CHAPTER 6

H-Theorems for Markoffian Processes

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Perspectives in Statistical Physics
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Contents

1. Introduction

The *H*-theorem was first introduced to statistical mechanics by Boltzmann in 1872 [1]. His original proof of the theorem was based on the assumption of the existence of inverse collisions or the symmetry of the collision kernel with respect to the initial and final states of colliding molecules. As was noticed by Lorentz, this assumption is not generally true for polyatomic molecules or molecules with internal degrees of freedom. In his later treaties of the gas theory [2], Boltzmann himself extended his proof by considering cycles of collisions and thus without the use of the previous assumption. Since that time, probably many people must have noticed that the proof could be simplified. His attention to this problem aroused by Pauli, Stueckelberg [3] noted briefly that the unitarity of the scattering matrix of binary collisions is sufficient to prove the *H*-theorem. More recently Waldmann [4] discussed this in greater details in a paper given to the centennial celebration of the Boltzmann equation.

In non-equilibrium statistical mechanics, the so-called master equation is often used to formulate the irreversible evolution of a given system, which is assumed to be a Markoffian process. *H*-theorems for Markoffian processes are essentially much simpler than those for the Boltzmann equation, because the evolution equation for the former is linear whereas that for the latter is non-linear. For pedagogical reasons, however, the proof is usually made with the use of the detailed balance assumption or the symmetry of the transition probability rate. Many years ago Yosida [5] gave a proof of the *H*-theorem for a Markoffian process without any such assumption. Since Yosida's proof seems to have remained unnoticed by most physicists, I like to present here a simple version of his proof and also some generalizations of it which may be of some relevance to the general aspects of non-equilibrium statistical mechanics.

2. Markoffian processes

We consider a Markoffian process $x(t)$ assuming a continuous time t and a continuous random variable x which may be a multi-component vector. The process is generally non-stationary so that the Chapman–Kolmogorov equation is written as:

$$P(y, t \leftarrow x, s) = \int P(y, t \leftarrow z, \tau)\,\mathrm{d}z\, P(z, \tau \leftarrow x, s), \qquad t > \tau > s, \tag{1}$$

for the probability density of transition from x to y over the time interval (s, t). The transition probability satisfies the conditions,

$$\int \mathrm{d}y\, P(y, t \leftarrow x, s) = 1, \qquad P(y, t \leftarrow x, s) \geqq 0. \tag{2}$$

For an infinitesimal time interval Δt, the transition probability is assumed to take the form,

$$P(y, t \leftarrow x, t - \Delta t) = \delta(x - y) + \Delta t (y | \Gamma_t | x) + o(\Delta t), \tag{3}$$

where Dirac's bracket notation is used for convenience to represent the integral kernel of the evolution operator Γ_t. The forward equation is then written as:

$$\frac{\partial \psi(t)}{\partial t} = \Gamma_t \psi(t), \quad \text{or} \quad \frac{\partial}{\partial t}\psi(x, t) = \int (x | \Gamma_t | y)\,\mathrm{d}y\, \psi(y, t), \tag{4}$$

and the backward equation as:

$$\frac{\partial \psi^+(s)}{\partial s} = \psi^+(s)\Gamma_s^+, \quad \text{or} \quad \frac{\partial}{\partial s}\psi^+(x, s) = \int \psi^+(y, s)\,\mathrm{d}y (y | \Gamma_s | x). \tag{5}$$

The fundamental solution of eq. (4) or eq. (5) with the initial or the final condition,

$$\psi(y, s) = \delta(y - x), \quad \text{or} \quad \psi^+(x, t) = \delta(x - y),$$

is the transition probability $P(y, t \leftarrow x, s)$. The general solution of eq. (4) is given in the form,

$$\psi(y, t) = \int P(y, t \leftarrow x, s)\,\mathrm{d}x\, \psi(x) \tag{6}$$

for a given function $\psi(x)$ at time s. For eq. (5) it is

$$\psi^+(x, s) = \int \psi^+(y)\,\mathrm{d}y\, P(y, t \leftarrow x, s), \tag{7}$$

for a given function $\psi^+(y)$. The expression (7) may be written as

$\langle \psi^+(x(t)) \rangle_{x,s}$ which is the expectation of the random variable $\psi^+(x(t))$ at time t when the system has started from x at the initial time s. By the Markoffian property (1), $\psi(y, t)$ and $\psi^+(x, s)$ satisfy the equations,

$$\psi(y, t) = \int P(y, t \leftarrow z, \tau)\,\mathrm{d}z\, \psi(z, t) \quad t > \tau \tag{8}$$

and

$$\psi^+(x, s) = \int \psi^+(z, \tau)\,\mathrm{d}z\, P(z, \tau \leftarrow x, s), \quad \tau > s. \tag{9}$$

If the process is stationary, the transition probability $P(y, t \leftarrow x, s)$ depends only on the time difference $\tau = t - s$. In such a case it is more customary to write the expression (7) as:

$$T_\tau f(x) = f(x, \tau) = \int f(y)\,\mathrm{d}y\, P(y, \tau \leftarrow x, 0), \tag{10}$$

defining a semi-group transformation T_τ. As a function of x, it is equal to the expectation of $f(x(\tau))$ when the initial value $x(0)$ is specified to x. Corresponding to eq. (9) we have:

$$T_t f(x) = \int T_s f(z)\,\mathrm{d}z\, P(z, t - s \leftarrow x, 0). \tag{11}$$

A familiar example of eq. (4) is the diffusion process,

$$\frac{\partial \psi(y, t)}{\partial t} = \frac{\partial}{\partial y} a(y, t)\psi(y, t) + \frac{\partial^2}{\partial y^2} b(y, t)\psi(y, t), \tag{12}$$

for which the backward equation is:

$$-\frac{\partial \psi^+(x, s)}{\partial s} = -a(x, s)\frac{\partial}{\partial x}\psi^+(x, s) + b(x, s)\frac{\partial^2}{\partial x^2}\psi^+(x, s). \tag{13}$$

If the process is stationary, the backward equation can be written as:

$$\frac{\partial}{\partial \tau} f(x, \tau) = -a(x)\frac{\partial}{\partial x} f(x, \tau) + b(x)\frac{\partial^2}{\partial x^2} f(x, \tau). \tag{14}$$

3. *H*-Theorems

Yosida's original *H*-theorem may be stated as follows:

Theorem 1. Assume that the stationary Markoffian process has the invariant measure (equilibrium distribution) $\phi_e(x)$. Then it holds that:

$$\int \phi_e(x)\,\mathrm{d}x\, C(T_s f(x)) \geqq \int \phi_e(x)\,\mathrm{d}x\, C(T_t f(x)), \quad s<t, \tag{15}$$

where $C(\xi)$ is an arbitrary convex function of ξ over the interval which covers the set of all possible values of $T_\tau f(x)$.

For the proof, we first note that the convex property of $C(\xi)$ means the inequality:

$$\sum_i C(\xi_i) w_i \geqq C\Big(\sum w_i \xi_i\Big) \tag{16}$$

for

$$\sum_i w_i = 1, \qquad w_i \geqq 0.$$

By taking

$$\xi = T_s f(z) \quad \text{and} \quad w(\xi) = P(z, t-s \leftarrow x, 0) \geqq 0,$$

and replacing the weighted sum by a weighted integral, the inequality (16) gives:

$$\int C(T_s f(z))\,\mathrm{d}z\, P(z, t-s \leftarrow x, 0) \geqq C\Big(\int T_s f(z)\,\mathrm{d}z\, P(z, t-s \leftarrow x, 0)\Big)$$
$$= C(T_t f(x)).$$

Multiplying this with $\phi_e(x)$ and integrating the both sides, we obtain eq. (15) by noticing the equation:

$$\int P(y, \tau \leftarrow x, 0)\,\mathrm{d}x\, \phi_e(x) = \phi_e(y). \tag{17}$$

This theorem is very general. It holds true for arbitrary functions f and C as long as the required conditions are satisfied. However, it is concerned with the backward equation and is less appealing to physicists than the more familiar types of *H*-theorems concerned with the

forward equation. Such a theorem is states as:

Theorem 2. Let $\psi(x,t)$ be a solution of the forward equation of a *stationary* Markoffian process (eq. (4) with a time-independent evolution operator Γ) and $\phi_e(x)$ be its invariant measure satisfying the condition $\phi_e(x) > 0$. A generalized *H*-function is defined by:

$$H_C(t) = \int C\left(\frac{\psi(x,t)}{\phi_e(x)}\right)\phi_e(x)\,\mathrm{d}x, \tag{18}$$

using an arbitrary convex function $C(\xi)$. The *H*-function never increases in time, namely:

$$H_C(s) \geqq H_C(t), \quad \text{if} \quad s<t. \tag{19}$$

The proof is similar to the previous one. By choosing the weight function,

$$w(x) = P(y, t \leftarrow x, s)\phi_e(x)/\phi_e(y) \geqq 0,$$

which satisfies the condition,

$$\int w(x)\,\mathrm{d}x = 1,$$

we apply the inequality (16) to:

$$\int C\left(\frac{\psi(x,s)}{\phi_e(x)}\right) w(x)\,\mathrm{d}x \geqq C\left(\int \frac{\psi(x,s)}{\phi_e(x)} w(x)\,\mathrm{d}x\right)$$
$$= C(\psi(y,t)/\phi_e(y)),$$

where eqs. (8) and (17) are used. This means that:

$$\int C\left(\frac{\psi(x,s)}{\phi_e(x)}\right) P(y, t \leftarrow x, s)\phi_e(x)\,\mathrm{d}x \geqq C\left(\frac{\psi(y,t)}{\phi_e(y)}\right)\phi_e(y).$$

When integrated over y, this yields the required inequality.

The theorem can be generalized to:

Theorem 3. Let $\psi_1(x,t)$ and $\psi_2(x,t)$ be two different solutions of the forward equation (4) of a non-stationary Markoffian process. Assuming that $\psi_2(x,t)>0$, a generalized H-function is defined by:

$$H_{12}(t)=\int \mathrm{d}x\, C\left(\frac{\psi_1(x,t)}{\psi_2(x,t)}\right)\psi_2(x,t), \tag{20}$$

with an arbitrary convex function C. Then the H-function never increases in time, namely:

$$H_{12}(s)\geqq H_{12}(t) \quad \text{if} \quad s<t.$$

The proof is the same as before. We choose the weight function:

$$w(x)=P(y,t\leftarrow x,s)\psi_2(x,s)/\psi_2(y,t),$$

which satisfies the condition:

$$\int w(x)\,\mathrm{d}x=1.$$

Then the inequality (16) gives:

$$\int C\left(\frac{\psi_1(x,s)}{\psi_2(x,s)}\right)w(x)\,\mathrm{d}x \geqq C\left(\int \frac{\psi_1(x,s)}{\psi_2(x,s)}w(x)\,\mathrm{d}x\right)$$

$$=C\left(\frac{\psi_1(y,t)}{\psi_2(y,t)}\right).$$

Multiplying both sides by $\psi_2(y,t)$ and integrating them over y we get the required inequality. Obviously theorem 2 is a particular case of theorem 3 for the choice of $\psi_2(x,t)=\phi_e(x)$ which is possible for a stationary process having an invariant measure.

The most familiar choice of C is:

$$C(\xi)=\xi\log\xi, \tag{21}$$

which is important and useful because of its extensive property. Then the H-function (18) becomes:

$$H(t)=\int \mathrm{d}x\,\psi_1(x,t)\{\log\psi_1(x,t)-\log\phi_e(x)\} \tag{22}$$

for a stationary process. This corresponds to the free energy function generalized to a non-equilibrium system in a stationary environment.

For a more general non-stationary system, eq. (21) gives:

$$H_{12}(t)=\int \mathrm{d}x\,\psi_1(x,t)\log\psi_1(x,t)/\psi_2(x,t). \tag{23}$$

If $\psi_1(x,t)$ also satisfies the condition $\psi_1(x,t)>0$, ψ_1 and ψ_2 can be interchanged so that a symmetrical H-function can be defined as:

$$H(t)=\int \mathrm{d}x(\psi_1(x,t)-\psi_2(x,t))\log\frac{\psi_1(x,t)}{\psi_2(x,t)}, \tag{24}$$

which never increases in time.

4. Comments

Although it is not entirely new, theorem 3 is worth noting. In fact it was first noted more than twenty years ago by Lebowitz and Bergmann [6] who proved the theorem for the H-function of the form (23). As was discussed by these authors, it is an interesting theorem of some importance for statistical mechanics of non-equilibrium systems. It means under some appropriate conditions the asymptotic uniqueness of statistical behavior of a system exposed to a non-stationary environment. This is indeed what we experience in a great many cases of ordinary circumstances. Suppose that a system is subject to external forces or is in contact with external reservoirs which are changing in time. The response of the system to these external conditions is generally dependent on the initial condition in which the system is prepared. As the time goes on, however, the memory of the initial preparation usually is lost. The response becomes asymptotically independent of the initial conditions and is solely determined by the nature of the system and of its interaction with the environments. This asymptotic uniqueness is generally true in near equilibrium situations, where the response is linear in off-equilibrium parameters. Beyond the regime of linear response, the same uniqueness of asymptotic responses is very commonly observed. It should be emphasized, however, that the uniqueness theorem can be violated in some cases which are by no means rare. There are branching phenomena which may delicately depend on the initial states of the system and also on the non-linear interactions within the system as well as those with the environment.

The asymptotic approach to a unique distribution in non-stationary Markoffian processes is a generalization of the existence of an invariant measure and the approach to it in stationary Markoffian processes. Lebowitz and Bergmann proved their theorem much in the same spirit as that of theorem 3. Namely, they noticed that the detailed balance condition or the direct symmetry of transition rate kernel is not necessary but a weaker integral condition is sufficient to prove the asymptotic approach. Also they noted that the decreasing property of the function (23) or (24) is proved under a weak condition.

In order that the theorem be meaningful, the sets of x where the two functions ψ_1 and ψ_2 take non-vanishing values must be identical except a set of zero measure. The set must be indecomposable in the same sense of the word familiar in ergodic theories to guarantee the uniqueness. Furthermore the process must be such that no runaway is possible.

These are only qualitative statements of the condition for the uniqueness of asymptotic distribution which must be formulated in a more rigorous manner. At the same time it will be an important and interesting problem to study the ways how the uniqueness is violated. It may also happen that a solution of the evolution equation ceases to be analytic at a certain time point, in which case a sort of phase change may occur or even an explosion may take place. Such a study will be useful for understanding of various phenomena in non-equilibrium non-stationary physical processes.

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CHAPTER 7

Energy Flow and Thermal Conductivity in One-dimensional, Harmonic, Isotopically Disordered Crystals.

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