Nonequilibrium Fluctuations for a Single-Particle Analog of Gas in a Soft Wall

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We investigate the motion of a colloidal particle driven out of equilibrium by a time-varying stiffness of the optical trap that produces persistent nonequilibrium work. Measurements of work production for repeated cycles composed of the compression and expansion processes for the optical potential show huge fluctuations due to thermal motion. Using a precise technique to modulate the stiffness in time, we accurately estimate the probability distributions of work produced for the compression and expansion processes. We confirm the fluctuation theorem from the ratio of the two distributions. We also show that the average values of work for the two processes comply with the Jarzynski equality. This system has an analogy with a gas in a breathing soft wall. We discuss about its applicability to a heat engine and an information engine operated by feedback control.

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The fluctuation theorem for entropy production in a heat bath was discovered for a deterministic dynamics in the early 1990s [1,2]. Later it was also proved theoretically in a wide class of stochastic systems and extended to other thermodynamic quantities such as work and heat [3–8]. Since it deals with the stochastic distribution for the fluctuation of a thermodynamic quantity, small systems with large fluctuations have been of interest in experimental studies. The first experiment and the following were done for a colloidal particle driven out of equilibrium by moving the center of the trap [9,10], which is regarded as a prototype of nonequilibrium process driven by an external field. Similar experimental systems were studied, such as a molecule in the atomic force microscopy or a colloidal particle in the optical trap pulled by an external force [11], an electrical dipole driven by a small current [12], and a harmonic oscillator under an external force [13,14]. These systems are well described by the overdamped Langevin equation, and theoretical works were accompanied or performed separately [15,16]. There were also experimental studies for biological systems with unknown dynamical details, such as an RNA molecule unfolded and refolded by optical tweezers [17,18] and a rotating motor protein F_1-ATPase [19], for which agreement with theory is less accurate.

In this Letter, we consider the motion of a colloidal particle in an optical trap with a time-varying stiffness. It is characterized by a different nonequilibrium prototype where a protocol changes the shape of potential in time. The theoretical approach is more difficult than that for nonequilibrium driven by an external field [9–14], and the probability distribution for the work production is not known rigorously. However, there have been recent theoretical works [20,21] where the moments of the work distribution are obtained. On the other hand, no experimental study on nonequilibrium fluctuations for this system has been done to date, partly due to difficulty in modulating the stiffness accurately. In this work, we use a liquid crystal device to control the stiffness precisely in time, from which we accurately measure large fluctuations for the work production in repeated cycles composed of the two processes given by compressing and expanding the trap potential. By estimating the work distributions for the two processes, we confirm the fluctuation theorem for the work production [4,7] along with an excellent agreement of the measured free-energy difference with the theoretical value. We also show the average values of work for the two processes to comply with the Jarzynski equality [3]. This system has an analogy with a gas in a soft-wall cylinder and has recently been exploited for a microscopic heat engine [22]. Our experimental method will be useful for further study on a microscopic engine constructed from this system.

The Brownian motion of the particle in a liquid (heat bath) at temperature [$T = (k_B\beta)^{-1}$] can be described by the stochastic differential equation for position $x(t)$ in one dimension, given as $\gamma\dot{x} = -kx + \xi$ where k is a time-varying stiffness, γ the dissipation coefficient, and $\xi(t)$ is a white noise with zero mean and correlation $\langle\xi(t)\xi(t')\rangle = 2\gamma\beta^{-1}\delta(t-t')$. This equation represents well the experimental situation in which the motion can be regarded as overdamped owing to large γ/m used and the nearly isotropic harmonic potential [23,24].

The particle is initially in equilibrium with an initial stiffness k_i. Then, for $t > 0$ the stiffness is changed from k_i to k_f. The process for $k_i < k_f$ ($k_i > k_f$) is called a forward (reverse) process, analogous to the compression

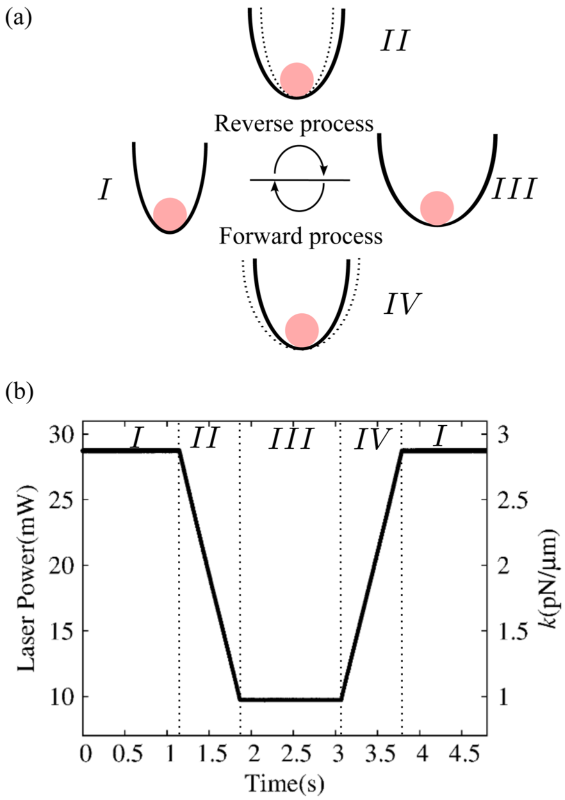

FIG. 1 (color online). (a) The colloidal particle is trapped inside the optical harmonic potential. During the forward (reverse) process, the trap stiffness is linearly increased (decreased) in time. (b) Trapping laser power and trap stiffness as a function of time for the case of $|\dot{k}| = 0.536\,\mathrm{pN}/\mu\mathrm{m\,s}$.

(expansion) of gas [See Fig. 1(a)]. The nonequilibrium work by an external agent that controls the trap potential is given by $W = \int_0^\tau dt \partial V/\partial t = (1/2)\int_0^\tau dt \dot{k} x^2$ where V is the instantaneous potential energy for $k = k(t)$ at time t [3].

The Jarzynski equality [3] relates the free energy difference ΔF between the initial and final equilibrium states associated with the stiffness k_i and k_f, respectively, given as

$$\langle e^{-\beta(W-\Delta F)} \rangle = 1, \tag{1}$$

where the bracket denotes the ensemble average over all possible trajectories. It gives rise to the inequality

$$\langle W \rangle - \Delta F \geq 0. \tag{2}$$

It is the second law of thermodynamics stated in terms of irreversible work $W - \Delta F$, where the equality holds for a reversible process. The Crooks-Tasaki fluctuation theorem [4,7], the sufficient condition for the Jarzynski equality, is given as

$$\frac{P_F(W)}{P_R(-W)} = e^{\beta(W-\Delta F)}. \tag{3}$$

Here, P_F (P_R) is a probability distribution function of the nonequilibrium work performed during the forward (reverse) process. In this study, we experimentally estimate these probability distribution functions and confirm Eqs. (2) and (3).

The analytic expression for the probability distribution of work fluctuation is not known except for special cases: the quasistatic limit ($\dot{k} \to 0$) and the sudden change limit ($|\dot{k}| \to \infty$) [21]. In the quasistatic process, the particle is in equilibrium at any instant so that $\langle x^2 \rangle = \beta^{-1} k(t)^{-1}$, as expected from the equipartition theorem. Then, the definition of work gives $\langle W \rangle_F = 1/(2\beta) \int dt \dot{k}/k = (2\beta)^{-1} \ln(k_f/k_i) = \Delta F = \langle -W \rangle_R$. Therefore, we expect the corresponding work distribution to be a Gaussian-like delta function with a peak at ΔF. In the case of sudden change limit, however, the particle still remains in its initial distribution even after a sudden change of k is made. Therefore, $\langle x^2 \rangle_F = \beta^{-1} k_i^{-1}$ and $\langle W \rangle_F = (k_f - k_i)/(2\beta k_i)$. Similarly, $\langle x^2 \rangle_R = \beta^{-1} k_f^{-1}$ and $\langle W \rangle_R = (k_i - k_f)/(2\beta k_f)$. The work distribution function can be found exactly by using $P(W) \propto p_{\mathrm{eq}}(x)$ and $W_{F,R} = \pm(k_f - k_i)x^2/2$ [21], which leads to $P_{F,R}(W) \propto \theta(\pm W)(\pm\beta W)^{-1/2} \exp(-a_\pm \beta |W|)$, where $+(-)$ denotes the forward (reverse) process, $a_+ = k_i/(k_f - k_i)$, $a_- = k_f/(k_f - k_i)$, and $\theta(W)$ is the Heaviside step function. Two probability distributions in the extremely fast nonequilibrium limit meet each other at $W = \Delta F$ as expected by the Crooks-Tasaki fluctuation theorem; see the Supplemental Material Fig. S1 [25].

From these two extreme limits, one can easily guess that, as $|\dot{k}|$ increases from 0, the work distribution function, starting from the delta function with a peak at ΔF, spreads with the peak moving towards the origin and is finally frozen to an exponential function. When $|\dot{k}|$ has a finite value and the stiffness is changed faster than the characteristic equilibration time of the system, the position of the particle does not follow the Boltzmann distribution corresponding to the stiffness $k(t)$ at any instant and the system is in nonequilibrium. Therefore, in the forward process where the shape of the potential becomes narrower in time; therefore, the position distribution of the particles is wider than the equilibrium distribution at every instant, so $\langle x^2 \rangle_F > \langle x^2 \rangle_{\mathrm{eq}}$. In reverse process, $\langle x^2 \rangle_R < \langle x^2 \rangle_{\mathrm{eq}}$. From the definition of work, therefore, we expect

$$\langle -W \rangle_R \leq |\Delta F| \leq \langle W \rangle_F, \tag{4}$$

which is the restatement of Eq. (2). Here, the equality again corresponds to the quasistatic limit.

In this study, we consider the case where the trap stiffness changes linearly in time; i.e., $\dot{k}$ is constant in time. To construct a trap potential with a time-dependent stiffness, a set of homemade optical tweezers is used; see the Supplemental Material Fig. S2 [25]. An inverted microscope (IX-70, Olympus) equipped with a $\times 100$ (NA $= 1.3$) oil immersion objective lens is used as a stable base on an air-cushioned optical table for tightly focusing two infrared lasers beams ($\lambda = 1064$ nm, 980 nm, Laser lab) required for trapping a colloidal particle and tracking its position. To measure the position of the particle, the light diffracted from the trapped particle is detected using a quadrant photodiode detector (QPD) (S5980, Hamamatsu). The electrical signal from the QPD is preamplified in a signal amplifier (OT-301, On-Trak Photonics, Inc.) and sampled at every 0.1 ms with a PCI data acquisition card (PCI-6230, National Instruments), which allows the measurements of particle position with a 2 nm resolution without appreciable data distortion. During the experiment, to reduce long-term laser power fluctuations, we set up a feedback laser power control system to limit laser power fluctuation to $\pm 0.5\%$. A highly dilute solution of 2 μm diameter poly methyl methacrylate particles in dodecane liquid is used in a 0.1 mL sample cell. The sample cell is sealed by epoxy to prevent vaporization and flow of the dodecane. The temperature of the sample cell is kept at 300 ± 0.1 K.

The laser beam power is very accurately controlled by using a liquid-crystal variable retarder (LCVR, LCC1113-C, Thorlabs). This retarder manipulates the polarization state of the output beam by applying an ac voltage difference across the liquid crystal. By switching the polarization state, it can control the laser beam intensity every 1 ms. To change the trap strength linearly, an amplitude-modulated 2 kHz square-wave signal is fed to the LCVR from an arbitrary function generator (33250a, Agilent).

Calibrating the trap stiffness as a function of laser power is done before the main experiment. The optical trap stiffness for each protocol of ac input voltage to LCVR is calibrated by using three different techniques based on the equipartition theorem, the Boltzmann distribution, and the forced oscillation [26]. The first method uses the relation $k\langle x^2\rangle/2 = k_B T/2$ and determines k from measured $\langle x^2\rangle$. The second uses the principle that the position of the particle should follow the equilibrium Boltzmann distribution $p_{\mathrm{eq}}(x) \propto \exp(-\beta k x^2/2)$ and determines k so as to best fit the measured distribution. The third uses the forced oscillation by a sinusoidal optical force given by oscillating optical tweezers with frequency ω. Then, the equation of motion becomes $m\ddot{x} + \gamma\dot{x} + kx = A\cos\omega t$, as noise is filtered out. The phase delay is given by $\delta(\omega) = \tan^{-1}(\omega/k)$ in overdamped limit $\gamma/m \gg 1$. From the measured phase delay, k can be determined. The values of the trap stiffness from three different methods agree with each other within 4% error; see the Supplemental Material Fig. S3 [25].

To control the stiffness accurately in time, each protocol is composed of 360 steps in this experiment. According to this protocol, at the lowest laser power corresponding to step 0, the trap stiffness is $k_i = 0.94$ pN/μm and at the highest laser power corresponding to step 360, $k_f = 2.87$ pN/μm. From these two values, the theoretical free energy difference is calculated as $\beta\Delta F = 0.558$. In each cycle of measurement, the trapping laser power is changed with time as shown in Fig. 1(b); the reverse (II) and forward process (IV) are separated by plateaus (I,III). For plateaus at $k = 2.87, 0.94$ pN/μm, the particle is equilibrated for a few seconds, which is much longer than the characteristic equilibration time. For each stiffness rate, the measurement is repeated for 40000 cycles.

The periods for the change in trap stiffness are chosen as $\tau = 7.20$, 3.60, 0.720, and 0.360 s, corresponding to $\dot{k} = 0.268$, 0.536, 2.68, and 5.36 pN/μm s, respectively. Using the definition of work, the work done in each process is given as

$$W = \pm \frac{|\dot{k}|\Delta t}{2} \sum_{n=1}^{N} x_n^2, \tag{5}$$

where $\Delta t = \tau/N$, $N = 360$ and $+(-)$ denotes the forward (reverse) process. x_n is the position of the particle at time $n\Delta t$ after the stiffness change is turned on. For a given $|\dot{k}|$,

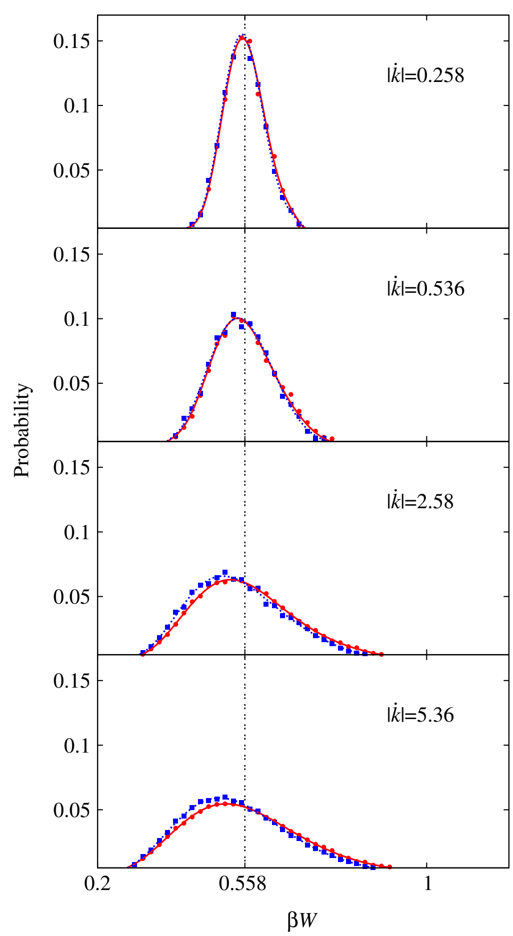

FIG. 2 (color online). Work probability distributions for four different $|\dot{k}|$ values. The unit of $|\dot{k}|$ is pN/μm s. The red solid circles correspond to $P_F(W)$ for the forward process, and the blue solid squares to $P_R(-W)$ for the reverse process. The solid curves are splined fits to guide readers' eye. The dashed vertical line corresponds to $|\beta\Delta F|$.

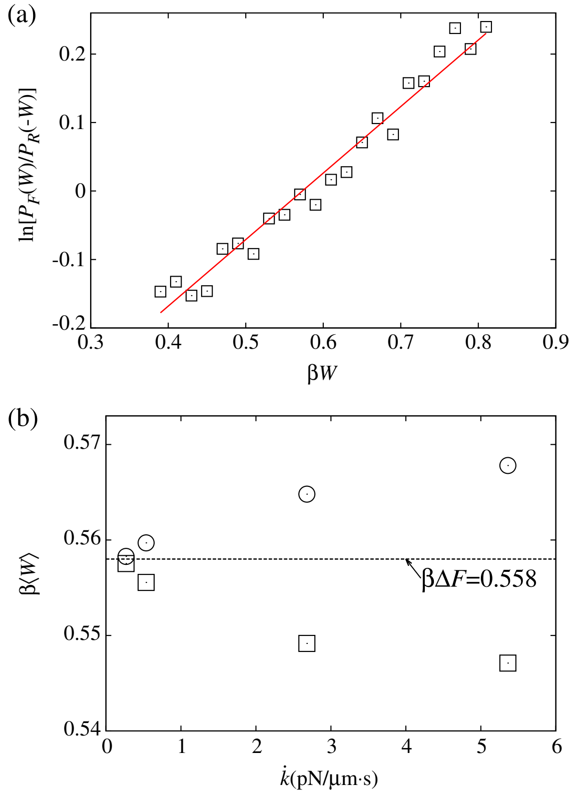

FIG. 3 (color online). (a) $\ln P_F(W)/P_R(-W)$ versus βW for $|\dot{k}| = 5.36$ pN/μm s. (b) Mean work values in the forward and reverse process depending on the trap stiffness rate. The circles (squares) represent $\beta\langle W\rangle_F$ ($\beta\langle -W\rangle_R$).

the probability distribution function for W is estimated from the 40 000-cycle data set. Figure 2 shows the work probability distributions for four different $|\dot{k}|$ values. In this figure the dashed vertical line corresponds to the theoretical value $|\beta\Delta F| = 0.558$. The red solid circles and the blue solid squares represent, respectively, the distribution function $P_F(W)$ for the forward process and the flipped distribution $P_R(-W)$ for the reverse process. The characteristic equilibration time for the stiffness in the range of $k(t) = 0.94$–2.87 pN/μm is $\gamma/k = 10$–30 ms. For $|\dot{k}| = 0.258, 0.536$ pN/μm s, the switching times are about 20, 10 ms, respectively. For these stiffness rates, the isothermal processes are not far from the quasistatic regime. In Fig. 2, the work distributions are observed to be nearly Gaussian with a small shift of mean from $\pm|\Delta F|$, agreeing with the theoretical expectation [21]. As a result, $P_F(W)$ and $P_R(-W)$ almost overlap each other for these rates. For higher rates of $|\dot{k}| = 2.58, 5.36$ pN/μm s, however, the corresponding switching times are about 2,1 ms, respectively, which are much smaller than the local equilibration times. For these rates, nonequilibrium nature can be more observable. $P_F(W)$ and $P_R(-W)$ are separable enough to estimate W at which point the two graphs meet. Figure 2 shows that the crossing occurs close to $|\Delta F|$, expected from the Crooks fluctuation theorem in Eq. (3). $P(W)$ tends to move to the left towards the origin, as expected from the theoretical study [21].

Figure 3(b) shows the mean values of the work performed in the forward and reverse processes, $\langle W\rangle_F$ and $\langle W\rangle_R$, as a function of the trap stiffness rate. When $|\dot{k}|$ is small, $\langle W\rangle_F$ and $\langle -W\rangle_R$ are close to $|\beta\Delta F|$. This is because the work distribution is sharply peaked with a peak close to $\beta\Delta F$ near the quasistatic limit. In contrast, when $|\dot{k}|$ becomes larger, the difference between the two values becomes larger because the nonequilibrium nature becomes dominant. This observation agrees very well with Eq. (4), which is a direct result of the Jarzynski equality.

To check the Crooks-Tasaki fluctuation theorem more quantitatively, we plot $\ln[P_F(W)/P_R(-W)]$ versus βW, which is expected to be equal to $\beta(W - \Delta F)$ according to Eq. (3). The data for $|\dot{k}| = 2.68, 5.36$ pN/μm s are fitted very well by the straight line with a slope of 1.0 within the experimental accuracy. Figure 3(a) shows the plot for $|\dot{k}| = 5.36$ pN/μm s, where $|\beta\Delta F| = 0.574 \pm 0.024$ and the slope is 1.02 ± 0.04. This also supports the validity of the fluctuation theorem. For the case of smaller stiffness rates, the data fittings are not satisfactory. This is because much more data are needed to confirm the fluctuation theorem for a system close to equilibrium as a consequence of the near overlap of the two probability distributions.

In conclusion, the fluctuation theorem is confirmed experimentally for the Brownian motion of a colloidal particle in an optical trap with a time-varying harmonic potential. It is always remarkable to witness that the theoretical prediction from the simple Langevin equation complies well with a real experiment. We are pursuing further investigation for issues related with this study such as the efficiency at maximum power for the stochastic heat engine [27,28] and the information thermodynamics for an information engine operated by feedback control [29,30].

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[1] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
[2] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
[3] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
[4] G. E. Crooks, J. Stat. Phys. **90**, 1481 (1998).
[5] J. Kurchan, J. Phys. A **31**, 3719 (1998).
[6] J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999).
[7] H. Tasaki, arXiv:cond-mat/0009244.
[8] C. M. Van Vliet, Phys. Rev. E **86**, 051106 (2012).

[9] G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **89**, 050601 (2002).
[10] E. H. Trepagnier, C. Jarzynski, F. Ritort, G. E. Crooks, C. J. Bustamante, and J. Liphardt, Proc. Natl. Acad. Sci. U.S.A. **101**, 15038 (2004).
[11] G. Hummer and A. Szabo, Proc. Natl. Acad. Sci. U.S.A. **98**, 3658 (2001).
[12] N. Garnier and S. Ciliberto, Phys. Rev. E **71**, 060101 (2005).
[13] F. Douarche, S. Joubaud, N. B. Garnier, A. Petrosyan, and S. Ciliberto, Phys. Rev. Lett. **97**, 140603 (2006).
[14] S. Joubaud, N. B. Garnier, and S. Ciliberto, Europhys. Lett. **82**, 30007 (2008).
[15] R. van Zon and E. G. D. Cohen, Phys. Rev. Lett. **91**, 110601 (2003); R. van Zon, S. Ciliberto, and E. G. D. Cohen, Phys. Rev. Lett. **92**, 130601 (2004).
[16] K. Kim, C. Kwon, and H. Park, Phys. Rev. E **90**, 032117 (2014).
[17] J. Liphardt, S. Dumont, S. B. Smith, I. Tinico, Jr., and C. Bustamante, Science **296**, 1832 (2002).
[18] D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco, Jr., and C. Bustamante, Nature (London) **437**, 231 (2005).
[19] K. Hayashi, H. Ueno, R. Iino, and H. Noji, Phys. Rev. Lett. **104**, 218103 (2010).
[20] A. Engel, Phys. Rev. E **80**, 021120 (2009).
[21] C. Kwon, J. D. Noh, and H. Park, Phys. Rev. E **88**, 062102 (2013).
[22] V. Blickle and C. Bechinger, Nat. Phys. **8**, 143 (2012).
[23] M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945).
[24] C. M. Van Vliet, *Equilibrium and Non-Equilibrium Statistical Mechanics* (World Scientific, Singapore and Hackensack NJ, 2010), Part F, Sec. 18.8.
[25] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.114.060603 for explaining the probability distribution at extreme limits, the experimental setup, and the calibration of the optical trap strength.
[26] C. Ha, H. D. Ou-Yang, and H. K. Pak, Physica (Amsterdam) **392A**, 3497 (2013).
[27] T. Schmiedl and U. Seifert, Europhys. Lett. **81**, 20003 (2008).
[28] M. Esposito, R. Kawai, K. Lindenberg, and C. Van den Broeck, Phys. Rev. Lett. **105**, 150603 (2010).
[29] T. Sagawa and M. Ueda, Phys. Rev. Lett. **104**, 090602 (2010); **109**, 180602 (2012).
[30] D. Abreu and U. Seifert, Europhys. Lett. **94**, 10001 (2011).