Nonintegral form of the reciprocal relation associated with violation of the fluctuation response relation

Kotaro Kasuga and Akira Yoshimori
Department of Physics, Niigata University, Niigata 950-2181, Japan

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We extend Onsager's reciprocal relation to systems in a nonequilibrium steady state. While Onsager's reciprocal relation concerns the kinetic (Onsager) coefficient, the extended reciprocal relation concerns violation of the fluctuation response relation (FRR) for mechanical and thermal perturbations. This extended relation holds at each frequency when the extent of the FRR violation is expressed in a frequency domain. This nonintegral form distinguishes the extended relation from previous relations expressed by integration over a frequency. To obtain this relation, we consider one-particle one-dimensional systems described by an overdamped Langevin equation with a force driving the system away from equilibrium. We assume a special property of the potential in the system. From this Langevin equation, we obtain the Fokker-Planck (FP) equation describing the time evolution of the distribution function of the particle. Using the FP equation, we calculate the responses of the particle velocity and heat current by applying time-dependent perturbations of the driving force and temperature. We express the extent of the FRR violation in terms of these responses with time correlation functions and expand them in powers of the FP operator. This reciprocal relation is valid far from equilibrium. One can also confirm this reciprocal relation through experiments with systems such as colloidal suspensions because the FRR violation can be experimentally observed.

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I. INTRODUCTION

Thermal and mechanical perturbations to an equilibrium or nonequilibrium system has a cross effect on thermal and mechanical responses of the system. An example of perturbation to an equilibrium system is a heat engine, because thermal perturbations change mechanical variables such as energy [1–3]. For an equilibrium cross effect, there are many relations including Onsager's reciprocal relation [4] and the fluctuation response relation (FRR) [5,6], while nonequilibrium effects are less well studied [7–9]. These studies contrast with those on mechanical perturbations because they provide many nonequilibrium relations such as the glassy system FRR [10–19], extended FRR [20–28], and reciprocal relation [29,30]. Some nonequilibrium studies have also dealt with perturbations other than mechanical ones [31–36], although the cross effect is out of the scope of these studies.

Yamada and Yoshimori have derived a reciprocal relation between thermal and mechanical responses by considering the nonequilibrium cross effect of perturbations [7,8]. When the perturbations are applied to a nonequilibrium steady state (NESS) [7,8,20–23,25–32,37–43], neither Onsager's reciprocal relation nor the FRR is valid. Yamada and Yoshimori showed that a reciprocal relation is valid for the extent of the FRR violation in nonequilibrium Brownian systems. Their reciprocal relation is valid for any type of system potential and for any driving force strength, which causes the system to deviate from an equilibrium state. In addition, their relation can be experimentally confirmed because it consists of measurable quantities.

Yamada and Yoshimori expressed their reciprocal relation by integrating the extent of the FRR violation over a frequency [7,8]. The integral over a frequency shows that the reciprocal relation in the time domain does not hold for all time, but only at zero time. Thus, their reciprocal relation contrasts with Onsager's reciprocal relation, which has a nonintegral form holding at each frequency and for all time. In a special case, they numerically found that their relation has a nonintegral form when the potential of the system is proportional to a cosine [8]. This result, however, has not exactly been proven.

In this study, we exactly derive a nonintegral form of a reciprocal relation valid for the extent of the FRR violation by assuming a condition of the potential $U(x)$ of the system. This condition is given by $U''(x) \propto U(x)$, where $U''(x)$ represents the second derivative of $U(x)$. Using the potential, we calculate responses to force and temperature perturbations on the basis of the one-dimensional one-particle overdamped Langevin equation with a driving force. We do not assume the strength of the force driving the system out of equilibrium; thus, our reciprocal relation holds even far from an equilibrium state. In addition, we confirm our reciprocal relation for various values of the driving force by numerically calculating the extent of the FRR violation.

II. MAIN RESULTS

We study a one-particle one-dimensional system described by the overdamped Langevin equation

$$\dot{x}(t) = \gamma^{-1}[F(x(t)) + \epsilon_1 f_p(t) + \xi(t)], \tag{1}$$

where $x(t)$ and $\dot{x}(t)$ are the position and velocity of the particle, γ is the coefficient of friction, $\epsilon_1 f_p(t)$ represents the time-dependent mechanical perturbation, and we assume a periodic boundary condition of length l. We write the force term $F(x)$ as

$$F(x) = f - \frac{dU(x)}{dx} \tag{2}$$

with the periodic potential

$$U(x+l) = U(x), \tag{3}$$

where f is the time-independent driving force shifting the system out of equilibrium. In Eq. (1), the Gaussian noise $\xi(t)$ satisfies

$$\langle \xi(t)\xi(s)\rangle_\epsilon = 2\gamma(T + \epsilon_2 T_p(t))\delta(t-s), \tag{4}$$

where T is the time-independent temperature, $\epsilon_2 T_p(t)$ represents the time-dependent thermal perturbation, and $\langle\cdots\rangle_\epsilon$ is the average in the presence of $\epsilon_1 f_p(t)$ and $\epsilon_2 T_p(t)$. In this paper, we set the Boltzmann constant to unity. The perturbations $\epsilon_1 f_p(t)$ and $\epsilon_2 T_p(t)$ are applied to the steady-state system at $t = t_{\mathrm{ini}} \to -\infty$.

In the system described by the Langevin equation, we express the entropy production using the currents and the affinities. We define entropy production as [1]

$$\Delta S \equiv \int_{-\infty}^{t} ds \beta(s)\langle \dot{Q}(s)\rangle_\epsilon, \tag{5}$$

where $\beta(s) \equiv 1/[T + \epsilon_2 T_p(s)]$ and

$$\dot{Q}(t) \equiv (\gamma \dot{x}(t) - \xi(t)) \circ \dot{x}(t) \tag{6}$$

with the Stratonovich product $\circ$ [44]. We rewrite Eq. (5) in the form [7,8]

$$\Delta S = \sum_{i=1}^{2} \int_{-\infty}^{t} ds A_i(s)\langle J_i(t)\rangle_\epsilon \tag{7}$$

$$= \int_{-\infty}^{t} ds A_1(s)\langle \dot{x}(s)\rangle_\epsilon + \int_{-\infty}^{t} ds A_2(s)\langle \dot{Q}(s)\rangle_\epsilon, \tag{8}$$

where $J_1(t) \equiv \dot{x}(t)$ and $J_2(t) \equiv \dot{Q}(t)$ (currents), and $A_1(t) \equiv (f + \epsilon_1 f_p(t))/T$ and $A_2(t) \equiv 1/(T + \epsilon_2 T_p(t)) - 1/T$ (affinities). To derive Eq. (7) from Eq. (5), we have used $\langle U(x(t))\rangle_\epsilon = \langle U(x(-\infty))\rangle_\epsilon$, which is obtained from the assumptions of $f_p(s) = T_p(s) = 0$ for $s > t_f$ and $t_f \ll t$ [7,8]. After enough time from the time t_f when the perturbations are turned off, the system reaches the same steady state as that at $t = -\infty$.

By expanding the currents using the affinities, we define the nonequilibrium kinetic coefficients (Onsager's coefficients). By expanding $\langle \dot{x}(s)\rangle_\epsilon$ and $\langle \dot{Q}(s)\rangle_\epsilon$ in powers of the perturbed parts of the affinities $\delta A_1(t) \equiv \epsilon_1 f_p(t)/T$ and $\delta A_2(t) \equiv -\epsilon_2 T_p(t)/T^2$, we define the nonequilibrium kinetic coefficients $L_{ij}(t)$ as

$$\langle \dot{x}(t)\rangle_\epsilon = J_1^{st} + \int_{-\infty}^{t} ds L_{11}(t-s)\frac{\epsilon_1 f_p(s)}{T} - \int_{-\infty}^{t} ds L_{12}(t-s)\frac{\epsilon_2 T_p(s)}{T^2}\cdots, \tag{9}$$

$$\langle \dot{Q}(t)\rangle_\epsilon = J_2^{st} + \int_{-\infty}^{t} ds L_{21}(t-s)\frac{\epsilon_1 f_p(s)}{T} - \int_{-\infty}^{t} ds L_{22}(t-s)\frac{\epsilon_2 T_p(s)}{T^2}\cdots. \tag{10}$$

Here, J_1^{st} and J_2^{st} are the particle velocity and the heat current in the steady state with $\epsilon_1 = \epsilon_2 = 0$, respectively. We assume $L_{ij}(t) = 0$ for $t < 0$.

Using the kinetic coefficients, we express the FRR and Onsager's reciprocal relation in an equilibrium state while defining their violation in a nonequilibrium state. To express these relations, the time correlation function $C_{ij}(t)$ is defined as

$$C_{ij}(t) \equiv \langle J_i(t)J_j(0)\rangle_0, \tag{11}$$

where $\langle\cdots\rangle_0$ is the average in the absence of perturbations. Using $C_{ij}(t)$, the FRR is given by [5,8]

$$C_{ij}(t) = L_{ij}(t) \qquad (t > 0), \tag{12}$$

and Onsager's reciprocal relation is given by [4,45]

$$L_{12}(t) = L_{21}(t). \tag{13}$$

While Eqs. (12) and (13) are valid for the perturbations applied to the equilibrium state ($f = 0$), they are violated for perturbations applied to the NESS ($f \neq 0$). For the NESS, if we define the extent of the FRR violation $\Delta_{ij}(t)$ as

$$\Delta_{ij}(t) \equiv \begin{cases} C_{ij}(t) - L_{ij}(t) & (t > 0) \\ 0 & (t \leqslant 0), \end{cases} \tag{14}$$

then the following reciprocal relation holds [7,8]:

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\tilde{\Delta}_{12}(\omega) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\tilde{\Delta}_{21}(\omega) \tag{15}$$

with $\tilde{\Delta}_{ij}(\omega) \equiv \int_{-\infty}^{\infty} dt \Delta_{ij}(t)\exp(-i\omega t)$.

In Sec. IV, we will use the extent of the FRR violation in the NESS to prove the following reciprocal relation expressed in a nonintegral form:

$$\tilde{\Delta}_{12}(\omega) = \tilde{\Delta}_{21}(\omega). \tag{16}$$

To prove Eq. (16), we assume

$$\frac{d^2U(x)}{dx^2} \propto U(x). \tag{17}$$

Equation (16) can be expressed in the time domain as

$$\Delta_{12}(t) = \Delta_{21}(t), \tag{18}$$

which holds for all time. Equations (16) and (18) are independent of the strength of the driving force f, which shows the extent of deviation from the equilibrium state. In Sec. IV, we will prove Eq. (18), which is equivalent to Eq. (16).

The reciprocal relation Eq. (16) expressed in the nonintegral form is equivalent to Eq. (18), holding for all time in the time domain. Equation (18) holds for a wider time range than previous nonequilibrium relations, which hold only at zero time [7,8,20,21,30] (see the next paragraph). For the property, we need to assume Eq. (17), which is satisfied by an experimentally constructible potential used in many studies, as explained later. In addition, because we do not need the frequency integration, our relation is less difficult to confirm experimentally than those in the integral form.

Equation (16) contrasts with nonequilibrium relations previously expressed in integral forms [7,8,20,21,30]. Harada and Sasa have expressed the relationship between the heat current and FRR violation through an integral identity [20,21]. Shimizu and Yuge also used an integral form to obtain a reciprocal relation between two mechanical perturbations [30]. In addition, Yamada and Yoshimori have obtained an integral form of the reciprocal relation between the same thermal and mechanical perturbations as those used by this study [Eq. (15)] [7,8]. Onsager's reciprocal relation differs from these nonequilibrium relations in that it can be expressed in a nonintegral form.

To prove that the reciprocal relation holds for all time, we need to assume Eq. (17). The potential satisfying Eq. (17) has often been used in theoretical and experimental studies [20,46–49]. The potential can be expressed in the form $U(x) = A\sin(kx + c)$ or $U(x) = A\cos(kx + c)$, where A, k, and c are constants independent of x. Such a function has only one wave length; thus, we can consider it to be simplest of the periodic functions assumed in Eq. (3). The potential satisfying Eq. (17) can experimentally be constructed and, in fact, has been constructed by some experimental studies [46,47].

Equations (16) and (18) can be confirmed by performing experiments on cross effects between thermal and mechanical perturbations. In Eq. (16), $\tilde{\Delta}_{12}(\omega)$ and $\tilde{\Delta}_{21}(\omega)$ are measurable quantities that can be obtained in experimental systems, such as a colloidal suspension. If the potential of the experimental system satisfies Eq. (17), one need not integrate the extent of the violation over a frequency. In addition, Eqs. (16) and (18) include responses to both thermal and mechanical perturbations. Thus, the nonequilibrium cross effect between these perturbations can more deeply be understood though our reciprocal relations.

III. A BRIEF SKETCH OF THE PROOF

We will give a brief sketch of the proof before describing its details. We begin the proof by expressing the extent of the FRR violation $\Delta_{ij}(t)$ using the nonperturbed stationary distribution function with the Fokker-Planck (FP) operator. To obtain the expression, we derive $L_{ij}(t)$ by expanding the FP equation in powers of ϵ_1 and ϵ_2 and derive $C_{ij}(t)$ using the Furutsu-Novikov-Donsker formula. Combining the derived expressions of $L_{ij}(t)$ and $C_{ij}(t)$, we derive the expression of $\Delta_{ij}(t)$ on the basis of Eq. (14). Details of the derivation have been given by Yamada and Yoshimori [7,8].

From this expression of $\Delta_{ij}(t)$, we obtain Eq. (18) or $\Delta_{21}(t) - \Delta_{12}(t) = 0$ by introducing the new operator $\hat{L}_1^\dagger$. To define $\hat{L}_1^\dagger$, we divide the conjugate FP operator into two operators: one that includes $F(x)$ and one that does not include $F(x)$. The operator $\hat{L}_1^\dagger$ is defined by one including $F(x)$. The exponential operators including $\hat{L}_1^\dagger$ give the time dependence of $\Delta_{21}(t) - \Delta_{12}(t)$.

Using the operator $\hat{L}_1^\dagger$, we divide $\Delta_{21}(t) - \Delta_{12}(t)$ into two parts. This is an important step of the proof and will be explained as follows. First, we expand the exponential operators in powers of the conjugate FP operator and count the number of $\hat{L}_1^\dagger$ operators included in the expanded term. Next, using this number, we divide the exponential operators into a term including an odd number of $\hat{L}_1^\dagger$ operators and a term including an even number. This division of the exponential operators allows us to divide $\Delta_{21}(t) - \Delta_{12}(t)$ into two parts.

Finally, we show that the two divided parts of $\Delta_{21}(t) - \Delta_{12}(t)$ vanish respectively. We can show that one of the parts vanishes without assuming Eq. (17). In contrast, the other part vanishes only when Eq. (17) is satisfied. To prove this, the second part is given by the x integration, whose integrand is expressed using the product of $F(x)$ and $dF(x)/dx$. By integrating the expression by parts, we show that the second part vanishes.

IV. PROOF

We express the extent of the FRR violation $\Delta_{ij}(t)$ in terms of the Fokker-Planck (FP) operator $\hat{L}$,

$$\hat{L} \equiv -\gamma^{-1}\frac{\partial}{\partial x}\left(F(x) - T\frac{\partial}{\partial x}\right), \tag{19}$$

with the stationary distribution function in a nonperturbed system. Using $\hat{L}$, we describe the time development of the distribution function for the particle $P_\epsilon(x,t)$ using the FP equation:

$$\frac{\partial P_\epsilon(x,t)}{\partial t} = \hat{L}P_\epsilon(x,t) - \gamma^{-1}\frac{\partial}{\partial x}\left(\epsilon_1 f_p(t) - \epsilon_2 T_p(t)\frac{\partial}{\partial x}\right) \times P_\epsilon(x,t). \tag{20}$$

The FP equation (20) is equivalent to the overdamped Langevin equation (1). The nonperturbed stationary distribution function $P_{st}(x)$ is defined as the steady-state equation with $\epsilon_1 = \epsilon_2 = 0$:

$$\frac{\partial P_{st}(x)}{\partial t} = \hat{L}P_{st}(x) = 0. \tag{21}$$

Using the FP operator $\hat{L}$ with the stationary distribution function $P_{st}(x)$, we can express $\Delta_{12}(t)$ and $\Delta_{21}(t)$ as follows [7,8]:

$$\Delta_{12}(t) = \gamma^{-2}\int_0^l dxF(x)e^{t\hat{L}}\hat{J}^2P_{st}(x), \tag{22}$$

$$\Delta_{21}(t) = \gamma^{-2}\int_0^l dxF(x)\hat{J}e^{t\hat{L}}\hat{J}P_{st}(x), \tag{23}$$

where $\hat{J}$ is the operator defined as

$$\hat{J} \equiv F(x) - T\frac{d}{dx}. \tag{24}$$

Using Eqs. (22) and (23), which express $\Delta_{12}(t)$ and $\Delta_{21}(t)$, respectively, we calculate $\Delta_{21}(t) - \Delta_{12}(t)$. From Eqs. (22) and (23), we obtain

$$\Delta_{21}(t) - \Delta_{12}(t) = \gamma^{-2}\int_0^l dxF(x)[\hat{J}, e^{t\hat{L}}]\hat{J}P_{st}(x), \tag{25}$$

where $[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$ with the operators $\hat{A}$ and $\hat{B}$. Because the differential equation

$$\frac{\partial}{\partial t}[\hat{J}, e^{t\hat{L}}] = \hat{L}[\hat{J}, e^{t\hat{L}}] + [\hat{J}, \hat{L}]e^{t\hat{L}} \tag{26}$$

provides

$$[\hat{J}, e^{t\hat{L}}] = \gamma^{-1}\int_0^t dse^{(t-s)\hat{L}}F'(x)\hat{J}e^{s\hat{L}}, \tag{27}$$

substituting into Eq. (25) yields

$$\Delta_{21}(t) - \Delta_{12}(t) = \gamma^{-3}\int_0^l dx \int_0^t ds F(x) e^{(t-s)\hat{L}} F'(x)\hat{J} e^{s\hat{L}} \hat{J} P_{st}(x), \quad (28)$$

where $F'(x) = dF(x)/dx$. From integrating Eq. (28) by parts with respect to x, we obtain

$$\Delta_{21}(t) - \Delta_{12}(t) = \gamma^{-3}\int_0^l dx \int_0^t ds [e^{(t-s)\hat{L}^\dagger} F(x)] \times F'(x)\hat{J} e^{s\hat{L}} \hat{J} P_{st}(x), \quad (29)$$

where the conjugate operator of $\hat{L}$ is defined as

$$\hat{L}^\dagger \equiv \gamma^{-1}\left(T\frac{d}{dx} + F(x)\right)\frac{d}{dx}. \quad (30)$$

In Eq. (29), $[\hat{O}g(x)]$ indicates that an operator $\hat{O}$ operates only on a function $g(x)$ and not on functions outside of $[\cdots]$.

By expanding $\Delta_{21}(t) - \Delta_{12}(t)$ in powers of conjugate operators, we divide $\Delta_{21}(t) - \Delta_{12}(t)$ into two parts. To expand $\Delta_{21}(t) - \Delta_{12}(t)$, we rewrite Eq. (29) in the form

$$\Delta_{21}(t) - \Delta_{12}(t) = \gamma^{-3}\int_0^l dx \int_0^t ds [e^{(t-s)\hat{L}^\dagger} F(x)] \times F'(x)[e^{s\hat{L}^{\dagger\star}} F(x)]\hat{J} P_{st}(x) \quad (31)$$

using the formula (Appendix A)

$$\hat{J} e^{s\hat{L}} \hat{J} P_{st}(x) = [e^{s\hat{L}^{\dagger\star}} F(x)]\hat{J} P_{st}(x), \quad (32)$$

where $\hat{L}^{\dagger\star} = \hat{L}_0^\dagger - \hat{L}_1^\dagger$ with

$$\hat{L}_0^\dagger \equiv \gamma^{-1} T\frac{d^2}{dx^2}, \quad (33)$$

$$\hat{L}_1^\dagger \equiv \gamma^{-1} F(x)\frac{d}{dx}. \quad (34)$$

In Eq. (31), we expand $e^{t\hat{L}^\dagger}F(x)$ and $e^{t\hat{L}^{\dagger\star}}F(x)$ in powers of $\hat{L}^\dagger$ and $\hat{L}^{\dagger\star}$, respectively, via

$$e^{t\hat{L}^\dagger}F(x) = \sum_{n=0}^\infty \frac{t^n}{n!}(\hat{L}^\dagger)^n F(x), \quad (35)$$

$$e^{t\hat{L}^{\dagger\star}}F(x) = \sum_{n=0}^\infty \frac{t^n}{n!}(\hat{L}^{\dagger\star})^n F(x). \quad (36)$$

Using $\hat{L}^{\dagger\star} = \hat{L}_0^\dagger - \hat{L}_1^\dagger$ and $\hat{L}^\dagger = \hat{L}_0^\dagger + \hat{L}_1^\dagger$ obtained from Eq. (30) with Eqs. (33) and (34), we obtain

$$e^{t\hat{L}^\dagger}F(x) = \sum_{n=0}^\infty \frac{t^n}{n!}(\hat{L}^\dagger)^n F(x) = g_o(x,t) + g_e(x,t), \quad (37)$$

$$e^{t\hat{L}^{\dagger\star}}F(x) = \sum_{n=0}^\infty \frac{t^n}{n!}(\hat{L}^{\dagger\star})^n F(x) = -g_o(x,t) + g_e(x,t), \quad (38)$$

with

$$g_o(x,t) \equiv \frac{1}{2}[e^{t\hat{L}^\dagger}F(x) - e^{t\hat{L}^{\dagger\star}}F(x)] = \frac{1}{2}\sum_{n=0}^\infty \frac{t^n}{n!}[(\hat{L}_0^\dagger + \hat{L}_1^\dagger)^n F(x) - (\hat{L}_0^\dagger - \hat{L}_1^\dagger)^n F(x)], \quad (39)$$

$$g_e(x,t) \equiv \frac{1}{2}[e^{t\hat{L}^\dagger}F(x) + e^{t\hat{L}^{\dagger\star}}F(x)] = \frac{1}{2}\sum_{n=0}^\infty \frac{t^n}{n!}[(\hat{L}_0^\dagger + \hat{L}_1^\dagger)^n F(x) + (\hat{L}_0^\dagger - \hat{L}_1^\dagger)^n F(x)], \quad (40)$$

where $\hat{L}_1^\dagger$ operates on $F(x)$ an odd and even number of times, respectively. By substituting Eqs. (37) and (38) into Eq. (31), we can divide Eq. (31) into two parts,

$$\Delta_{21}(t) - \Delta_{12}(t) = \Delta_o(t) + \Delta_e(t), \quad (41)$$

where

$$\Delta_o(t) \equiv -\gamma^{-3}\int_0^l dx \int_0^t ds g_e(x,t-s)F'(x)g_o(x,s)\hat{J}P_{st}(x) + \gamma^{-3}\int_0^l dx \int_0^t ds g_o(x,t-s)F'(x)g_e(x,s)\hat{J}P_{st}(x), \quad (42)$$

$$\Delta_e(t) \equiv \gamma^{-3}\int_0^l dx \int_0^t ds g_e(x,t-s)F'(x)g_e(x,s)\hat{J}P_{st}(x) - \gamma^{-3}\int_0^l dx \int_0^t ds g_o(x,t-s)F'(x)g_o(x,s)\hat{J}P_{st}(x). \quad (43)$$

One of the two divided parts $\Delta_o(t)$ vanishes. To show this, we transform the variable s into $\tau = t - s$ in the first term of Eq. (42) to obtain

$$\Delta_o(t) = -\gamma^{-3}\int_0^l dx \int_0^t d\tau g_e(x,\tau)F'(x)g_o(x,t-\tau)\hat{J}P_{st}(x) + \gamma^{-3}\int_0^l dx \int_0^t ds g_o(x,t-s) \times F'(x)g_e(x,s)\hat{J}P_{st}(x). \quad (44)$$

On the right side of Eq. (44), the absolute value of the first term is equivalent to that of the second term if $\tau = s$. These terms cancel out, so we obtain

$$\Delta_o(t) = 0. \quad (45)$$

We have not assumed Eq. (17) to derive Eq. (45).

The other of the two divided parts, $\Delta_e(t)$, can be expressed as a product of $F(x)$ and $F'(x)$, assuming Eq. (17). Using

$$\frac{d^2F(x)}{dx^2} = \alpha[F(x) - f] \quad (46)$$

derived from Eq. (17) with $U'(x) = \alpha U(x)$, we rewrite Eqs. (39) and (40) in the forms

$$g_o(x,t) = \sum_{p=0}^{\infty}\sum_{q=0}^{\infty} h_o^{pq}(t)[F(x)]^p[F'(x)]^{2q+1}, \quad (47)$$

$$g_e(x,t) = \sum_{p=0}^{\infty}\sum_{q=0}^{\infty} h_e^{pq}(t)[F(x)]^p[F'(x)]^{2q}, \quad (48)$$

where $h_o^{pq}(t)$ and $h_e^{pq}(t)$ are functions of t independent of x (Appendix B). By substituting Eqs. (47) and (48) into Eq. (43), we obtain

$$\Delta_e(t) = \gamma^{-3}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\int_0^l dx\int_0^t ds h^{pq}(t,s)[F(x)]^p \times [F'(x)]^{2q+1}\hat{J}P_{st}(x), \quad (49)$$

where $h^{pq}(t,s)$ is a function of t and s independent of x.

Using Eq. (49), expressed in terms of $F(x)$ and $F'(x)$, we show that $\Delta_e(t)$ vanishes. We rewrite the integral part of Eq. (49), using $[F(x)]^pF'(x) = (p+1)^{-1}d([F(x)]^{p+1})/dx$, in the form

$$\int_0^l dx[F(x)]^p[F(x)']^{2q+1}\hat{J}P_{st}(x) = \frac{1}{p+1}\int_0^l dx\frac{d[F(x)]^{p+1}}{dx}\left[\frac{dF(x)}{dx}\right]^{2q}\hat{J}P_{st}(x). \quad (50)$$

Using Eqs. (21) and (46), integrating Eq. (50) by parts yields

$$\frac{1}{p+1}\int_0^l dx\frac{d[F(x)]^{p+1}}{dx}\left[\frac{dF(x)}{dx}\right]^{2q}\hat{J}P_{st}(x) = a_0\int_0^l dx[F(x)]^{p+2}\left[\frac{dF(x)}{dx}\right]^{2q-1}\hat{J}P_{st}(x) + a_1\int_0^l dx[F(x)]^{p+1}\left[\frac{dF(x)}{dx}\right]^{2q-1}\hat{J}P_{st}(x), \quad (51)$$

where a_0 and a_1 are x-independent constants determined by p, q, and α. By integrating Eq. (51) p times by parts, we obtain

$$\int_0^l dx[F(x)]^p\left[\frac{dF(x)}{dx}\right]^{2q+1}\hat{J}P_{st}(x) = \sum_{i=0}^{q}C_i\int_0^l dx[F(x)]^{p+q+i}\left[\frac{dF(x)}{dx}\right]\hat{J}P_{st}(x) = \sum_{i=0}^{q}\frac{C_i}{p+q+i+1}\int_0^l dx\frac{d[F(x)]^{p+q+i+1}}{dx}\hat{J}P_{st}(x) = -\sum_{i=0}^{q}\frac{C_i}{p+q+i+1}\int_0^l dx[F(x)]^{p+q+i+1}\frac{d}{dx}\hat{J}P_{st}(x) = 0, \quad (52)$$

where C_i is a constant expressed in terms of a_0 and a_1. Because Eq. (52) shows

$$\Delta_e(t) = 0, \quad (53)$$

we finally obtain Eq. (18) from Eqs. (45) and (53) with Eq. (41).

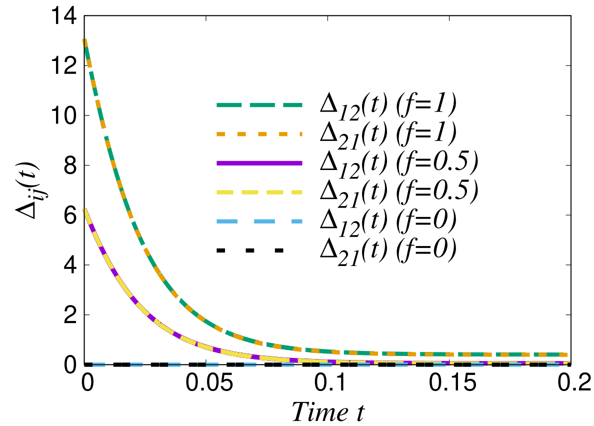

FIG. 1. Time dependence of the extent of the FRR violation $\Delta_{12}(t)$ or $\Delta_{21}(t)$ [Eq. (14)] calculated using the potential in Eq. (54) and the driving forces $f = 0$, 0.5, and 1 with $a = 0$. We use a one-particle one-dimensional model described by a driving overdamped Langevin equation. We convert all quantities into dimensionless forms using the time unit $\gamma T^{-1}l^2$, energy T, and length l, where γ is the friction coefficient.

V. NUMERICAL CALCULATIONS

We demonstrate the reciprocal relation derived in the previous section by numerically calculating $\Delta_{12}(t)$ and $\Delta_{21}(t)$ using the following form of the potential $U(x)$:

$$\frac{U(x)}{T} = \cos\frac{2\pi x}{l} + a\cos\frac{4\pi x}{l}, \quad (54)$$

where a is a parameter independent of x. The potential given by Eq. (54) does not satisfy the condition of Eq. (17) for $a \neq 0$, but satisfies the condition for $a = 0$. To calculate $\Delta_{ij}(t)$, we convert all quantities to dimensionless forms using the time unit $\gamma T^{-1}l^2$, energy T, and length l.

We numerically calculate $\Delta_{12}(t)$ and $\Delta_{21}(t)$ on the basis of Eqs. (22) and (23) using the FP equation [7,8]. Because Eqs. (22) and (23) do not include the perturbations $\epsilon_1 f_p(t)$ and $\epsilon_2 T_p(t)$, the calculations do not need the explicit forms of the perturbations. Equations (22) and (23) are represented by

$$\Delta_{12}(t) = \gamma^{-2}\int_0^l dxF(x)P_{12}(x,t), \quad (55)$$

$$\Delta_{21}(t) = \gamma^{-2}\int_0^l dxF(x)\hat{J}P_{21}(x,t), \quad (56)$$

where $P_{12}(x,t)$ and $P_{21}(x,t)$ are given by $P_{12}(x,t) = e^{t\hat{L}}\hat{J}^2P_{st}(x)$ and $P_{21}(x,t) = e^{t\hat{L}}\hat{J}P_{st}(x)$. We obtain the distribution functions $P_{12}(x,t)$ and $P_{21}(x,t)$ by solving Eq. (20) with $\epsilon_1 = \epsilon_2 = 0$ under the initial conditions $P_{12}(x,0) = \hat{J}^2P_{st}(x)$ and $P_{21}(x,0) = \hat{J}P_{st}(x)$. We numerically solve the FP equation with the Euler method and spatial finite difference method, setting the time and length steps at $\Delta t = 6.25 \times 10^{-7}$ and $\Delta x = 1.25 \times 10^{-3}$, respectively.

First, we numerically confirm that Eq. (18) is valid using a range of values of the driving force f, which shows the extent of deviation from an equilibrium state (Fig. 1). Because Eq. (18) is valid at $a = 0$ in Eq. (54), we calculate $\Delta_{ij}(t)$ for the potential at $a = 0$. For $f = 0$, $\Delta_{12}(t) = \Delta_{21}(t) = 0$ because the FRR is valid in the equilibrium state. We

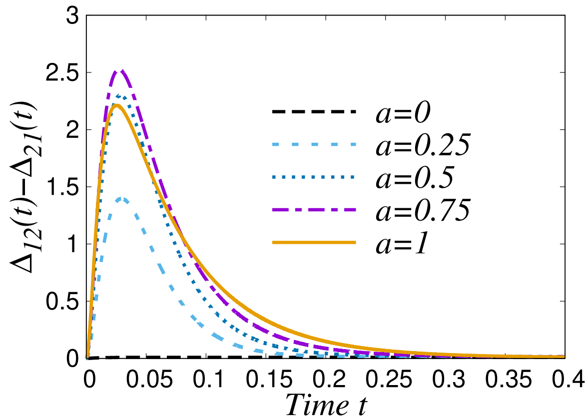

FIG. 2. Time dependence of the difference in extent of the FRR violations $\Delta_{12}(t)$ and $\Delta_{21}(t)$ [Eq. (14)] calculated using the potential in Eq. (54) for five values of the parameter a. We use a one-particle one-dimensional model described by an overdamped Langevin equation with the driving force $f = 1.0$. We convert all quantities into dimensionless forms using the time unit $\gamma T^{-1} l^2$, energy T, and length l, where γ is the friction coefficient.

confirm $\Delta_{12}(t) = \Delta_{21}(t)$ for all the calculated values. This result shows that our reciprocal relation is valid in some nonequilibrium states.

Second, we calculate $\Delta_{12}(t) - \Delta_{21}(t)$ when the potential $U(x)$ does not satisfy Eq. (17) (Fig. 2). At $t = 0$, $\Delta_{12}(t) - \Delta_{21}(t) = 0$ for all values of a, as Yamada and Yoshimori showed [7,8]. When t increases from zero, $\Delta_{12}(t) - \Delta_{21}(t)$ increases from zero to a positive value and reaches a peak between $t = 0.02$ and 0.03. The peak value increases with a except for $a = 1.0$, where the peak is lower than at $a = 0.75$. In contrast, for a longer time, $\Delta_{12}(t) - \Delta_{21}(t)$ is larger at $a = 1.0$ than at $a = 0.75$.

VI. DISCUSSION

We have exactly proven the reciprocal relations of Eqs. (16) and (18) assuming Eq. (17). We now discuss why Eq. (17) was necessary for deriving Eqs. (16) and (18). Equation (17) has been used to show $\Delta_e(t) = 0$, where $\Delta_e(t)$ is given by the division of $\Delta_{21}(t) - \Delta_{12}(t)$ into $\Delta_o(t)$ and $\Delta_e(t)$. To show $\Delta_e(t) = 0$, we have to express $g_o(x, t)$ and $g_e(x, t)$ in the forms of Eqs. (47) and (48), where any higher derivative of $F(x)$ is expressed by $F(x)$ and $F'(x)$. The expressions of the higher derivative can be obtained using Eq. (46) derived from Eq. (17) and have also been applied to Eq. (51).

In the following, we discuss whether our result can be transferred to nonequilibrium systems other than the systems considered in this study. First, we discuss the transferability to systems where the potential does not satisfy Eq. (17). Because we can prove $\Delta_o(t) = 0$ without Eq. (17), Eqs. (16) and (18) are valid for systems with $\Delta_e(t) = 0$. Thus, even if Eq. (17) is not satisfied, we can obtain $\Delta_{21}(t) - \Delta_{12}(t) = 0$, for instance, in the case of $g_e(x, t) = g_o(x, t)$ in Eq. (43). Because it is not clear whether such a system exits, we have to study the possibility in future work.

Next, we discuss the transferability to the underdamped Langevin case, where we have to consider the particle momentum p as well as the position x. Because of the consideration of p, we cannot divide $\Delta_{21}(t) - \Delta_{12}(t)$ in the same way as in the overdamped case. Even if we can divide it in another way, we cannot show that the two divided parts vanish. This is because considering p does not allow us to obtain equations valid in the overdamped case. We obtain $\Delta_o(t) = 0$ from Eq. (31) and $\Delta_e(t) = 0$ from Eqs. (47) and (48), but we cannot obtain such equations in the underdamped case.

Finally, we discuss the transferability to a many-particle three-dimensional system described by the overdamped Langevin equation [8]. In this case, we assume

$$\frac{d^2 U(\{\mathbf{x}_i\})}{d\mathbf{x}_i^2} \propto U(\{\mathbf{x}_i\}), \tag{57}$$

where $U(\{\mathbf{x}_i\})$ is the potential including particle interaction terms, $\mathbf{x}_i$ is the position of particle i, and $\{\mathbf{x}_i\} = \mathbf{x}_1, \mathbf{x}_2, \ldots$. In this system, we can divide $\Delta_{21}(t) - \Delta_{12}(t)$ in the same way as in the one-particle one-dimensional system, so we obtain $\Delta_o(t)$ and $\Delta_e(t)$. Nevertheless, we cannot show $\Delta_o(t) = 0$ because Eq. (31) is not valid in this system. In addition, we cannot show $\Delta_e(t) = 0$ even using Eq. (57) because it is not possible to obtain equations similar to Eqs. (47) and (48).

VII. CONCLUSION

In this work, we have exactly derived the reciprocal relation (16), which is valid in the NESS, from an overdamped Langevin equation assuming Eq. (17). Our reciprocal relation can be expressed in a nonintegral form with respect to the frequency, in contrast to other relations derived by previous studies. This relation is valid far from an equilibrium state because the derivation of the relation is independent of the driving force f representing the extent of the nonequilibrium state. Because our reciprocal relation is expressed only with measurable quantities, one can verify its validity through experiments on systems such as a colloidal suspension. Our reciprocal relation gives deeper understanding of the cross effect between thermal and mechanical perturbations to the NESS.

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APPENDIX A: DERIVATION OF EQ. (32)

In this Appendix, we derive Eq. (32) by expanding $e^{s\hat{L}}$ in powers of $\hat{L}$. We expand $e^{s\hat{L}}$ on the left side of Eq. (32) to obtain

$$\hat{J} e^{s\hat{L}} \hat{J} P_{st}(x) = \hat{J} \sum_{n=0}^{\infty} \frac{s^n}{n!} \hat{L}^n \hat{J} P_{st}(x). \tag{A1}$$

Substituting Eqs. (19) and (24) into Eq. (A1), we obtain

$$\hat{J} \sum_{n=0}^{\infty} \frac{s^n}{n!} \hat{L}^n \hat{J} P_{st}(x) = \hat{J} \sum_{n=0}^{\infty} \frac{s^n}{n!} \left(-\gamma^{-1} \frac{d}{dx} \hat{J} \right)^n \hat{J} P_{st}(x). \tag{A2}$$

We rewrite the right side of Eq. (A2) in the form

$$\hat{J}\sum_{n=0}^{\infty}\frac{s^n}{n!}\left(-\gamma^{-1}\frac{d}{dx}\hat{J}\right)^n\hat{J}P_{st}(x)$$
$$=\sum_{n=0}^{\infty}\frac{s^n}{n!}\left(-\gamma^{-1}\hat{J}\frac{d}{dx}\right)^n\hat{J}^2P_{st}(x). \tag{A3}$$

From Eq. (A3) with $\hat{L}^{\dagger\star}=-\gamma^{-1}\hat{J}d/dx$ and

$$e^{s\hat{L}^{\dagger\star}}=\sum_{n=0}^{\infty}\frac{s^n}{n!}(\hat{L}^{\dagger\star})^n, \tag{A4}$$

we obtain

$$\hat{J}e^{s\hat{L}}\hat{J}P_{st}(x)=e^{s\hat{L}^{\dagger\star}}\hat{J}^2P_{st}(x). \tag{A5}$$

We can derive Eq. (32) from Eq. (A5), obtained by expanding $e^{s\hat{L}}$, using the property of the stationary distribution function $P_{st}(x)$. Because Eq. (24) leads to the property

$$\frac{d}{dx}\hat{J}P_{st}(x)=0, \tag{A6}$$

we obtain

$$e^{s\hat{L}^{\dagger\star}}\hat{J}^2P_{st}(x)=e^{s\hat{L}^{\dagger\star}}F(x)\hat{J}P_{st}(x). \tag{A7}$$

By applying the operator $e^{s\hat{L}^{\dagger\star}}$ to $F(x)\hat{J}P_{st}(x)$ in Eq. (A7) and using $\hat{L}^{\dagger\star}=-\gamma^{-1}\hat{J}d/dx$ and Eq. (A6), we rewrite the right side of Eq. (A7) in the form

$$e^{s\hat{L}^{\dagger\star}}F(x)\hat{J}P_{st}(x)=[e^{s\hat{L}^{\dagger\star}}F(x)]\hat{J}P_{st}(x). \tag{A8}$$

From Eqs. (A5), (A7), and (A8), we finally obtain Eq. (32).

APPENDIX B: DERIVATION OF EQS. (47) AND (48)

Using Eq. (46), we obtain

$$\hat{L}_1^{\dagger}[F(x)]^m[F'(x)]^n$$
$$=c_1[F(x)]^m[F'(x)]^{n+1}+c_2[F(x)]^{m+2}[F'(x)]^{n-1}$$
$$+c_3[F(x)]^{m+1}[F'(x)]^{n-1}\ (m\geqslant 0, n\geqslant 1), \tag{B1}$$

$$\hat{L}_0^{\dagger}[F(x)]^m[F'(x)]^n$$
$$=c_1'[F(x)]^{m+2}[F'(x)]^{n-2}+c_2'[F(x)]^m[F'(x)]^n$$
$$+c_3'[F(x)]^{m-2}[F'(x)]^{n+2}+c_4'[F(x)]^{m+1}[F'(x)]^{n-2}$$
$$+c_5'[F(x)]^{m-1}[F'(x)]^n+c_6'[F(x)]^m$$
$$\times[F'(x)]^{n-2}\ (m\geqslant 2, n\geqslant 2), \tag{B2}$$

where m and n are integers, and c_i and c_i' are constants independent of x. Equation (B1) shows that $\hat{L}_1^{\dagger}$ changes the exponent of $F'(x)$ into an odd number when n is even. When n is odd, $\hat{L}_1^{\dagger}$ changes the exponent into an even number. In contrast, we find from Eq. (B2) that $\hat{L}_0^{\dagger}$ does not change the parity of the exponent of $F'(x)$. Because the same situations are valid for $n<2$ or $m<2$, we can rewrite Eqs. (39) and (40) in the forms of Eqs. (47) and (48).

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