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Entropy Production Rate of Non-equilibrium Systems from the Fokker-Planck Equation

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Abstract The entropy production rate of non-equilibrium systems is studied via the Fokker-Planck equation. This approach, based on the entropy production rate equation given by Schnakenberg from a master equation, requires information on the transition rate of the system under study. We obtain the transition rate from the conditional probability extracted from the Fokker-Planck equation and then derive a new and more operable expression for the entropy production rate. A few examples are presented as applications of our approach.

Keywords Entropy production · Non-equilibrium system · Fokker-Planck equation

1 Introduction

Non-equilibrium phenomena are ubiquitous in nature. A general description of non-equilibrium systems is therefore desirable. An available framework uses the notion of entropy production. It has been recognized that the distinguishing feature of a system out of thermodynamic equilibrium is the continuous production of entropy [1]. The variation of entropy per unit time can be divided into two parts: the exchange of entropy with the environment and the internal entropy production [2–4], that is,

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt}, \quad (1)$$

where S is the system entropy, $\frac{d_e S}{dt}$ is the flow of entropy per unit time between the environment and the system, and $\frac{d_i S}{dt}$ is

the internal entropy production rate. When the system is in a stationary state, $\frac{dS}{dt}$ vanishes and $\frac{d_i S}{dt} = -\frac{d_e S}{dt}$. If the stationary state is also an equilibrium state, then $\frac{d_i S}{dt} = 0$; if it is a non-equilibrium state, $\frac{d_i S}{dt} > 0$.

Since the notion of entropy plays an important role in the development of statistical mechanics, the entropy production of a non-equilibrium system is regarded as a matter of primary importance. The interest in this quantity is not only focused on why the entropy increases as the non-equilibrium system evolves but also on how the entropy is produced. These two topics have been the subject of many theories. Perhaps, the most famous among them is the principle of minimum entropy production, introduced by Prigogine [4]. A much less known theorem, the principle of maximum entropy production was proposed by Jaynes [5] as a universal method for constructing the microscopic probability distributions of equilibrium and non-equilibrium statistical mechanics [6]. The fluctuation theorem, which is related to the probability distribution of the time-averaged irreversible entropy production, has been studied and developed in many aspects [7–12]. Even after such powerful theorems were proved, however, one can hardly say that the non-equilibrium problem has been solved. Much more research is needed.

This work describes a method to derive the entropy production rate for out-of-equilibrium systems. This new method follows a line analogous to Schnakenberg's; certain differences nonetheless distinguish the two methods. In Sect. 2, we will first introduce a few basic notions, including the entropy production expression suggested by Schnakenberg on the basis of a master equation and a few elements of probability theory. In Sect. 3, we will combine the transition rate in a master equation with the transition probability density that describes a continuous stochastic variable, and in Sect. 4, a new expression for the entropy production rate will be obtained. Examples will be presented in Sect. 5, and finally, our conclusions will be summarized in Sect. 6.

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2 Basic Notions

The common definition of a non-equilibrium Gibbs entropy is given by

$$S = -k_B \sum_n p_n(t) \ln p_n(t), \quad (2)$$

where k_B is the Boltzmann constant and $P_n(t)$ is the probability of state n at time t . For a system that can be described by the master equation [13],

$$\frac{\partial p_n(t)}{\partial t} = \sum_m [p_m(t)w_{m,n}(t) - p_n(t)w_{n,m}(t)], \quad (3)$$

where $w_{m,n}(t)$ is the transition rate from state m to state n at time t ; Schnakenberg [14] suggested the following expression for the entropy production rate:

$$\begin{aligned} \frac{d_i S}{dt} &= \frac{k_B}{2} \sum_{m,n} [p_m(t)w_{m,n}(t) - p_n(t)w_{n,m}(t)] \ln \frac{p_m(t)w_{m,n}(t)}{p_n(t)w_{n,m}(t)} \\ &= k_B \sum_{m,n} p_m(t)w_{m,n}(t) \ln \frac{p_m(t)w_{m,n}(t)}{p_n(t)w_{n,m}(t)}. \end{aligned} \quad (4)$$

This result was derived by constructing a fictitious system, a materially open homogeneous system containing chemical species and allowing chemical reactions between pairs of the components. Equation (4), which satisfies all the requirements imposed on entropy production, has been considered by several authors [1, 15–18].

One difficulty associated with the derivation of the entropy production from Eq. (4) is to obtain an expression for the transition rate $w_{m,n}(t)$. To circumvent this obstacle, we take advantage of elementary probability theory. Consider a stochastic variable X , and let $p(x, t)$ be the probability density that X takes the value x at time t . We then have that

$$p(x, t + \tau) = \int dx' P(x, t + \tau | x', t) p(x', t), \quad (5)$$

where $P(x, t + \tau | x', t)$ is the conditional probability density for the variable X to take value x at time $t + \tau$ given that it had value x' at time t .

If the process dynamics is Markovian, i.e., if the memory of the stochastic variable is limited to its immediate past, then the conditional probability density $P(x, t + \tau | x', t)$ is the transition probability density [19]. We shall see that the two concepts, $w_{m,n}(t)$ and $P(x, t + \tau | x', t)$ are nearly the same. They are different only because the former is discrete, and the latter, continuous. The following derivation will show how $w_{m,n}(t)$ is linked to $P(x, t + \tau | x', t)$, after which a new expression for the entropy production rate for continuous states will be derived. And to some extent, since $P(x, t + \tau | x', t)$ can be precisely

determined, the new expression is more operable than the one following from Eq. (4).

3 From the Transition Probability Density to the Transition Rate

If a non-equilibrium process described by a continuous stochastic variable X is Markovian, condition (5) is satisfied. One example is a Brownian particle in a viscous fluid, for which the time evolution of the probability density follows the Fokker-Planck equation. We want to describe the system states with a small quantity ε . If the stochastic variable X takes values between $(n - 1/2)\varepsilon$ and $(n + 1/2)\varepsilon$, we say that the system is in the n th state. And then the probability that the system be in the n th state is the probability that the stochastic variable X lie between $(n - 1/2)\varepsilon$ and $(n + 1/2)\varepsilon$, that is,

$$p_n(t) = \int_{n\varepsilon - \frac{\varepsilon}{2}}^{n\varepsilon + \frac{\varepsilon}{2}} d\xi p(x, t), \quad (6)$$

where $p(x, t)$ is the probability density.

As mentioned before, for a Markovian process, the conditional probability density $P(x, t + \tau | x', t)$ is the transition probability density. The difference between the transition probability density $P(x, t + \tau | x', t)$ and the transition rate $w_{m,n}(t)$ is that while $P(x, t + \tau | x', t)$ describes a continuous stochastic variable, $w_{m,n}(t)$ describes a discrete one. While the former is the transition during the time interval $t \rightarrow t + \tau$, the latter is the transition per unit time.

Physically, $w_{m,n}(t)$ represents the probability of the transition from state m to state n per unit time. Therefore, $w_{m,n}(t)\tau$ is the probability of transition from state m to state n during the time interval $t \rightarrow t + \tau$. And $w_{m,n}(t)p_m(t)\tau$ is the joint probability that the system be in state n at time $t + \tau$ and in state m at time t . We use $p_{m,n}(t, \tau)$ to denote $P_{m,n}(t, \tau) = w_{m,n}(t)p_m(t)\tau$. The following equation is then a consequence of elementary probability theory combined with Eqs. (5) and (6), the equation is

$$P_{m,n}(t, \tau) = \int_{n\varepsilon - \frac{\varepsilon}{2}}^{n\varepsilon + \frac{\varepsilon}{2}} dx \int_{m\varepsilon - \frac{\varepsilon}{2}}^{m\varepsilon + \frac{\varepsilon}{2}} dx' P(x, t + \tau | x', t) p(x', t), \quad (7)$$

and so

$$w_{m,n}(t) = \frac{\int_{n\varepsilon - \frac{\varepsilon}{2}}^{n\varepsilon + \frac{\varepsilon}{2}} dx \int_{m\varepsilon - \frac{\varepsilon}{2}}^{m\varepsilon + \frac{\varepsilon}{2}} dx' P(x, t + \tau | x', t) p(x', t)}{\tau p_m(t)} \quad (8)$$

We now try to obtain simpler expressions for the discrete probability (6) and the transition rate (8) from the integral mean-value theorem. This theorem states that if $G: [a, b] \rightarrow R$ (where R is the real domain) is a continuous function and φ is an integrable function that does not change sign in the interval

(a, b), then value x in (a, b) can be found such that

$$\int_a^b G(t)\varphi(t)dt = G(x)\int_a^b \varphi(t)dt.$$

In particular, if $\varphi(t)=1$ for all t in $[a, b]$ we have that

$$\int_a^b G(t)dt = G(x)(b-a).$$

The mean-value theorem reduces Eq. (7) to the relation

$$p_n(t) = \int_{n\varepsilon-\frac{\varepsilon}{2}}^{n\varepsilon+\frac{\varepsilon}{2}} d\xi p(\xi, t) = \varepsilon p(\lambda, t), \quad (9)$$

where $\lambda \in (n\varepsilon - \varepsilon/2, n\varepsilon + \varepsilon/2)$. When ε is very small, $n\varepsilon$ can be approximately chosen as λ , so that

$$p_n(t) = \varepsilon p(n\varepsilon, t). \quad (10)$$

With the same approach, we convert Eq. (8) to the form

$$\begin{aligned} w_{m,n}(t) &= \frac{\varepsilon P(n\varepsilon, t + \tau | m\varepsilon, t) P_m(t)}{\tau P_m(t)} \\ &= \frac{\varepsilon}{\tau} P(n\varepsilon, t + \tau | m\varepsilon, t). \end{aligned} \quad (11)$$

Equation (11) exactly shows the relation between the transition probability density and the transition rate.

4 Entropy Production Rate

Substitution of the right-hand sides of Eqs. (10) and (11) for $p_n(t)$ and $w_{m,n}(t)$, respectively, in Eq. (4) yields the expression

$$\frac{d_i S}{dt} = k_B \sum_{m,n} \frac{\varepsilon^2}{\tau} P(n\varepsilon, t + \tau | m\varepsilon, t) p(m\varepsilon, t) \ln \frac{P(n\varepsilon, t + \tau | m\varepsilon, t) p(m\varepsilon, t)}{P(m\varepsilon, t + \tau | n\varepsilon, t) p(n\varepsilon, t)}. \quad (12)$$

With $\varepsilon \rightarrow 0$, the sum in the above equation turns into an integral, and we have that

$$\frac{d_i S}{dt} = k_B \int dx \int dx' \frac{1}{\tau} P(x, t + \tau | x', t) p(x', t) \ln \frac{P(x, t + \tau | x', t) p(x', t)}{P(x', t + \tau | x, t) p(x, t)}, \quad (13)$$

which is a new expression for the entropy production rate for a continuous stochastic variable. To proceed and derive the entropy production rate from Eq. (13), we need an exact expression for $P(x, t + \tau | x', t)$. Fortunately, for the one-variable Fokker-Planck equation [20],

$$\frac{\partial p(x, t)}{\partial t} = -\frac{\partial}{\partial x} \left(D^{(1)}(x, t) p(x, t) \right) + \frac{\partial^2}{\partial x^2} \left(D^{(2)}(x, t) p(x, t) \right), \quad (14)$$

where $D^{(1)}(x, t)$ and $D^{(2)}(x, t)$ are the drift coefficient and the diffusion coefficient, respectively; the conditional probability density $P(x, t + \tau | x', t)$ can be expressed as

$$P(x, t + \tau | x', t) = \left[1 - \tau D^{(1)}(x', t) \frac{\partial}{\partial x} + \tau D^{(2)}(x', t) \frac{\partial^2}{\partial x^2} + O(\tau^2) \right] \delta(x - x'). \quad (15)$$

The omission of the higher-order small quantities, $O(\tau^2)$, and the use of the Fourier integral representation of δ function then yield the result

$$P(x, t + \tau | x', t) = \frac{1}{2\sqrt{\pi D^{(2)}(x', t)\tau}} \exp \left(-\frac{[x - x' - D^{(1)}(x', t)\tau]^2}{4D^{(2)}(x', t)\tau} \right) \quad (16)$$

There are two ways to obtain an exact formula of the entropy production for a non-equilibrium process. One is to insert Eq. (16) into Eq. (13),

$$\begin{aligned} \frac{d_i S}{dt} &= k_B \int dx \int dx' \frac{p(x', t) e^{-\frac{[x - x' - D^{(1)}(x', t)\tau]^2}{4b(x')\tau}}}{2\tau\sqrt{\pi b(x')\tau}} \ln \frac{\sqrt{b(x)} p(x', t) e^{-\frac{[x - x' - D^{(1)}(x', t)\tau]^2}{4b(x')\tau}}}{\sqrt{b(x')} p(x, t) e^{-\frac{[x' - x - D^{(1)}(x, t)\tau]^2}{4b(x)\tau}}}, \end{aligned} \quad (17)$$

with $a(x) = D^{(1)}(x, t)$ and $b(x) = D^{(2)}(x, t)$.

The other is to substitute the right-hand side of Eq. (15) for $P(x, t + \tau | x', t)$ before the logarithm on the right-hand side of Eq. (13) and carry out the integration over x' with help of the δ function to obtain the result

$$\begin{aligned} \frac{d_i S}{dt} &= k_B \int dx D^{(1)}(x, t) p(x, t) \left[\frac{\partial}{\partial x} \ln \frac{P(x', t + \tau | x, t) p(x, t)}{P(x, t + \tau | x', t) p(x', t)} \right]_{x'=x} \\ &\quad + k_B \int dx D^{(2)}(x, t) p(x, t) \left[\frac{\partial^2}{\partial x^2} \ln \frac{P(x', t + \tau | x, t) p(x, t)}{P(x, t + \tau | x', t) p(x', t)} \right]_{x'=x}. \end{aligned} \quad (18)$$

Insertion of Eq. (16) into Eq. (18) yields an expression that may be different from Eq. (17), but is more manageable. Either way yields an exact expression, distribution-dependent for the entropy production.

Notwithstanding the exact Eq. (17), a difficulty arises. Equation (14) is usually used to describe a system whose states are continuous, such as a Brownian motion. Nonetheless, we have used the probability (4), with discrete states described by a master equation. When we try to calculate the entropy production rate with Eq. (4), should we use the Fokker-Planck equation once again? We see that all the above derivations, and also the ones below, rely on Eq. (5). From Eq. (5), one can derive the master equation [19] and also the Fokker-Planck equation [20], provided only that the Markov condition is satisfied. We see that the master equation and the Fokker-Planck equation are simply two different

phenomenological descriptions for one system. As Eq. (17) shows, these descriptions depend on the parameter τ , which describes the shortest transition time, which sets the time scale of the target system.

5 Examples of the Smoluchowski Equation and Ornstein-Uhlenbeck Process

An important example of one-variable Fokker-Planck equation is the Smoluchowski equation, which describes the probability distribution of a Brownian particle moving in a strong friction medium [21]. In this case, the coordinate undergoes a creeping motion leading to the Smoluchowski equation,

$$\frac{\partial p(x, t)}{\partial t} = \frac{1}{m\gamma} \left[-\frac{\partial}{\partial x} F(x) + k_B T \frac{\partial^2}{\partial x^2} \right] p(x, t), \quad (19)$$

where m is the mass of the Brownian particle, γ is the friction coefficient, and $F(x)$ is the force acting on the particle. The comparison between Eqs. (14) and (19) yields

$$D^{(1)}(x, t) = \frac{F(x)}{m\gamma}; D^{(2)}(x, t) = \frac{k_B T}{m\gamma}. \quad (20)$$

In inserting Eq. (20) into Eq. (16), we then find that

$$P(x, t + \tau | x', t) = \frac{1}{2\sqrt{\pi b\tau}} \exp\left(-\frac{[x - x' - a(x')\tau]^2}{4b\tau}\right), \quad (21)$$

with $a(x) = F(x)/m\gamma$ and $b = k_B T/m\gamma$.

Insertion of Eq. (21) into Eq. (13) yields the equality

$$\frac{d_i S}{dt} = k_B \int dx \int dx' \frac{p(x', t) e^{-\frac{[x - x' - a(x')\tau]^2}{4b\tau}}}{2\tau\sqrt{\pi b\tau}} \ln \frac{p(x', t) e^{-\frac{[x - x' - a(x')\tau]^2}{4b\tau}}}{p(x, t) e^{-\frac{[x' - x - a(x)\tau]^2}{4b\tau}}}. \quad (22)$$

Alternatively, the insertion of Eq. (21) into Eq. (18) followed by the integration by parts and the limit $\tau \rightarrow 0$ shows that

$$\frac{d_i S}{dt} = k_B \int \frac{[J(x, t)]^2}{bp(x, t)} dx, \quad (23)$$

where

$$J(x, t) = a(x)p(x, t) - b \frac{\partial}{\partial x} p(x, t) \quad (24)$$

is the probability current in Eq. (19).

Equation (24) is equivalent to the result derived by Tomé [22] in the multi-particles case. And as a by-product, the entropy flux term, which is the negative of the entropy production rate, is also the same. Our approach to calculate the entropy production rate is equivalent to Tomé's, but the equivalence is limited to constant

diffusion coefficients. When the diffusion coefficient is a function of x , Eq. (23) will be no longer valid, and even the probability current will no longer be given by Eq. (24).

To derive and express for the entropy production rate from Eq. (22), we need to know $F(x)$. For the simple case is $F(x) = 0$, Eq. (19) reduces to the diffusion equation

$$\frac{\partial p(x, t)}{\partial t} = D \frac{\partial^2 p(x, t)}{\partial x^2}. \quad (25)$$

Equation (25) describes a Wiener process. The solution is

$$p(x, t) = \frac{1}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (26)$$

with the initial condition $p(x, 0) = \delta(x)$.

The transition probability is simply

$$P(x, t + \tau | x', t) = \frac{1}{2\sqrt{\pi D\tau}} \exp\left(-\frac{(x - x')^2}{4D\tau}\right). \quad (27)$$

When we insert Eqs. (26) and (27) into Eq. (13), the following expression for the entropy production rate of the diffusion process results in the following:

$$\frac{d_i S}{dt} = \frac{k_B}{2t}. \quad (28)$$

The parameter τ has disappeared from Eq. (28). It is clear that for a Wiener process, the entropy production rate will reduce to zero when $t \rightarrow \infty$, as the system approaches equilibrium.

Another important example is the Ornstein-Uhlenbeck process, with

$$D^{(1)}(x) = -\gamma x; D^{(2)}(x) = D = \text{const.} \quad (29)$$

The probability distribution equation for this process,

$$\frac{\partial p(x, t)}{\partial t} = \gamma \frac{\partial}{\partial x} (xp(x, t)) + D \frac{\partial^2 p(x, t)}{\partial x^2}. \quad (30)$$

has the following stationary solution $p(x)$, which satisfies $\partial p / \partial t = 0$ for $\gamma > 0$:

$$p(x) = \sqrt{\frac{\gamma}{2\pi D}} \exp\left(-\frac{\gamma x^2}{2D}\right), \quad (31)$$

and the corresponding differential equation reduces to

$$\gamma \frac{\partial}{\partial x} (xp(x)) + D \frac{\partial^2 p(x)}{\partial x^2} = 0 \quad (32)$$

with the boundary conditions $p(x) \rightarrow 0$ when $x \rightarrow \pm\infty$.

With the initial condition $P(x, t | x', t) = \delta(x - x')$ and $p(x) = \int_{-\infty}^{\infty} P(x, t + \tau | x', t) p(x') dx'$, Eq. (30) shows that the transitions probability density $P(x, t + \tau | x', t)$ [20] is

$$P(x, t + \tau | x', t) = \sqrt{\frac{\gamma}{2\pi D(1 - e^{-2\gamma\tau})}} \exp \left[-\frac{\gamma(x - e^{-\gamma\tau}x')^2}{2D(1 - e^{-2\gamma\tau})} \right], \quad (33)$$

We now insert Eqs. (31) and (33) into Eq.(13). The entropy production rate $\frac{d_s S}{dt} = 0$ then results, which shows that Eq. (31) is an equilibrium state of the Ornstein-Uhlenbeck process.

6 Conclusion

We have presented a procedure to calculate the entropy production rate based on Eq.(4), derived by Schnakenberg. We have used the conditional probability density easily obtained from the Fokker-Planck to derive the transition rate in the master equation description and then obtain the new expression (17) for the entropy production rate.

Compared with the Schnakenberg's expression, Eq.(4), our entropy production rate, Eq. (17), is more operable. The entropy production rate can be calculated exactly if the drift and diffusion coefficients are known. By contrast, the transition rate in Eq.(4) is usually difficult to compute, unless phenomenological methods or conjectures are adopted.

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References

1. T. Tomé, M. Oliveira, Phys Rev Lett **108**, 020601 (2012)
2. I. Prigogine, *Introduction to thermodynamics of irreversible processes* (Thomas, Springfield, 1955)
3. S.R. de Groot, P. Mazur, *Non-equilibrium thermodynamics* (North-Holland, Amsterdam, 1962)
4. P. Glansdorff, I. Prigogine, *Thermodynamics of structure, stability and fluctuations* (Wiley, New York, 1971)
5. E. T. Jaynes, *The Maximum Entropy Formalism*, R. D. Levine and M. Tribus (eds.), (MIT Press, Cambridge, 1979)
6. R.C. Dewar, J Phys A Math Gen **38**, 4519 (2005)
7. J. Kurchan, J Phys A Math Gen **31**, 3719 (1998)
8. D.J. Evans, D.J. Searles, Adv Phys **51**, 7 (2002)
9. C. Maes, K.U. Leuven, Séminaire Poincaré **2**, 29 (2003)
10. U. Seifert, Phys Rev Lett **95**, 040602 (2005)
11. R. J. Harris, G. M. Schütz, J. Stat. Mech. (2007) P07020.
12. D. Andrieux, P. Gaspar, J Stat Phys **127**, 107 (2007)
13. N.G. van Kampen, *Stochastic processes in physics and chemistry* (North-Holland, Amsterdam, 1981)
14. J. Schnakenberg, Rev Mod Phys **48**, 571 (1976)
15. C.Y. Mou et al., J Chem Phys **84**, 7011 (1986)
16. B. Gaveau et al., Phys Rev E **79**, 010102 (2009)
17. G. Szabó et al., Phys Rev E **82**, 011105 (2010)
18. T. Tomé, M.J. de Oliveira, Phys Rev E **82**, 021120 (2010)
19. L.E. Reichl, *A modern course in statistical physics* (Wiley, New York, 1998)
20. H. Risken, *The Fokker-Planck equation* (Springer, Berlin, 1989)
21. W.T. Coffey, Y.P. Kalmykov, J.T. Waldron, *The Langevin equation: with applications to stochastic problems in physics chemistry and electrical engineering* (World Scientific, Singapore, 2004)
22. T. Tomé, Braz J Phys **36**, 1285 (2006)