

Persistency, Pseudo-Entropy, and the Thermokinetic Potential

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The microscopic concepts of persistency, pseudo-entropy, and the rate of pseudo-entropy production, introduced by Kikuchi from the viewpoint of path probability, and the macroscopic concept of thermokinetic potential, proposed by the author from the viewpoint of Carathéodory's inaccessibility postulate or of the principle of macroscopic separability, are shown to agree with each other within a constant numerical factor near the steady state for the two examples treated by Kikuchi.

THE three recently introduced concepts, persistency and pseudo-entropy production, deduced from microscopic considerations, and the thermokinetic potential, deduced from macroscopic considerations, will be shown in what follows to differ from each other by only a constant factor around the steady state at which all these quantities become extrema. Such an agreement between two entirely different approaches is considered to be of importance as an indication of coming vast improvement in our understanding of the nonequilibrium steady state. Briefly, the three concepts are described as follows:

Persistency was introduced by Kikuchi¹ in examining systems undergoing Markoffian irreversible changes of state. It is the probability that a certain nonequilibrium state will remain in the same state during a short time period τ along the most probable path. The logarithm of this probability is found to be proportional to τ for small τ and the proportionality factor is thus only a function of the state. This proportionality factor assumes a maximum value at the steady state; or, for the same τ , the steady state undergoing Markoffian irreversible processes is a state of maximum persistency.

Proceeding further to find the probability for a change of state during a longer time period, Kikuchi and Gottlieb² introduced the concept of pseudo-entropy which, when divided by the Boltzmann constant, is the logarithm of the probability for the system to deviate from the steady state along a special but most probable path called the anticausal path. This special path, under the condition that detailed balance holds, is simply the reversed natural path. The steady state is thus a state of maximum pseudo-entropy. Furthermore, the probability for the system originally at the steady state to deviate to a second state along the anticausal path is always larger than the probability for the same system to deviate to a third state along the anticausal path and then drift to the second state along the natural path. Since the probability of the natural path is very nearly unity, the pseudo-entropy of the third state is always smaller than that of the second state or the pseudo-entropy increases in all

natural processes. The rate of pseudo-entropy production, defined as the change of pseudo-entropy per unit time along the natural path, vanishes at the steady state but is positive everywhere else around it. The steady state is thus a state of minimum pseudo-entropy production. Unlike persistency, the pseudo-entropy is defined between any nonequilibrium state and the steady state, is a function of the variables of both states, and can be calculated only with a knowledge of the steady state.

The concept of thermokinetic potential, introduced by the present author, is based on Kelvin's separability postulate.³ Alternatively, it results from application⁴ of Carathéodory's principle to the integration of the following Pfaffian differential equation:

$$d\mathfrak{F} = \sum_i J_i dX_i, \quad (1)$$

where the J 's and X 's are the usual macroscopic fluxes and forces, respectively, and \mathfrak{F} is the thermokinetic potential, which exists if Eq. (1) is integrable without specifying the path. To ascertain this integrability in general, it is found that either we have to postulate the separability of independent processes or to assume the existence in the neighborhood of any nonequilibrium state of states inaccessible by an "isodynamic process" defined by $d\mathfrak{F}=0$ calculated from Eq. (1). Without these assumptions, Eq. (1) is also integrable under any of the following conditions: (a) there are only two fluxes and two forces; (b) the phenomenological coefficients, including all first-order and higher-order coefficients, are totally symmetric; or (c) the deviation from the steady state is small. Once the existence of the thermokinetic potential is ascertained, its property of decreasing in all natural processes is a result of the second law of thermodynamics⁴ and to the consideration that macroscopic variables are definable in a nonequilibrium system only if the system is stable when all the irreversible effects considered are frozen. Unlike the pseudo-entropy production which is defined relative only to the steady state, the thermokinetic potential is calculable relative to any state and can be minimized without knowledge of the steady state.

¹ R. Kikuchi, *Phys. Rev.* **124**, 1682 (1961).

² R. Kikuchi and P. Gottlieb, *Phys. Rev.* **124**, 1691 (1961).

³ J. C. M. Li, *J. Appl. Phys.* **33**, 616 (1962); see also J. C. M. Li, *J. Chem. Phys.* **29**, 747 (1958).

⁴ J. C. M. Li, *J. Phys. Chem.* (to be published).

Since all three concepts are definable near the steady state which is the region of greatest interest, the comparison among them will be made in this region for the following two examples treated by Kikuchi.

THE TWO-LEVEL SYSTEM

The two-level problem is the example treated by Klein⁵ and his symbols will be used. A system of N noninteracting particles capable of assuming two energy states 0 and ϵ is subjected to radiation whose quanta have energy ϵ . Interacting with the radiation, the particles have a transition probability b , per unit time for both directions, from one energy state to another. The system can also interact with a heat bath at temperature T with a transition probability, a per unit time for the upward transition, and $a\alpha$ per unit time for the downward transition. For any given distribution, let p_1 and p_2 be the fraction of particles in the lower and upper energy states, respectively. As shown by Klein,⁵ a state with minimum rate of entropy production is not the steady state. It has been shown⁴ that the steady state corresponds to the minimum of the thermokinetic potential. Let p_1^0 and p_2^0 be the fraction of particles in the lower and upper energy states, respectively, at the steady state. The thermokinetic potential relative to the steady state is found to be⁴:

$$\Delta\mathcal{F} = Nk(a\alpha + a + 2b) \times [p_1^0 \ln(p_1^0/p_1) + p_2^0 \ln(p_2^0/p_2)], \quad (2)$$

which reduces to the following near the steady state:

$$\Delta\mathcal{F} = \frac{1}{2}Nk(p_1 - p_1^0)^2 \frac{(a\alpha + a + 2b)^2}{(a+b)(a\alpha+b)}. \quad (3)$$

For the same problem, Kikuchi¹ found that the persistency \mathcal{G} near the steady state is given by (using Klein's symbols):

$$(\tau N)^{-1} \ln \mathcal{G} = -\frac{1}{4}(p_1 - p_1^0)^2 \frac{(a\alpha + a + 2b)^2}{(a+b)(a\alpha+b)}. \quad (4)$$

A comparison of Eqs. (3) and (4) reveals the simple relation near the steady state:

$$\Delta\mathcal{F} = -2k(\tau^{-1} \ln \mathcal{G}). \quad (5)$$

From the definition,² pseudo-entropy \tilde{S} is the following for this problem:

$$\tilde{S} = Nk[p_1 \ln(p_1^0/p_1) + p_2 \ln(p_2^0/p_2)]. \quad (6)$$

It is interesting to notice that this is also the function W proposed by Klein and Rosenbaum.⁵ The rate of pseudo-entropy production is simply

$$d\tilde{S}/dt = Nk(a\alpha + a + 2b) \times (p_1^0 - p_1)[\ln(p_1^0/p_1) - \ln(p_2^0/p_2)], \quad (7)$$

⁵ M. J. Klein, in *Transport Processes in Statistical Mechanics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958), p. 311.

which reduces to the following near the steady state:

$$\frac{d\tilde{S}}{dt} = Nk(p_1^0 - p_1)^2 \frac{(a\alpha + a + 2b)^2}{(a+b)(a\alpha+b)}. \quad (8)$$

A comparison of Eqs. (3) and (8) reveals the following simple relation near the steady state:

$$\Delta\mathcal{F} = \frac{1}{2}d\tilde{S}/dt. \quad (9)$$

It is seen that the thermokinetic potential near and relative to the steady state is simply one half the rate of pseudo-entropy production. Both approach zero at the steady state. Furthermore, the same thermokinetic potential, when divided by twice the Boltzmann constant, is simply the negative of the logarithm of persistency divided by the time interval. At the steady state when the thermokinetic potential becomes a minimum, the persistency approaches a maximum which is unity. To illustrate these relations further, it is advisable to analyze a more complicated problem.

THE MANY-LEVEL SYSTEM

This is a problem treated by Mathews, Shapiro, and Falkoff⁶ and analyzed by Kikuchi and Gottlieb² from the viewpoint of path probability. The set of symbols of the latter authors will be used. A system of L particles capable of assuming many energy states E_i ($i=1,2,\dots$), interacts with two heat baths with temperatures at T' and T'' . The transition from state i to j takes place with a quantum mechanical transition probability θ_{ij}' by interacting with the bath at T' and with a probability θ_{ij}'' by interacting with the bath at T'' . A state is described by p_i ($i=1,2,\dots$) to be the fraction of particles at the energy state i . The probability G that a steady state with distribution $p_{i\infty}$ deviates to a state with distribution p_i along the anticausal path is given by

$$G = \exp[L \sum_i p_i \ln(p_{i\infty}/p_i)]. \quad (10)$$

By definition, the pseudo-entropy is

$$\tilde{S} = kL \sum_i p_i \ln(p_{i\infty}/p_i), \quad (11)$$

and the rate of pseudo-entropy production is

$$d\tilde{S}/dt = kL \sum_i \dot{p}_i \ln(p_{i\infty}/p_i), \quad (12)$$

where \dot{p}_i is the rate of the change of p_i along the natural path. This rate is

$$\dot{p}_i = \sum_{j \neq i} [p_j \Theta_{ji} - p_i \Theta_{ij}], \quad (13)$$

where

$$\Theta_{ij} = \theta_{ij}' \exp[(E_i - E_j)/2kT'] + \theta_{ij}'' \exp[(E_i - E_j)/2kT'']. \quad (14)$$

Let the deviation from the steady state be small, so that

$$p_i = p_{i\infty}(1 + \alpha_i). \quad (15)$$

⁶ P. M. Mathews, I. I. Shapiro, and D. L. Falkoff, *Phys. Rev.* **120**, 1 (1960).

Equation (12) reduces to simply

$$d\tilde{S}/dt = kL \sum_i \sum_{j<i} p_{i\infty}(\alpha_i - \alpha_j)^2 \Theta_{ij}, \quad (16)$$

under the condition that the detailed balance holds at the steady state:

$$p_{i\infty} \Theta_{ij} = p_{j\infty} \Theta_{ji}. \quad (17)$$

Under the same condition, the persistency \mathcal{G} calculated by considering the most probable path to be composed of a natural path and an anticausal path is given by

$$\tau^{-1} \ln \mathcal{G} = -(L/4) \sum_i \sum_{j<i} p_{i\infty}(\alpha_i - \alpha_j)^2 \Theta_{ij}. \quad (18)$$

It is seen that at the steady state, the rate of pseudo-entropy production becomes a minimum (zero) while the persistency becomes a maximum (unity).

To construct a macroscopic treatment for this problem, the system can be considered to consist of L molecules of many different chemical species. A reversible first-order chemical reaction exists between any two species i and j with a heat of reaction $E_j - E_i$ absorbed from either of the heat baths. The first-order rate constants are

$$k_{ij}' = \theta_{ij}' \exp(E_i - E_j)/2kT' \quad (19)$$

for the bath at T' and

$$k_{ij}'' = \theta_{ij}'' \exp(E_i - E_j)/2kT'' \quad (20)$$

for the bath at T'' . For any distribution p_i , these chemical reactions give the following fluxes with the corresponding forces:

$$J_{ij}' = L(p_i k_{ij}' - p_j k_{ji}'), \quad (21)$$

$$J_{ij}'' = L(p_i k_{ij}'' - p_j k_{ji}''), \quad (22)$$

$$X_{ij}' = k \ln(p_i/p_j) + [(E_i - E_j)/T'], \quad (23)$$

$$X_{ij}'' = k \ln(p_i/p_j) + [(E_i - E_j)/T'']. \quad (24)$$

From Eq. (1), the change of thermokinetic potential is

$$\begin{aligned} d\mathcal{F} &= \sum_i \sum_{j<i} (J_{ij}' dX_{ij}' + J_{ij}'' dX_{ij}'') \\ &= k \sum_i \sum_{j<i} (p_i \Theta_{ij} - p_j \Theta_{ji}) d \ln(p_i/p_j). \end{aligned} \quad (25)$$

This can be integrated when the deviation from the steady state is small; the thermokinetic potential relative to the steady state is, using Eqs. (15) and (17),

$$\Delta \mathcal{F} = \frac{1}{2} kL \sum_i \sum_{j<i} p_{i\infty}(\alpha_i - \alpha_j)^2 \Theta_{ij}. \quad (26)$$

Inspection of Eqs. (16), (18), and (26) confirms the simple relations, Eqs. (5) and (9), near the steady state.

Although it has been shown that the three quantities, persistency, pseudo-entropy production, and the thermokinetic potential, are related by a constant numerical factor from each other near the steady state, their relation away from the steady state remains to be studied. In the many-level system, detailed balance at the steady state is still assumed. The concept of pseudo-entropy is still connected with a special anticausal path and is calculable only with a knowledge of the steady state. These and many other problems still have to be studied before a complete understanding of the steady state is possible.

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