due to the surface integral in the previous quantity is zero, and the expression may be reduced to the form

$$- \int_V dV S_{,ij} \nabla \cdot \mathbf{J}_i da_j \quad (13)$$

or by means of (8)

$$\int_V dV S_{,ij} (\partial a_i / \partial t) da_j \quad (14)$$

The foregoing quantity may be regarded as the differential of a functional F . Suppose that the differential form dF along a time evolution path of a dynamic trajectory is defined in the space of $n + 1$ coordinates $(a_1, a_2, \dots, a_n, t)$; then it is possible to define the time derivative of the function $F(t)$ by

$$\dot{F}(t) = \int_V dV S_{,ij} \dot{a}_i \dot{a}_j \leq 0 \quad (15)$$

or

$$dF = \int_V dV S_{,ij} \dot{a}_i da_j \leq 0$$

where \dot{a}_i , $i = 1, 2, \dots, n$ are the total derivative of a_i with respect to time. Since $\dot{F}(t)$ is a quadratic function of \dot{a}_i , the inequality is proved in view of (7).

Integrating Eq. (15) along the time path, one obtains

$$F(t) = \int_{t_0}^t \dot{F}(t) dt + F(t_0) \quad (16)$$

where t_0 is the initial instant of the nonequilibrium state. It follows from (15) that

$$F(t_0) \geq F(t_1) \geq \dots \geq F(t_\infty) \quad (17)$$

for

$$t_0 < t_1 < \dots < t_\infty$$

Hence, $F(t)$ decreases monotonically with respect to increasing time and must eventually reach the minimum value $F(t_\infty)$ as the system evolves to its steady state a^* . Obviously, the evolutionary criterion stated in (15) is a direct consequence of the principle of local stable equilibrium, and may be regarded as an alternative postulate in the theory of nonequilibrium thermodynamics.

It is worth noting here that $F(t)$ is closely related to the familiar concept of Liapunor function in the stability theory of differential equations.⁹ If one defines a Liapunor function

$$V(t) = \int_{t_0}^t \dot{F}(t) dt \geq 0 \quad (18)$$

for the set of partial differential equations in (9), stability of the steady-state solution a_i^* that satisfies

$$\nabla \cdot \mathbf{J}_i^* = 0 \quad (19)$$

can be determined by observing the signs of $V(t)$ and $\dot{V}(t)$. Since $V(t)$ is positive semidefinite and $\dot{V}(t)$ is negative semidefinite for all motions defined by (9), one may easily conclude that all irreversible processes that are governed by the evolutionary criterion (15) must possess a stable steady state.

III. Variational Principle of Stable Steady State

Since the definition of the universal criterion (15) is analogous to that of the second law inequality in the theory of

equilibrium thermodynamics, one may proceed to establish a variational principle for the steady state that corresponds to the entropy maximum principle in the equilibrium case. In specific, it will be shown that if the steady state is stable, then there exists a functional Φ of the conservative variables a_i that has an absolute minimum at the steady state a_i^* with respect to all admissible varied states a_i .

Suppose that

$$a_i = a_i^* + \delta a_i \text{ in } V \quad (20)$$

where the variation δa_i is taken in time frozen state, then the first variation of \dot{F} may be formed as

$$\begin{aligned} \delta \dot{F} = \int_V dV [S_{,ij} \dot{a}_i \dot{a}_j - S_{,ij} \dot{a}_i^* \dot{a}_j^*] = \\ \int_V dV [S_{,ij} \dot{a}_i^* \delta \dot{a}_j + S_{,ij} \dot{a}_j^* \delta \dot{a}_i] + \\ \int_V dV S_{,ij} \delta \dot{a}_i \delta \dot{a}_j + \int_V dV S_{,ijk} \dot{a}_i^* \dot{a}_j^* \delta a_k \end{aligned} \quad (21)$$

When the process is at the steady state, \dot{a}_i^* identically vanishes, and in view of the conservative law of the perturbed state variables

$$\delta \dot{a}_i + \nabla \cdot \mathbf{J}_i = 0 \quad (22)$$

(21) can be written as

$$\delta \dot{F} = \int_V dV S_{,ij} \delta \dot{a}_i \delta \dot{a}_j = - \int_V dV S_{,ij} \nabla \cdot \mathbf{J}_i \delta \dot{a}_j \leq 0 \quad (23)$$

where the inequality is the consequence of the stable steady state.

Integrating (23) with respect to time and observing that the variation of the initial state is δa_j and the variation of the final state δa_j^* is zero, one obtains

$$\begin{aligned} - \int_0^\infty \int_V dV S_{,ij} \nabla \cdot \mathbf{J}_i \delta \dot{a}_j dt = - \int_V dV S_{,ij} \nabla \cdot \mathbf{J}_i \times \\ (\delta a_j^* - \delta a_j) = \int_V dV S_{,ij} \nabla \cdot \mathbf{J}_i \delta a_j \leq 0 \end{aligned} \quad (24)$$

Now one may define the thermokinetic potential Φ of the steady state by

$$\delta \Phi = - \int_V dV S_{,ij} \nabla \cdot \mathbf{J}_i \delta a_j \geq 0 \quad (25)$$

This is exactly the desired extremum property of the steady state. By means of (10), and the divergence theorem, (25) can be rewritten as

$$\begin{aligned} \delta \Phi = \int_V dV \mathbf{J}_i \cdot \nabla S_{,ij} \delta a_j - \int_A dA \mathbf{n} \cdot \mathbf{J}_i S_{,ij} \delta a_j = \\ \int_V dV \mathbf{J}_i \cdot \delta \mathbf{X}_i \geq 0 \end{aligned} \quad (26)$$

where the surface integral vanishes due to $\delta a_j = 0$ on A .

Although the variational principle obtained here is identical to the one stated in the previous papers,^{6,7} the introduction of two functionals F and Φ here enable one to derive the inequalities (15) and (29) from separate mathematical considerations and, at the same time, to distinguish the functional characteristics between the universal evolution criterion [Eq. (15)], which is valid for all dissipative processes along a time evolutionary path, and the minimum thermokinetic potential (26) which is only valid for a process in steady states.

IV. Integrability of Thermokinetic Potential

Suppose Φ exists and it can be expressed as

$$\Phi = \int_V L(u_1, u_2, \dots, u_n) dV \quad (27)$$

where u_1, u_2, \dots, u_n are functions of the space variables defined in the sense of the variational calculus and L is the Lagrangian density function; then the first variation of Φ gives

$$\delta \Phi = \int_V \delta L dV = 0 \quad (28)$$

or

$$\delta L = (\partial L / \partial u_i) \delta u_i = 0 \quad (29)$$

According to a well-known theorem on the integrability of the Pfaffian differential equation,¹⁰ a Pfaffian form of

$$g_i du_i = 0 \quad (30)$$

is integrable if, and only if,

$$\partial g_i / \partial u_j = \partial g_j / \partial u_i \quad i, j = 1, \dots, n \quad i \neq j \quad (31)$$

are satisfied.

The conditions on the integrability of (26) are thus specified by the $n(n-1)/2$ relationships in (31). Obviously, when the fluxes \mathbf{J}_i are functions of the thermodynamic forces \mathbf{X}_i ,

$$\mathbf{J}_i = L_{ij} \mathbf{X}_j \quad (32)$$

Equation (31) may be seen to be equivalent to the Onsager's reciprocal relationship, i.e.,

$$L_{ij} = L_{ji} \quad (33)$$

However, if the phenomenological coefficients L_{ij} are also explicit functions of the state variables a_i , as it is in the case of heat conduction, the previous conditions (33) are no longer sufficient. To examine this case, it is convenient to express the relationship in (26) in terms of a_i , and the conditions in (31) now become

$$(\partial / \partial a_i) [\mathbf{J}_k \cdot \nabla S_{,kj}] = (\partial / \partial a_j) [\mathbf{J}_k \cdot \nabla S_{,ki}]$$

or

$$\mathbf{J}_{k,i} \cdot \nabla S_{,kj} = \mathbf{J}_{k,j} \cdot \nabla S_{,ki} \quad (34)$$

Again, if one assumes that the fluxes \mathbf{J}_k can be written as (32), but now the phenomenological coefficients L_{km} are functions of a_i and X_i , then (34) can be expressed as

$$\left[\frac{\partial L_{km}}{\partial a_i} + \frac{\partial L_{km}}{\partial \mathbf{X}_i} \cdot \nabla S_{,i,i} \right] \cdot \nabla S_{,kj} = \left[\frac{\partial L_{km}}{\partial a_j} + \frac{\partial L_{km}}{\partial \mathbf{X}_i} \cdot \nabla S_{,i,j} \right] \cdot \nabla S_{,ki} \quad (35)$$

The mathematical implications of the previous relationship for the general case are difficult to judge, but it is obvious that this again expresses a reciprocal relationship similar to that of (33). When L_{km} are independent of a_i , then (35) reduces directly to (34).

Since the phenomenological coefficient L_{ij} is an experimentally determined quantity, the $n(n-1)/2$ conditions in Eq. (31), in general, will not be met, and the thermokinetic potential cannot be found. However, for most practical purposes, it is often sufficient to replace the nonlinear flux \mathbf{J}_i by the following form:

$$\mathbf{J}_i \cong L_{ij}^* \mathbf{X}_j \quad (36)$$

where the L_{ij}^* is evaluated at the steady state, then to integrate the functional Φ in the neighborhood of the steady state to obtain

$$\Phi^0 = \frac{1}{2} \int_V dV L_{ij}^* \mathbf{X}_i \cdot \mathbf{X}_j \quad (37)$$

This functional Φ^0 is positive definite and vanishes identically at the steady state, and thus may be used to represent the true potential in the neighborhood of the steady state. Φ^0 has been given the name of the local potential by Glansdorff and Prigogine.⁸ It is worth noting here that by taking the variation of Φ^0 , one does not arrive at the steady-state equation directly. Instead, one obtains

$$\delta \Phi^0 = \int_V dV L_{ij}^* \mathbf{X}_i \cdot \delta \mathbf{X}_j = 0$$

or

$$\nabla \cdot [L_{ij}^* \mathbf{X}_j] = 0 \quad (38)$$

Obviously, Eq. (30) does not reduce to the Euler-Lagrange equation of (26)

$$\nabla \cdot [L_{ij} \mathbf{X}_j] = 0 \quad (39)$$

In order to remove such an inconsistency, Prigogine has introduced a subsidiary condition

$$a_i = a_i^* \quad (40)$$

so that (38) may be brought back to the form of (39) by means of (40). This is known as the self-consistent variational technique. Although the previous approach enables one to treat a large class of nonlinear problems by the method of local potential, the mathematical implication on the self-consistent technique and the conditions on convergence have not been stated correctly in the previous work.

The validity of the self-consistent technique and the precise definition of the local potential can be shown in the following manner. First, expand the nonlinear flux \mathbf{J}_i in terms of \mathbf{X}_i , then define the linearized flux \mathbf{J}'_i by

$$\mathbf{J}'_i = \mathbf{J}_i^0 + (\partial \mathbf{J}_i^0 / \partial \mathbf{X}_i) (\mathbf{X}_j - \mathbf{X}_j^0) \quad (41)$$

According to Kalaba,¹¹ \mathbf{J}_i may be replaced by the maximization of \mathbf{J}'_i over \mathbf{X}_i^0 , $a_i^0 = a_i$, if \mathbf{J}_i is a convex function of \mathbf{X}_i ;

$$\mathbf{J}_i = \text{Max}_{\mathbf{X}_i^0} [\mathbf{J}'_i] = \mathbf{J}'_i + \mathbf{P}_i \quad (42)$$

where \mathbf{P}_i is a positive function of \mathbf{X}_i .

Substituting (42) into (26), the variation of Φ becomes

$$\delta \Phi = \int_V dV [\text{Max}_{\mathbf{X}_i^0} \mathbf{J}'_i] \cdot \delta \mathbf{X}_i \quad (43)$$

We now define the local potential Φ' as the variational integral of the following equation:

$$\delta \Phi' = \int_V dV \mathbf{J}'_i \cdot \delta \mathbf{X}_i \quad (44)$$

Equation (43) may be written as

$$\delta \Phi = \delta \Phi' + \int_V dV \mathbf{P}_i \cdot \delta \mathbf{X}_i$$

or

$$\Phi = \text{Max}_{\mathbf{X}_i^0} \Phi'(\mathbf{X}, \mathbf{X}^0) \geq \Phi'(\mathbf{X}, \mathbf{X}^0) \quad (45)$$

Consequently,

$$\delta \Phi = \delta [\text{Max}_{\mathbf{X}_i^0} \Phi'] = \text{Max}_{\mathbf{X}_i^0} [\delta \Phi'] \quad (46)$$

if the maximum and the variational operations are assumed to be interchangeable.^{11,12} Since the local potential Φ' gives a lower bound for the functional Φ , the previous scheme may be used to compute approximate solutions whose convergence is now insured by (46).

For example, if L_{ij} are functions of the state variables only, then

$$\mathbf{J}'_i = L_{ij}^0 \mathbf{X}_j^0 + L_{ij}^0 (\mathbf{X}_j - \mathbf{X}_j^0)$$

and Φ' becomes

$$\begin{aligned} \delta \Phi' &= \int_V dV L_{ij}^0 \mathbf{X}_i \cdot \delta \mathbf{X}_j \\ &= \delta \left[\frac{1}{2} \int_V dV L_{ij}^0 \mathbf{X}_i \cdot \mathbf{X}_j \right] \end{aligned}$$

This is exactly the form of the local potential given in (37).

When L_{ij} are functions of the thermodynamic forces and state variables,

$$\mathbf{J}'_i = L_{ij}^0 \mathbf{X}_j + (\partial L_{ik}^0 / \partial \mathbf{X}_j) \mathbf{X}_k^0 (\mathbf{X}_j - \mathbf{X}_j^0)$$

and

$$\begin{aligned} \Phi' &= \frac{1}{2} \int_V dV L_{ij}^0 \mathbf{X}_i \cdot \mathbf{X}_j + \\ &\quad \frac{1}{2} \int_V dV (\partial L_{ik}^0 / \partial \mathbf{X}_j) \mathbf{X}_k^0 (\mathbf{X}_i - \mathbf{X}_i^0) \cdot (\mathbf{X}_j - \mathbf{X}_j^0) \end{aligned}$$

The form of Φ' now differs from that of the local potential defined by Prigogine. We shall illustrate these two cases in the example given in the next section.

V. Steady-State Heat Conduction

For the case of a simple heat-conduction problem, the only conservative variable of interest is the internal energy E (per unit volume), and the corresponding functions in Eq. (26) can be readily found as

$$\begin{aligned}\partial^2 S / \partial E^2 &= -1 / c_p T^2 \\ \delta E &= c_p \delta T \\ \delta \dot{E} &= -\nabla \cdot \mathbf{J}\end{aligned}\quad (47)$$

and

$$\mathbf{J} = -k_\alpha \partial T / \partial x_\alpha, \alpha = 1, 2, 3$$

where c is the specific heat and ρ is the density of the volume element, and k_α is the thermal conductivity in the x_α direction. Now, substituting the corresponding expressions of (47) into (25), one obtains the following variational form:

$$\delta \Phi = -\int_V dV (1/T^2) (\partial / \partial x_\alpha) (k_\alpha \partial T / \partial x_\alpha) \delta T = 0 \quad (48)$$

It is readily seen that the foregoing expression directly leads to the Euler-Lagrange equation of a steady-state heat-conduction problem

$$(\partial / \partial x_\alpha) (k_\alpha \partial T / \partial x_\alpha) = 0 \quad (49)$$

when T is specified on the boundary surface A .

In order to derive the local potential, it is more convenient to use the alternative form of (48);

$$\delta \Phi = \int_V dV (k_\alpha / T^2) (\partial T / \partial x_\alpha) \delta (\partial T / \partial x_\alpha) \quad (50)$$

When k_α are functions of T , we obtain

$$\Phi' = \Phi^0 = \frac{1}{2} \int_V dV k_\alpha^0 [(1/T_0) (\partial T / \partial x_\alpha)]^2 dV \quad (51)$$

Set the first variation of Φ^0 equal to zero, we have

$$(\partial / \partial x_\alpha) [k_\alpha^0 \partial T / \partial x_\alpha] = 0$$

The Euler-Lagrange equation of (51) is apparently different from that of (49). Since the local potential is equivalent to one-half of the entropy production, it is obvious that the direct minimization of Φ^0 or the entropy production does not lead to a true extremum principle.^{6,7} For the case of a simple heat-conduction problem, the true thermokinetic potential Φ may be constructed as follows. First, multiply an integration factor $g = 2k_\alpha T^2$ to the integrand of Eq. (48); then,

$$\delta \Phi = -2 \int_V dV (\partial / \partial x_\alpha) (k_\alpha \partial T / \partial x_\alpha) k_\alpha \delta T$$

Now suppose that the heat conductivity k_α is a function of temperature only, and T is fixed on A ; then,

$$\delta \Phi = 2 \int_V dV k_\alpha (\partial T / \partial x_\alpha) \delta (k_\alpha \partial T / \partial x_\alpha)$$

and Φ becomes

$$\Phi = \int_V dV (k_\alpha \partial T / \partial x_\alpha)^2 = \int_V dV (k_\alpha T^2 \partial T^{-1} / \partial x_\alpha)^2 \quad (52)$$

It is easy to verify that the minimization of Φ indeed leads to the steady-state equation in (49).

When k_α are functions of $\partial T / \partial x_\alpha$, quasi-linearization of (50) gives

$$\begin{aligned}\delta \Phi' &= \int_V dV (1/T_0^2) (k_\alpha^0 \partial T / \partial x_\alpha) \delta \partial T / \partial x_\alpha + \\ &\quad \int_V dV (1/T_0^2) (k'_\alpha \partial T_0 / \partial x_\alpha) (\partial T / \partial x_\alpha - \partial T_0 / \partial x_\alpha) \delta \partial T / \partial x_\alpha\end{aligned}$$

Thus,

$$\begin{aligned}\Phi' &= \frac{1}{2} \int_V dV (k_\alpha^0 / T_0^2) (\partial T / \partial x_\alpha)^2 + \\ &\quad \frac{1}{2} \int_V dV (k'_\alpha / T_0^2) (\partial T_0 / \partial x_\alpha) (\partial T / \partial x_\alpha - \partial T_0 / \partial x_\alpha)^2\end{aligned}\quad (53)$$

The variation of Φ' yields

$$\frac{\partial}{\partial x_\alpha} \left[\left(k_\alpha^0 + k'_\alpha \frac{\partial T_0}{\partial x_\alpha} \right) \frac{\partial T}{\partial x_\alpha} \right] = \frac{\partial}{\partial x_\alpha} \left[k'_\alpha \left(\frac{\partial T_0}{\partial x_\alpha} \right)^2 \right] \quad (54)$$

If the maximization $T = T_0$ is applied to (54), it reduces directly to (49).

A true thermokinetic potential for $k_\alpha = k_\alpha^0 + k'_\alpha \partial T / \partial x_\alpha$, where k_α^0 , k'_α are constants, can be obtained if we take $g = T^2$. Equation (48) now becomes

$$\delta \Phi = -\int_V dV (\partial / \partial x_\alpha) (k_\alpha \partial T / \partial x_\alpha) \delta T$$

and

$$\Phi = \int_V dV [(k_\alpha^0 / 2) (\partial T / \partial x_\alpha)^2 + (k'_\alpha / 3) (\partial T / \partial x_\alpha)^3] \quad (55)$$

The similarity between the two expressions in (53) and (55) again can easily be observed.

The method of local potential is, in fact, equivalent to the Newton-Raphson technique applied to variational equations. It differs from the direct linearization of (49) in that the iterative solutions converge monotonically to the true solution and it thus provides a more efficient computation scheme.

VI. Conclusion

We have presented a variational principle of steady-state transport process based on a basic inequality in the theory of nonequilibrium thermodynamics. The emphasis has been placed on the formulation of a true extremum principle which is valid even if the fluxes are nonlinear functions of thermodynamics forces and state variables. It is shown that the rate of entropy production in fact corresponds to the local representation of the thermokinetic potential, and that the principle of minimum entropy production is valid only if the Onsager's coefficients are constants. The so-called self-consistent variational technique for local potential is examined from the viewpoint of Min-Max operation, and the iteration scheme by means of local potential is shown to be equivalent to the Newton-Raphson technique applied to the universal criterion. A simple heat-conduction problem is used to illustrate the correct derivations of the local potentials when the thermoconductivities are either functions of temperature or the gradients of temperature.

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