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, new relations in statistical mechanics such as the fluctuation theorems\cite{1, 2, 3, 4} and the Jarzynski equality\cite{5, 6} have been discovered for small systems driven out of equilibrium. These new ideas have been experimentally tested\cite{7, 8, 9, 10, 11} 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 readily obtainable quantities.

Firstly, we introduce this equality. In the overdamped case, the Langevin equation is written as

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

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 $\tilde{\xi}(t)$ is a white Gaussian random force: \(\langle \tilde{\xi}(t) \rangle = 0\), \(\langle \tilde{\xi}(t)\tilde{\xi}(s) \rangle = 2\gamma k_B T\delta(t-s)\). In the systems described by this Langevin equation, Harada and Sasa derived the following equality\cite{15, 16, 17}, which relates the ensemble average of the energy dissipation rate $J(t)$ to experimentally accessible quantities as:

$$\langle J(t) \rangle_0 = \gamma \int_{-\infty}^{\infty} \left[ \tilde{C}(\omega) - 2k_B T \tilde{R}^R(\omega) \right] \frac{d\omega}{2\pi},$$

(1)

where Fourier transform of an arbitrary function $A(t)$ is defined as $\tilde{A}(\omega) = \int_{-\infty}^{\infty} A(t) \exp(i\omega t) dt$. $A^R(\omega)$ denotes the real part of $\tilde{A}(\omega)$. $C(t)$ is the auto correlation function of the velocity: $C(t) = \langle \dot{x}(t)\dot{x}(0) \rangle$. $R(t)$ is the linear response function of the velocity to a small external probe force $\varepsilon f^p(t)$:

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

(2)

where $\langle \cdots \rangle_o$ 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 $\tilde{R}^R(\omega)$ 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 of the first kind\cite{19}: $C(\omega) = 2k_B T \tilde{R}^R(\omega)$. 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\cite{20}. 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, 1064 nm) 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[mm]) 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

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

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

To know the response function \( R(\omega) \), we shifted the position of the tweezer at \( t = 0 \) with a distance of \( d = 190.2\pm0.11[mm] \) (Fig. 2) 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 2 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 \( \omega_c = 27.61\pm0.05[rad/sec] \), which yields the friction coefficient \( \gamma = k/\omega_c = 1.763 \times 10^{-6}[kg/s] \).

From the fitting curve in Fig. 2 we obtained the response function \( R'(\omega) = \omega^2/(\omega^2 + \omega_0^2)\gamma \). We compared this response function \( R'(\omega) \) and correlation functions of the velocity \( \bar{C}(\omega) \) obtained from the trajectories of the particle. In Fig. 3 we found a good coincidence between \( \bar{C}(\omega) \) and \( 2k_B T R'(\omega) \) 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 \( \bar{C}(\omega) \) from \( 2k_B T R'(\omega) \) was.

Equation 1 implies that the product of \( \gamma \) and the
FIG. 4: (Color) Response Function: The trajectories of the relaxation processes in EQ (equilibrium state) and NESS (nonequilibrium steady states) with mean switching rates \( \lambda = 1.0, 2.0, 3.0, 4.0 \) [Hz]. Dashed line is the fitting curve: \( \langle x(t) \rangle / d = 1 - \exp(-\omega_c t) \) 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 \( \lambda = 2.0 \).

area between \( \tilde{C}(\omega) \) and \( 2k_B T \tilde{R}'(\omega) \) in Fig. 5 corresponds to the energy dissipation rate. The irreversible energy dissipation should be balanced with the energy input in steady states, thus \( \langle J \rangle = (F(x(t), t) \circ v(t)) \), where \( \circ \) denotes the Stratonovich multiplication\(^{22} \). 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 \( F(x(t), t) = -k(x(t) - \frac{1}{2} \sigma(t)) \). (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 statistical error. In one switching, the particle is supposed to

FIG. 5: (Color) \( \tilde{C}(\omega) \) and \( 2k_B T \tilde{R}'(\omega) \): Dashed line is the response function \( 2k_B T \tilde{R}'(\omega) = 2k_B T \omega^2 / (\omega^2 + \omega_c^2) \gamma \). 52 [runs] \( \times \) 69.17 [s] (1,703,884 [points]) in EQ and NESS at \( \lambda = 3.0, 4.0 \) respectively and 53 [runs] \( \times \) 69.17 [s] (1,736,651 [points]) in NESS at \( \lambda = 1.0 \) and 2.0 respectively were averaged for \( \tilde{C}(\omega) \). Moving averages were taken in \( \omega \) direction.

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 [k_B T/s] at all switching rates. (b) Validation of the equality for each \( \omega \) (Eq. 3); \( \tilde{I}(\omega) \) (blue line) vs \( \gamma(\tilde{C}(\omega) - 2k_B T \tilde{R}'(\omega)) \) (black line). We used the same data for \( \tilde{C}(\omega) \) and \( \tilde{R}'(\omega) \) in Fig. 5 to calculate \( \gamma(\tilde{C}(\omega) - 2k_B T \tilde{R}'(\omega)) \).
travel a distance of $L$ on an average. This corresponds

to an energy injection of $kL^2/2 = 12.5\text{[kB]}$ per one

switching and $kL^2/2 = 12.5\text{[kB]}$ per unit time. How-

ever, insufficient relaxation to the switched position due to

due to this deviation and height of the peak of the local

correlation function and response function of the par-

ticle 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 re-
cently. As we described, Deutsch and Narayan recently
generalized the equality to these situations, namely sys-
tems described by a generalized Langevin equation[18].
If this generalization is confirmed by experiments, it pro-
vides us applications of this equality to much wider sys-
tems. This will be the primary focus of the forthcoming
experiments.

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