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 the first 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.

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Experimental techniques of the manipulation and observation in small systems has developed significantly in these years. Recently, new relations in statistical mechanics such as the fluctuation theorems1,2,3,4 and the Jarzynski equality5,6 have been discovered in these years. Most of these new ideas have been experimentally tested7,8,9,10,11 mainly in the systems of macro-molecules and colloids using the optical tweezer.

Recently, Harada and Sasa derived an equality12,13,14 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 kernel15,16,17, relating the rate of energy dissipation to experimentally accessible quantities as:

\[ J = \gamma \int_{-\infty}^{\infty} \left[ C(\omega) - 2k_B T R'(\omega) \right] \frac{d\omega}{2\pi} \]

(1)

where Fourier transform of an arbitrary function \( A(t) \) is defined as \( \tilde{A}(\omega) = \int_{-\infty}^{\infty} A(t) \exp(i\omega t) dt \). \( \tilde{A}'(\omega) \) denotes the real part of \( \tilde{A}(\omega) \). \( C(t) \) is the auto correlation function of the velocity \( v \) and \( R(t) \) is the linear response function of the velocity to a small external probe force \( \varepsilon f_p(t) \):

\[ \langle \dot{x}(t) \rangle_v - v_s = \varepsilon \int_{-\infty}^{t} R(t-s) f_p(s) ds + o(\varepsilon^2) \]

(2)

where \( \langle \cdots \rangle_v \) denotes an ensemble average under the probe force \( f_p(t) \) of order \( \varepsilon \). \( v_s \) is the steady state velocity. Measurement of \( \tilde{C}(\omega) \) and \( \tilde{R}(\omega) \) is usually more accessible by experiments than that of \( J \). The right hand side of Eq. (1) vanishes near the equilibrium state due to the fluctuation dissipation relation of the first kind19; \( \tilde{C}(\omega) = 2k_B T R'(\omega) \). 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 particles20. Nonequilibrium steady states (NESS) can be established by introducing persistent forcing to the Brownian particle.

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

![FIG. 1: Experimental Setup](image)

To achieve nonequilibrium steady states(NESS), we switched the position of the tweezer between two sites ±L/2[L = 460.8 ± 0.14[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

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

where \(k\) is the stiffness of the tweezer. \(x(t)\) is the horizontal coordinate of the particle position (see Fig.2(a)). \(\bar{\sigma}(t) = \{-1, 1\}\) is a random variable obeying Poissonian process with a transition rate \(\lambda: \langle \bar{\sigma}(t) \bar{\sigma}(s) \rangle = \exp(-2\lambda|t-s|)\). 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 \(k = 117.5 \pm 0.48[kB/\mu m^2] = 0.4870 \pm 0.0020[pN/\mu m]\).

To know the response function \(R(\omega)\), we shifted the position of the tweezer at \(t = 0\) with a distance of \(d = 190.2\pm 0.11[nm]\) (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 \(kd(t \geq 0), 0(t < 0)\). Figure 3 shows that the ensemble averaged trajectories of the relaxation processes in EQ and NESSs coincided well. We fitted an exponential function \((x(t))/d = 1 - \exp(-\omega_c t)\) to the trajectory in EQ. The cutoff frequency was estimated as \(\omega_c = 27.61\pm 0.05[\text{rad/sec}]\), which yields the friction coefficient \(\gamma = k/\omega_c = 1.763 \times 10^{-3}[\text{kg/s}]\).

From the fitting curve in Fig.4 we obtained the response function \(\tilde{R}(\omega) = \omega^2/(\omega^2 + \omega_0^2)\gamma\). We compared this response function \(\tilde{R}(\omega)\) and correlation functions of the velocity \(\tilde{C}(\omega)\) obtained from the trajectories of the particle. In Fig.4 we found a good coincidence between \(\tilde{C}(\omega)\) and \(2k_B T \tilde{R}(\omega)\) in the equilibrium state. Thus, the fluctuation dissipation relation was confirmed. While, these had differences in nonequilibrium steady states. Also, the higher the switching rate \(\lambda\) was, the larger the deviation of \(\tilde{C}(\omega)\) from \(2k_B T \tilde{R}(\omega)\) was.

Equation 1 implies that the product of \(\gamma\) and the
the center of the tweezer as cause the force exerted by the optical tweezer can be cal-
trary, in our setup it is possible to evaluate this
de pressed in 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: \( \langle x(t) \rangle / \langle d \rangle = 1 - \exp(-\omega_c t) \) for
EQ, \( d = 190.2 \pm 0.11 \) [nm] and the cutoff frequency \( \omega_c \) was
27.61 \pm 0.05 [rad/sec]. We averaged 7,854 trajectories for EQ, \( \lambda = 1.0, 3.0, \) and \( 4.0 \) respectively and 8,085 trajectories for
\( \lambda = 2.0 \).

FIG. 6: (Color) (a) The left hand side (LHS) and the right hand side (RHS) of the equality (11) were plotted against the
mean switching rate \( \lambda \) [Hz]. For RHS, we integrated only in the region \( \omega < 850 \) because the difference between LHS and
RHS should vanish at sufficiently high frequencies. Dashed
line is the theoretical curve [22]. The standard errors of RHS were around \( 1 \) [kBT/s] at all switching rates. (b) Validation of
the equality for each \( \omega \) (Eq. 3): \( \gamma \langle C(\omega) - 2k_B T \hat{R}(\omega) \rangle \) (black line). We used the same data for \( C(\omega) \)
and \( \hat{R}(\omega) \) in Fig. 5 to calculate \( \gamma \langle C(\omega) - 2k_B T \hat{R}(\omega) \rangle \).

area between \( \tilde{C}(\omega) \) and \( 2k_B T \hat{R}(\omega) \) 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 con-
trary, in our setup it is possible to evaluate this \( \langle J \rangle \) be-
cause the force exerted by the optical tweezer can be
calculated from the displacement between the particle and
the center of the tweezer as \( F(x(t), t) = -k(x(t) - \frac{1}{2} \sigma(t)) \).
(Note that this is not always possible in other systems.)
We compared these two values in Fig. 5(a) and confirmed
that the equality is valid to good extent within statisti-
cal error. In one switching, the particle is supposed to
travel a distance of $L$ on an average. This corresponds to an energy injection of $kL^2/2 = 12.5[k_B T]$ per one switching and $kL^2/2 = 12.5[k_B T]$ 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)):

$$I(\omega) = \gamma \left[ \tilde{C}(\omega) - 2k_B T \tilde{R}'(\omega) \right],$$

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

$I(t) \equiv \langle [F(x(t), t) \circ v(0)]_0 + [F(x(0), 0) \circ v(t)]_0 \rangle / 2$.

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

We showed the first experimental demonstration of the 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 $1[k_B T/s]$ 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 Markovian Langevin 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-Markovian behaviour 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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