Experimental test of a new equality: Measuring heat dissipation in an optically driven colloidal system

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Measurement of energy dissipation in small nonequilibrium systems is generally a difficult task. Recently, Harada and Sasa [Phys. Rev. Lett. **95**, 130602 (2005)] derived an equality relating the energy dissipation rate to experimentally accessible quantities in nonequilibrium steady states described by the Langevin equation. Here, we show an experimental test of this new relation in an optically driven colloidal system. We find that this equality is validated to a fairly good extent, thus the irreversible work of a small system is estimated from readily obtainable quantities.

Experimental techniques of the manipulation and observation in small systems has developed significantly in these years. Recently, new relations in statistical mechanics such as fluctuation theorems [1–4] and the Jarzynski equality [5,6] have been discovered for small systems driven out of equilibrium. These new ideas have been experimentally tested [7–11] and utilized [12–14] mainly in the systems of macromolecules and colloids using the optical tweezer.

Recently, Harada and Sasa derived an equality [15–17] relating the rate of energy dissipation to experimentally accessible quantities described by Langevin equations. Although the energy dissipation rate is the fundamental quantity to characterize the nonequilibrium steady states, it is generally hard to measure it directly in small systems, especially in microrheological systems and biological systems such as molecular machines. The important aspect of this relation is that it enables us to evaluate the energy dissipation rate from experimentally accessible quantities such as correlation functions and response functions of fluctuating observables. Moreover, this equality was generalized to systems with a memory kernel [18]. In those systems, the fluctuating force has a colored spectrum, not a white one. Such a generalization provides us applications of the equality to much wider systems, including rheological systems and biological systems. In this paper, we showed the first experimental test of the prediction by Harada and Sasa in a colloidal system driven by an optical tweezer in a viscous fluid. Also, we evaluated the energy dissipation rate as a function of frequency using this equality.

First, we introduce this equality. In the over damped case, the Langevin equation is written as

$$\gamma \dot{x}(t) = F(x(t),t) + \varepsilon f^p(t) + \hat{\xi}(t),$$

where $x(t)$ denotes a certain degree of freedom such as the position of a Brownian particle. The force $F(x(t),t)$ acting on the particle at $x(t)$, can be periodically or randomly changing in time, or time independent in general. $\varepsilon f^p(t)$ is a small

probe force to measure the response and $\hat{\xi}(t)$ is a white Gaussian random force: $\langle \hat{\xi}(t) \rangle = 0$, $\langle \hat{\xi}(t)\hat{\xi}(s) \rangle = 2\gamma k_B T \delta(t-s)$. In the systems described by this Langevin equation, Harada and Sasa derived the following equality [15–17], which relates the ensemble average of the energy dissipation rate $J(t)$ to experimentally accessible quantities as

$$\langle J \rangle_0 = \gamma \int_{-\infty}^{\infty} [\widetilde{C}(\omega) - 2k_B T \widetilde{R}'(\omega)]\frac{d\omega}{2\pi}, \qquad (1)$$

where Fourier transform of an arbitrary function $A(t)$ is defined as $\widetilde{A}(\omega) \equiv \int_{-\infty}^{\infty} A(t)\exp(i\omega t)dt$. $\widetilde{A}'(\omega)$ denotes the real part of $\widetilde{A}(\omega)$. $C(t)$ is the autocorrelation function of the velocity: $C(t) \equiv \langle \dot{x}(t)\dot{x}(0) \rangle_0$. $R(t)$ is the linear response function of the velocity to a small external probe force $\varepsilon f^p(t)$:

$$\langle \dot{x}(t) \rangle_\varepsilon - v_s = \varepsilon \int_{-\infty}^{t} R(t-s)f^p(s)ds + o(\varepsilon^2), \qquad (2)$$

where $\langle \cdots \rangle_\varepsilon$ denotes an ensemble average under the probe force $f^p(t)$ of order ε. v_s is the steady state velocity. Measurement of $\widetilde{C}(\omega)$ and $\widetilde{R}'(\omega)$ is usually more accessible by experiments than that of $J(t)$. The right hand side of Eq. (1) vanishes near the equilibrium state due to the fluctuation dissipation relation (FDR) of the first kind [19]; $\widetilde{C}(\omega) = 2k_B T \widetilde{R}'(\omega)$, while it has a finite value in nonequilibrium states generally. Therefore the integral in Eq. (1) corresponds to the extent of the FDR violation.

We tested this equality [Eq. (1)] in an optically driven system, in which one small particle was trapped by an optical tweezer. The optical tweezer enables us to create a potential for small particles [20]. Nonequilibrium steady states (NESSs) can be established by introducing persistent forcing to the Brownian particle.

The experimental setup is shown in Fig. 1. Infrared laser (Spectra Physics, 1064 nm) was introduced to the microscope (Olympus, IX71) and focused by an objective lens (Olympus UPLSAPO, 100× NA=1.4) to create an optical tweezer. One carboxylated polystyrene particle of a diameter of 0.984±0.023 μm (Polysciences, 08226) was trapped in

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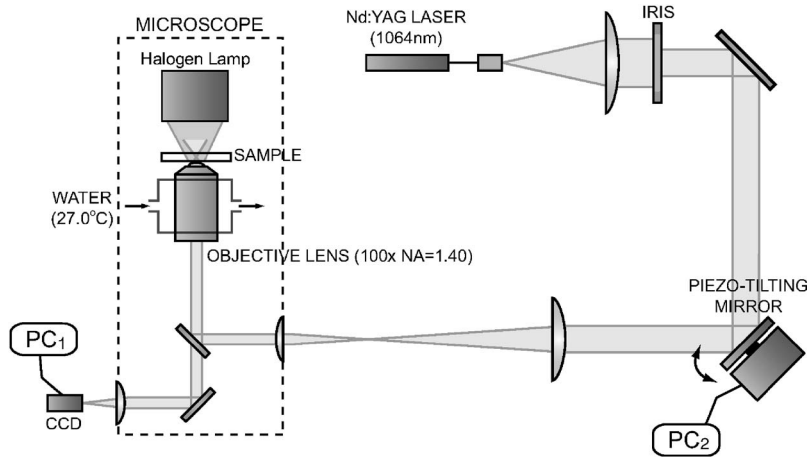†Electronic address: sano@phys.s.u-tokyo.ac.jp

FIG. 1. Experimental setup.

distilled water. Trajectory of the particle was captured by a charge-coupled device (CCD) camera (Hamamatsu, HISCA C6770) with 472 frames/s and analyzed to know the particle position. The temperature was kept at 27.0±0.1 °C by water circulation around the objective lens.

To achieve nonequilibrium steady states (NESSs), we switched the position of the tweezer between two sites $\pm L/2$ ($L=460.8\pm0.14$ nm) at random according to the Poissonian process by tilting the angle of a Piezo mounted mirror (PI, S-226) controlled by a PC. The corresponding Langevin equation becomes

$$\gamma \dot{x}(t) = -k\left[x(t) - \frac{L}{2}\hat{\sigma}(t)\right] + \varepsilon f^{p}(t) + \hat{\xi}(t),$$

where k is the stiffness of the tweezer. $x(t)$ is the horizontal coordinate of the particle position [see Fig. 2(a)]. $\hat{\sigma}(t) = \{-1, 1\}$ is a random variable obeying Poissonian process with a transition rate λ; $\langle\hat{\sigma}(t)\hat{\sigma}(s)\rangle = \exp(-2\lambda|t-s|)$. The particle is sufficiently small $(m/\gamma \sim 10^{-7}$ s) thus the over damped assumption is supposed to be valid.

At first, we trapped a particle with fixing the position of the tweezer and obtained a histogram of the particle location (1 703 884 points). Then, according to the Boltzmann distribution, we calculated the potential energy of the particle, which was well fitted by a harmonic potential with a spring constant of $k=117.5\pm0.48k_{\mathrm{B}}T/\mu\mathrm{m}^2=0.4870 \pm0.0020$ pN/μm.

To know the response function $\tilde{R}(\omega)$, we shifted the position of the tweezer at $t=0$ with a distance of $d=190.2\pm0.11$ nm (Fig. 3) and tracked particle trajectories in the relaxation processes in the equilibrium state (EQ) and four NESSs (the mean switching rates were varied from $\lambda=1.0$ to 4.0 with a step of 1.0 Hz). The corresponding probe force $\varepsilon f^{p}(t)$ becomes $kd(t\geq0)$, $0(t<0)$. Figure 4 shows that the ensemble averaged trajectories of the relaxation pro-

(a)

(b)
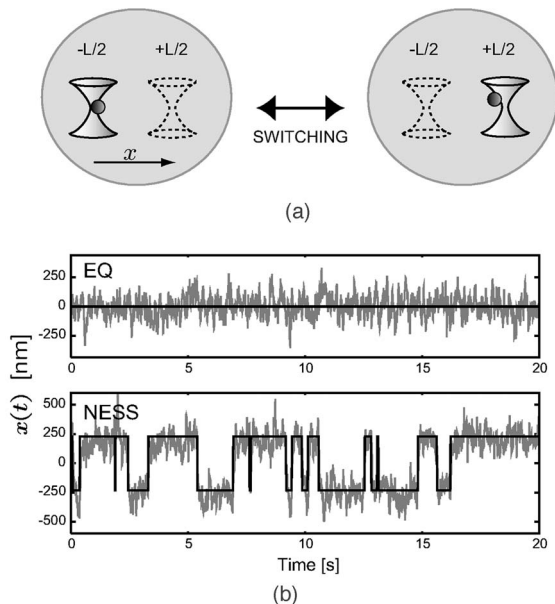
FIG. 2. Switching: (a) To achieve nonequilibrium steady states (NESSs), position of the optical tweezer was switched between two sites ($\pm L/2$) using a piezo mounted mirror at random with Poissonian process. In the equilibrium state (EQ), the position of the tweezer was fixed. In NESS, we decided whether to switch or not at random every 4 ms. One switching takes 5 ms due to the mechanical response of the mirror unit. (b) Typical trajectory for EQ and NESS ($\lambda=1.0$). Black line is the trajectory of the optical tweezer. Gray line is the trajectory of the particle. $L=460.8\pm0.14$ nm.

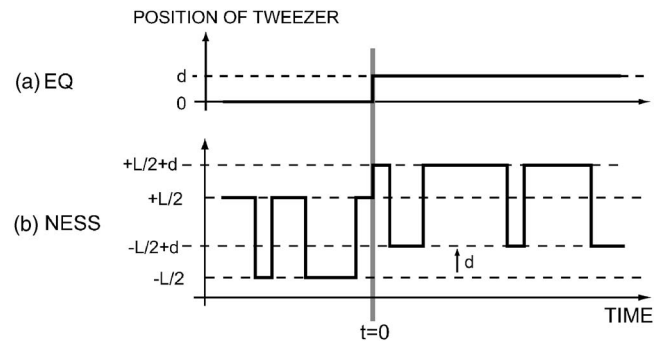FIG. 3. Measurement of response function: (a) We shifted the tweezer position with a distance of $d=190.2\pm0.11$ nm at $t=0$ and observed the relaxation processes to the new laser position. We repeated this and obtained an ensemble average. (b) Similarly in NESSs, we added a bias d and observed the relaxation processes.
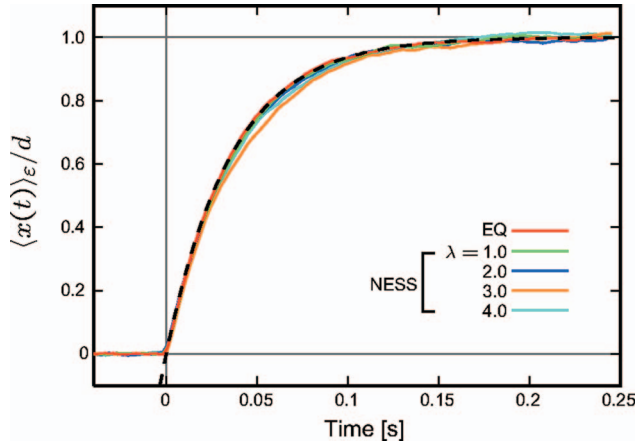
FIG. 4. (Color) response function: The trajectories of the relaxation processes in EQ [equilibrium state (no switching)] and NESSs (nonequilibrium steady states) with mean switching rates $\lambda=1.0$, 2.0, 3.0, and 4.0 Hz. Dashed line is the fitting curve: $\langle x(t)\rangle/d=1-\exp(-\omega_c t)$ for EQ. d was 190.2 ± 0.11 nm and the cutoff frequency ω_c was 27.61 ± 0.05 rad/sec. We averaged 7854 trajectories for EQ, $\lambda=1.0$, 3.0, and 4.0, respectively, and 8085 trajectories for $\lambda=2.0$.

cesses in EQ and NESSs coincided well. We fitted an exponential function $\langle x(t)\rangle/d=1-\exp(-\omega_c t)$ to the trajectory in EQ. The cutoff frequency was estimated as $\omega_c=27.61\pm0.05$ rad/sec, which yields the friction coefficient $\gamma=k/\omega_c=1.763\times10^{-8}$ kg/s [21].

From the fitting curve in Fig. 4, we obtained the response function $\widetilde{R}'(\omega)=\omega^2/(\omega^2+\omega_c^2)\gamma$. We compared this response function $\widetilde{R}'(\omega)$ and correlation functions of the velocity $\widetilde{C}(\omega)$ obtained from the trajectories of the particle. In Fig. 5, we found a good coincidence between $\widetilde{C}(\omega)$ and $2k_BT\widetilde{R}'(\omega)$ in the equilibrium state. Thus the fluctuation dissipation relation was confirmed, while these had differences in nonequilib-
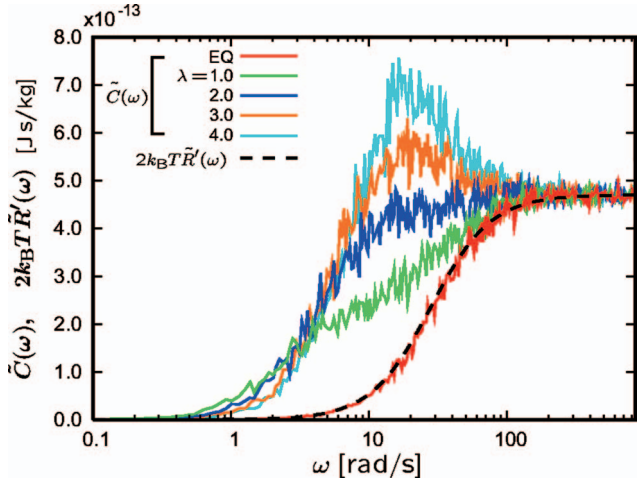

FIG. 5. (Color) $\widetilde{C}(\omega)$ and $2k_BT\widetilde{R}'(\omega)$: Dashed line is the response function $2k_BT\widetilde{R}'(\omega)=2k_BT\omega^2/(\omega^2+\omega_c^2)\gamma$. 52 runs $\times69.17$ s (1 703 884 points) in EQ and NESS at $\lambda=3.0$, 4.0, respectively, and 53 runs $\times69.17$ s (1 736 651 points) in NESS at $\lambda=1.0$ and 2.0, respectively, were averaged for $\widetilde{C}(\omega)$. Moving averages were taken in ω direction.
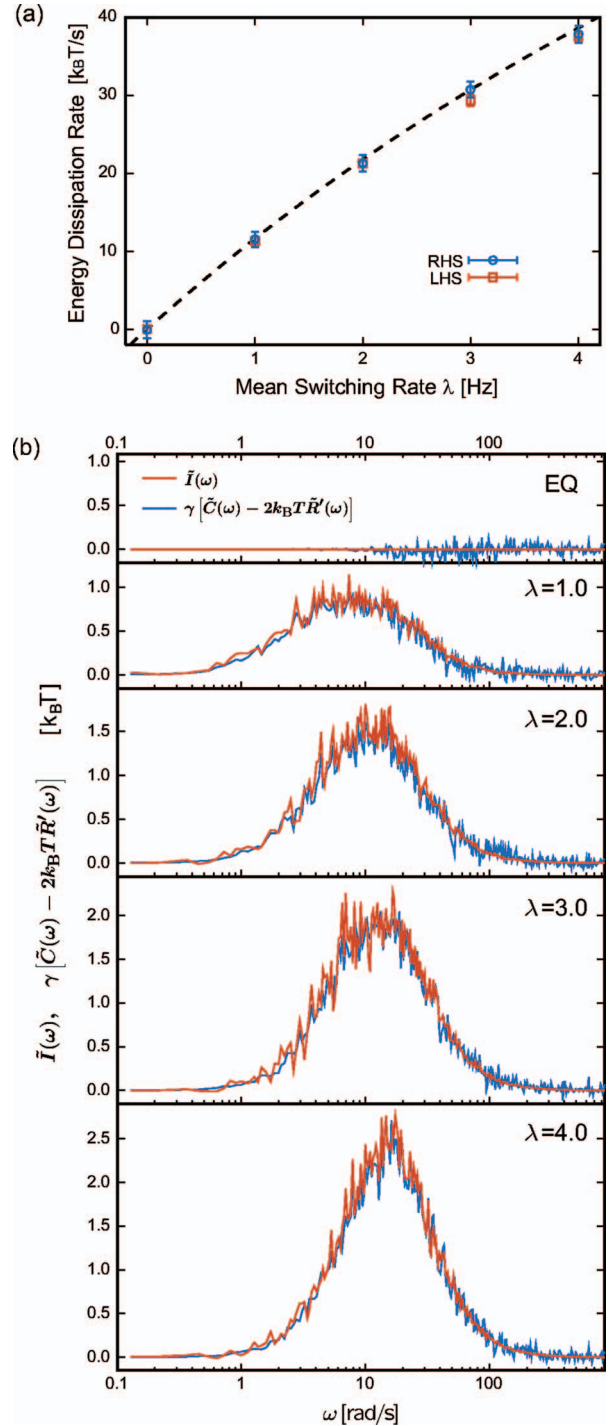

FIG. 6. (Color) (a) The left hand side (LHS) and the right hand side (RHS) of the equality (1) were plotted against the mean switching rate λ Hz. For the RHS, we integrated only in the region $\omega<850$ because the difference between the LHS and RHS should vanish at sufficiently high frequencies. Dashed line is the theoretical curve [22]. The standard errors of the RHS were around $1k_BT/s$ at all switching rates. (b) Validation of the equality for each ω [Eq. (3)]; $\widetilde{I}(\omega)$ (blue line) vs $\gamma[\widetilde{C}(\omega)-2k_BT\widetilde{R}'(\omega)]$ (black line). We used the same data for $\widetilde{C}(\omega)$ and $\widetilde{R}'(\omega)$ in Fig. 5 to calculate $\gamma[\widetilde{C}(\omega)-2k_BT\widetilde{R}'(\omega)]$.

rium steady states. Also, the higher the switching rate λ was, the larger the deviation of $\widetilde{C}(\omega)$ from $2k_{\mathrm{B}}T\widetilde{R}'(\omega)$ was.

Equation (1) implies that the product of γ and the area between $\widetilde{C}(\omega)$ and $2k_{\mathrm{B}}T\widetilde{R}'(\omega)$ in Fig. 5 corresponds to the energy dissipation rate. The irreversible energy dissipation should be balanced with the energy input in steady states, thus $\langle J \rangle = \langle F(x(t),t) \circ v(t) \rangle$, where $\circ$ denotes the Stratonovich multiplication [23]. On the contrary, in our setup it is possible to evaluate this $\langle J \rangle$ because the force exerted by the optical tweezer can be calculated from the displacement between the particle and the center of the tweezer as $F(x(t),t) = -k\left[x(t) - \frac{L}{2}\sigma(t)\right]$ (note that this is not always possible in other systems). We compared these two values in Fig. 6(a) and confirmed that the equality is valid to a good extent within statistical error. In one switching, the particle is supposed to travel a distance of L on an average. This corresponds to an energy injection of $kL^2/2 = 12.5k_{\mathrm{B}}T$ per one switching and $\lambda kL^2/2 = 12.5\lambda k_{\mathrm{B}}T$ per unit time. However, insufficient relaxation to the switched position due to fast switchings causes a deviation from this value. The dashed line in Fig. 6(a) is the theoretical value including this effect [22].

It is possible to derive a local equality [Eq. (1)]:

$$\widetilde{I}(\omega) = \gamma[\widetilde{C}(\omega) - 2k_{\mathrm{B}}T\widetilde{R}'(\omega)], \tag{3}$$

where $\widetilde{I}(\omega)$ is the Fourier transform of the cross correlation of the force $F(x(t),t)$ and velocity $v(t)$ at different times:

$$I(t) \equiv [\langle F(x(t),t) \circ v(0) \rangle_0 + \langle F(x(0),0) \circ v(t) \rangle_0]/2.$$

Equation (3) implies that the equality holds at each ω [16]. This local relation provides us a chance for the more detailed experimental test of the equality. Figure 6(b) shows a good agreement of the both sides of Eq. (3) at each ω. As we increased the mean switching rate λ, the frequency and height of the peak of the local dissipation rate increased.

We showed experimental demonstration of Harada and Sasa's equality. Using this equality, we evaluated the rate of the energy dissipation for an optically driven particle with a precision of around $1k_{\mathrm{B}}T/\mathrm{s}$ from the correlation function and response function of the particle velocity. Note that this equality is not applicable to systems with retarded friction, since it is based on a Markovnian Langevein equation. However, systems which are more interesting and practical often have a retarded friction. For example, molecular machines are working in extremely crowded environment in cells. In such a situation, non-Markovnian behavior is expected. Also, microrheology is attracting extensive studies recently. As we described, Deutsch and Narayan recently generalized the equality to these situations, namely systems described by a generalized Langevin equation [18]. If this generalization is confirmed by experiments, it provides us applications of this equality to much wider systems. This will be the primary focus of the forthcoming experiments.

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