Work and heat probability distribution of an optically driven Brownian particle: Theory and experiments

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We analyze the equations governing the evolution of distributions of the work and the heat exchanged with the environment by a manipulated stochastic system, by means of a compact and general derivation. We obtain explicit solutions for these equations for the case of a dragged Brownian particle in a harmonic potential. We successfully compare the resulting predictions with the outcomes of experiments, consisting in dragging a micron-sized colloidal particle through water with a laser trap.

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The study of the physics of small systems has recently received a boost by the possibility of manipulating nanosystems and biomolecules. The fluctuations of the work and heat that these small systems exchange with the environment while being manipulated can be of the order or even larger than the thermal energy, leading to "transient" violations of the second principle of thermodynamics. The distributions of heat and work have been experimentally studied for a few brownian systems [1, 2, 3, 4]. The probability distribution function (PDF) of the work done on a Brownian particle dragged by a moving quadratic potential was derived in [5, 6]. The distribution turns out to be gaussian, what has been taken as an ansatz in [6] and confirmed in [7] by means of a rather involved path integral calculation. On the other hand, obtaining the PDF of the transferred heat represents a much more difficult task: the Fourier transform of this function was obtained in refs. [6, 7] by exploiting the energy balance and the gaussian ansatz for the work PDF, valid when the potential is quadratic.

In the present paper we derive in a simple way the differential equations governing the evolution of the PDFs of the work and heat exchanged by a brownian particle, valid for any choice of the potential acting on the particle. The solutions of these equation turn out to fulfill the well-known fluctuation relations. We evaluate the solution of these equations for a moving harmonic potential. We then experimentally study the work and the heat exchanged by a colloidal particle dragged through water by an optical trap. The PDF's predicted by our equations result in an excellent agreement with the experimental data. We were inspired by the experiment of Wang *et al.* [1] where the work done on a similar system was measured. However, in that experiment, only the performed work, and not the heat transferred, was sampled. Moreover, the expected gaussian distribution of the performed work was not verified, and a detailed comparison with the theoretical predictions was not attempted. However in a subsequent paper [8], the authors stressed that the PDF of the work has to be gaussian in their experimental conditions.

Let us consider a Brownian particle in the overdamped regime, driven by a time-dependent potential $U(x, X(t))$, where X is an externally controlled parameter, that varies according to a fixed protocol $X(t)$. The Langevin equation is given by

$$\frac{dx}{dt} = -\Gamma U'(x, X) + f(t), \tag{1}$$

where $\langle f(t) f(t')\rangle = (2\Gamma/\beta)\delta(t - t')$ and the prime denotes derivative with respect to x. We have defined $\beta = (k_B T)^{-1}$, and $\Gamma = 1/6\pi r\eta$, for a spherical particle with radius r, in a medium of viscosity η.

The *thermodynamical* work done on the particle is defined by

$$W = \int dX\, \frac{\partial U}{\partial X} = \int_0^t dt'\, \dot{X}(t') \frac{\partial U}{\partial X}. \tag{2}$$

Besides work, the particle also exchanges with the environment heat, whose expression is

$$Q = \int dx\, \frac{\partial U}{\partial x} = \int_0^t dt'\, \dot{x}(t') U'(x(t'), X(t')). \tag{3}$$

If $Q > 0$ the particle receives heat by the environment. Note that the integrals appearing in the last equation are stochastic integrals that must be interpreted according to the Stratonovich integration scheme [9]. Let ΔU be the potential energy difference between the final and the initial state: the balance of energy for the manipulated particle reads $\Delta U = W + Q$, which follows immediately from eqs. (2,3). Note that the quantities Q and W have to be regarded as stochastic variables, whose value at time t depends on the specific stochastic trajectory.

The differential equation governing the time evolution of the PDF of the work is given by [10]

$$\partial_t \phi(x, W, t) = \Gamma \frac{\partial}{\partial x} \left[U' \phi\right] + \frac{\Gamma}{\beta} \frac{\partial^2 \phi}{\partial x^2} - \dot{X} \frac{\partial U}{\partial X} \frac{\partial \phi}{\partial W}. \quad (4)$$

It can be easily shown that the solution of eq. (4) satisfies the Jarzynski equality [10].

The differential equation for the joint PDF $\varphi(x, Q, t)$ of the position x and the heat Q is obtained as follows. In a short time interval δt the heat exchanged by the particle with the environment reads $\delta Q = dU - \partial_t U \, \delta t = U' dx$, and thus the time derivative of Q is given by

$$\frac{dQ}{dt} = U' \frac{dx}{dt} = U' \left(-\Gamma U' + f(t)\right). \quad (5)$$

Thus equations (1) and (5) describe two coupled stochastic processes. We now define the vectors of the stochastic variables $\mathbf{y}$ and of the forces $\mathbf{F}$ by

$$\mathbf{y} = \begin{pmatrix} x \\ Q \end{pmatrix}, \quad \mathbf{F} = \begin{pmatrix} -\Gamma U' \\ -\Gamma U'^2 \end{pmatrix}, \quad (6)$$

and the diffusion matrix

$$\underline{\mathbf{B}} = \begin{pmatrix} \Gamma/\beta, & (\Gamma/\beta) U' \\ (\Gamma/\beta) U' & (\Gamma/\beta) U'^2 \end{pmatrix}. \quad (7)$$

Then the differential equation governing $\varphi(x, Q, t)$ straightforwardly follows [11, 12]:

$$\partial_t \varphi(x, Q, t) = -\frac{\partial}{\partial \mathbf{y}} \left(\mathbf{F} \varphi\right) + \frac{\partial}{\partial \mathbf{y}} \left(\underline{\mathbf{B}} \cdot \frac{\partial}{\partial \mathbf{y}} \varphi\right). \quad (8)$$

By introducing the generating function $\chi(x, \lambda, t) = \int dQ \, \exp(\lambda Q) \varphi(x, Q, t)$, we obtain the simpler equation

$$\begin{aligned} \partial_t \chi(x, \lambda, t) \; &= \; \frac{\Gamma}{\beta} \frac{\partial^2 \chi}{\partial x^2} + \Gamma \left(1 - \frac{\lambda}{\beta}\right) \partial_x \left(U' \chi\right) \quad (9) \\ &\quad - \lambda \frac{\Gamma}{\beta} U' \partial_x \chi + \lambda \left(\frac{\lambda}{\beta} - 1\right) \Gamma U'^2 \chi, \end{aligned}$$

that was first derived by Lebowitz e Spohn [13]. Note that the operator appearing on the rhs of this equation changes into its adjoint by the substitution $\lambda \longrightarrow \beta - \lambda$. As discussed in ref. [13], this symmetry implies the Gallavotti-Cohen fluctuation relation [14] for our system.

By defining the function $g(x, \lambda, t)$ as $\chi(x, \lambda, t) = g(x, \lambda, t) \exp\left[-\delta(\lambda) U(x, t)/2\right]$, with $\delta(\lambda) = \beta - 2\lambda$, eq. (9) becomes

$$\partial_t g = \frac{\Gamma}{\beta} \frac{\partial^2 g}{\partial x^2} - \Gamma \beta \frac{U'^2}{4} g + \frac{\Gamma}{2} U'' g + \frac{\delta(\lambda)}{2} g \partial_t U. \quad (10)$$

This equation has the form of an imaginary-time Schrödinger equation.

It is worth remarking that eqs. (4), (8) and (9) hold for any choice of the potential $U(x, X(t))$. Moreover, the present approach can be easily generalized to the case of a Brownian particle with inertia [7, 15, 16].

We now consider the particular case of a harmonic potential

$$U(x, t) = \frac{k}{2} (x - X(t))^2, \quad (11)$$

with $X(t) = vt$, i.e., the center of the potential moves with a constant velocity v. We shall assume that the particle is initially in thermal equilibrium, with the potential centered at $X = 0$ at $t = 0$. It is then possible to solve directly equation (4), obtaining

$$\phi(x, W, t) = \mathcal{N}_t \exp\left[-\frac{\left(W - \widehat{W}(x, t)\right)^2}{2\sigma^2(t)} - \frac{\beta k}{2} \left(x - \xi(t)\right)^2\right]. \quad (12)$$

In this equation, having defined $\tau = 1/\Gamma k$ and $\alpha(t) = e^{-t/\tau}$, we have $\xi(t) = v\tau\left(\alpha(t) - 1 + t/\tau\right)$, $\sigma^2(t) = v^2 \tau^2 k \beta^{-1} [2t/\tau + 1 - (2 - \alpha(t))^2]$,

$$\begin{aligned} \widehat{W}(x, t) \; &= \; t v^2 \tau k (2 - \alpha(t)) - v x \tau k (1 - \alpha(t)) \quad (13) \\ &\quad - v^2 \tau^2 k \left(2 + \alpha^2(t) - 3\alpha(t)\right); \\ \mathcal{N}_t^{-1} \; &= \; \sqrt{4(\pi v \tau/\beta)^2 \left(2t/\tau + 1 - (2 - \alpha(t))^2\right)} \quad (14) \end{aligned}$$

The unconstrained PDF $\Phi(W, t) \equiv \int dx \, \phi(x, W, t)$, is given by

$$\Phi(W, t) = \mathcal{N}_t' \exp\left[-\beta \frac{\left(W - v^2 \tau^2 k \left(\alpha(t) - 1 + t/\tau\right)\right)^2}{4 v^2 \tau^2 k \left(\alpha(t) - 1 + t/\tau\right)}\right], \quad (15)$$

where $\mathcal{N}_t' = \left[4\pi\beta^{-1} v^2 \tau^2 k \left(\alpha(t) - 1 + t/\tau\right)\right]^{-1/2}$. A similar result was first obtained in [5] in a special case, and then in [6], by using qualitative arguments and by *assuming* that $\Phi(W, t)$ is gaussian, and more recently in [7], by a functional integral technique. We now see that eqs. (12,15) can be straightforwardly derived as solutions of eq. (4). An approach analogous to ours was used in ref. [17], leading again to eq. (15).

We now turn to the heat PDF: substituting eq. (11) into eq. (10) one obtains a Schrödinger-like equation for the harmonic oscillator, that can be solved exactly. Assuming that the particle is at thermal equilibrium at $t = 0$, with $v = 0$ for $t < 0$, the solution of eq. (9) reads

$$\begin{aligned} \chi(x, \lambda, t) \; &= \; \exp\left[-\frac{\delta(\lambda)}{2} U(x, X(t)) - \frac{\beta v}{2\Gamma} z(x, t)\right] \\ &\quad \times \sum_{n=0}^{\infty} e^{\gamma_n t} c_n(\lambda) \psi_n(z(x, t)), \quad (16) \end{aligned}$$

where $\gamma_n = \left(-n/\tau + \delta^2(\lambda) v^2/4\Gamma\beta - \beta v^2/4\Gamma\right)$, and $z(x, t) = x - vt + \delta(\lambda) v\tau/\beta$, and where $\psi_n(z)$ are the eigenfunctions of the Schrödinger equation for the harmonic oscillator, with the substitutions $\hbar^2/m \longrightarrow 2\Gamma/\beta$ and $m\omega^2 \longrightarrow \Gamma\beta k^2/2$. The value of coefficients $c_n(\lambda)$ is determined by the initial condition $\chi(x, \lambda, t = 0)$. Note that $\tau = 1/\Gamma k$ sets up the characteristic time scale for both work and heat fluctuations.

Case a): $v = 0$ for $t \geq 0$, i.e., a fixed potential. The behavior of the generating function $\Psi(\lambda, t) \equiv \int dx\, \chi(x, \lambda, t)$ in the long-time limit is governed by the eigenfunction $\psi_0(z(x,t))$ associated with the smallest eigenvalue. Thus, after some algebra, one finds $\Psi(\lambda, t \to \infty) = 1/\sqrt{1-(\lambda/\beta)^2}$. Therefore, in the case of constant potential, the heat unconstrained PDF in the long time limit has the expression

$$\varphi(Q, t{\to}\infty) = \int \frac{d\lambda}{2\pi i} \Psi(\lambda, t{\to}\infty) e^{-\lambda Q} = \beta \frac{K_0(\beta|Q|)}{\pi}, \tag{17}$$

where $K_0(x)$ is the zero-th order modified Bessel function of the second kind.

Case b): $v > 0$. Also in this case the long time behavior of the solution of eq. (9) will be dominated by the eigenfunction with $n = 0$, which is a gaussian function. Thus, in the long time limit, one finds

$$\Psi(\lambda, t \to \infty) = \exp\left\{ \frac{v^2\beta}{4\Gamma} \left[\frac{4\lambda}{\beta} \left(\frac{\lambda}{\beta} - 1 \right) t \right.\right. \tag{18}$$

$$\left.\left. + \frac{2\lambda(3 - 4(\lambda/\beta)^2)}{\Gamma k(\beta + \lambda)} \right] \right\} \left[1 - \left(\frac{\lambda}{\beta} \right)^2 \right]^{-1/2},$$

and, integrating by the saddle-point method, one finds

$$\varphi(Q, t \to \infty) = \frac{1}{2\pi \mathrm{i}} \int d\lambda\, \Psi(\lambda, t \to \infty)\, e^{\lambda Q} \tag{19}$$

$$= \exp\left[-\frac{\Gamma\beta}{4v^2 t} \left(Q + \frac{v^2 t}{\Gamma} \right)^2 \right] \sqrt{\frac{\Gamma\beta}{\pi 4 v^2 t}}, \tag{20}$$

Note that in the long time limit $\overline{W} + \overline{Q} = 0$. As discussed in ref. [6], some care has to be taken when calculating the integral (19) with the saddle point method. The resulting calculation shows that the function $\varphi(Q, t)$ is gaussian up to a subleading term of order $1/\sqrt{t}$ [6].

In order to test these results, we have experimentally observed the trajectories of a colloidal particle in an optical trap, which is well described by a quadratic potential (11) near its focus $X(t)$.

The Optical Tweezers system consisted of a home made optical microscope with a high numerical aperture water immersion objective lens (Olympus, UPLAPO60XW3, NA=1.2) and a frequency and amplitude stabilized Nd-YAG laser ($\lambda = 1.064\ \mu m$, 500 mW, Innolight Mephisto). The sample cell was made with a glass coverslip of 150 μm thickness and a microscope slide glued together by parafilm stripes of about 100 μm thickness. Polystyrene micro-spheres produced by Postnova (density: 1.06 g/cm^3, refractive index: 1.65) with a diameter of 2.00±0.05 μm were diluted in distilled water to a final concentration of about 1÷2 particles/μl. The sample cell was mounted on a closed-loop piezoelectric transducer stage (Physik Instrumente PI-517.3CL) which allowed movements with nanometer resolution. Moving

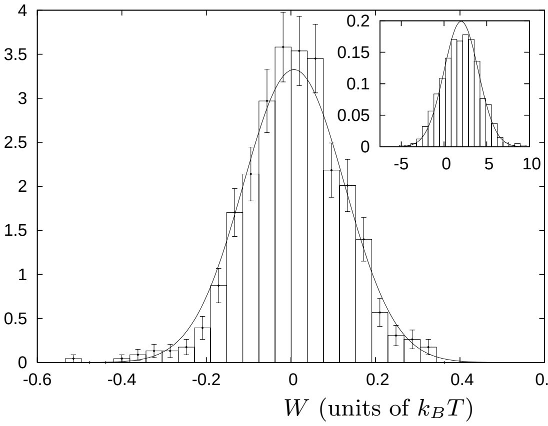

FIG. 1: Histogram of the work exerted on the colloidal particle by the optical trap, as given by eq. (2), for $t = 0.01\,\mathrm{s} < \tau$ (main figure) and $t = 0.5\,\mathrm{s} \gg \tau$ (inset). The lines correspond to the expected function (15), with no adjustable parameter.

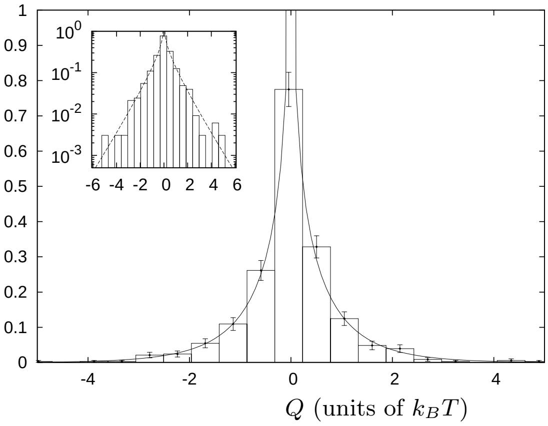

FIG. 2: Histogram of the heat exchanged by the colloidal particle with the environment, with fixed optical trap $v = 0$, as given by eq. (3), for $t = 0.5$ s. The line correspond to the expected PDF as given by eq. (17), with no adjustable parameter. Inset: same data, with logarithmic y-axis.

the stage in a given direction corresponds to moving the optical trap focus in the opposite direction. The sample temperature was not stabilized but continuously monitored using a negative temperature coefficient thermistor positioned on the top surface of the microscope slide. The temperature during a complete set of measurements remains constant $T = 296.5$ K, within 0.2 K. The trapped bead was positioned in the middle of the sample cell to avoid any surface effects. The thermally driven motion of trapped beads was monitored by a InGaAs quadrant photodiode (Hamamatsu G6849) placed in the back focal plane of the condenser lens [18]. The response of our quadrant photodiode was linear for displacements of about 300 nm with a resolution of 2 nm, and its bandwidth was about 250 kHz. The trajectories in the transverse x-y plane were sampled at 125 kHz using a digital oscilloscope (details on the experimental setup can be

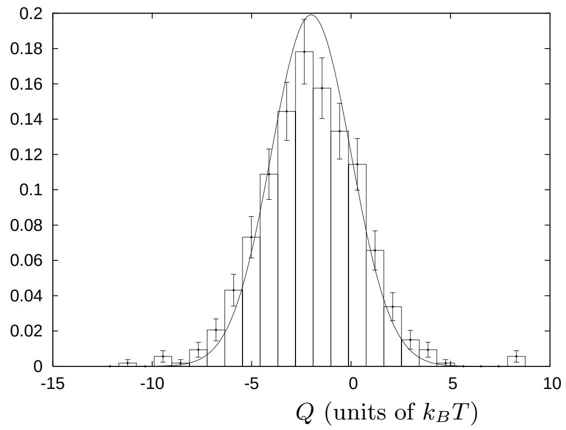

FIG. 3: Histogram of the heat exchanged by the colloidal particle with the environment, with $v = 1\,\mu$m/s, and $t = 0.5\,$s $\gg \tau$, as given by eq. (3). The line correspond to the expected PDF as given by eq. (20), with no adjustable parameter.

found elsewhere [19]). The duration of each trajectory measurement was 10 s. During the first 5 seconds the stage was at rest and we use this period to compute the power spectral density of the particle position to obtain the trap stiffness, which takes the value $k = 6.67 \times 10^{-7}$ N/m, and the calibration factor of the quadrant photodiode [20]. Then at $t = 5$ s the stage started to move with a speed of $v = 1\mu m$/s for 5 s along one axis. After a pause of 1 second the above described sequence started again, but the stage was moved in the opposite direction. We repeated this procedure 300 times and back and forth trajectories were recorded for further analysis. Thus the overall number of trajectories considered is 600. Note that for each trajectory we measure both the work done on the particle and the heat, as defined by eq. (2) and (3), respectively. We have, under our experimental conditions, $\Gamma = 1/6\pi r\eta = 5.76 \times 10^7\,\mathrm{s}^2/\mathrm{kg}$, yielding $\tau \simeq 0.026$ s.

In figure 1, we plot the histogram of the work exerted on the particle by the optical trap, finding a good agreement with the expected PDF $\Phi(W,t)$, as given by eq. (15): the distribution of the work turns out to be gaussian both at short and long times. At short times ($t = 0.01$ s) the gaussian is peaked around zero, but the peak moves to positive values of W as t increases.

In order to evaluate the heat Q from the particle trajectories, we exploit the discrete version of eq. (5): $Q = \sum_{t_i} \left(x_{t_i} - x_{t_{i-1}}\right) k/2 \left[\left(x_{t_i} - X(t_i)\right) + \left(x_{t_{i-1}} - X(t_{i-1})\right)\right]$. We plot the histogram of the measured heat for the motionless trap, with $t = 0.5$ s, in fig. 2. The histogram agrees nicely with eq. (17), in particular the tails of the distribution are found to be exponential. This behavior was also found at shorter times (data not shown).

Finally, in fig. (3) the histogram of the measured heat, for the trap moving with $v = 1\,\mu$m/ s, is plotted, in the long-time range $t = 0.5$ s $\gg \tau$. The distribution is found to be gaussian, in agreement with eq. (20). By comparing figures 1 and 3, it can also be seen that the mean values of the work and of the heat are the negative of each other, as expected in the long-time range. At shorter times we observe that the tails of the distribution of the measured heat fall off exponentially, with time-dependent slopes (data not shown). We have noticed that for observation times longer than 0.5 s both the heat and work distributions appear slightly broader than the theoretical predictions,whereas their centers remain in good agreement with the expected ones (data not shown). We ascribe this fact to the presence of low-frequency (smaller than 1 Hz) noise affecting our experimental set-up.

We have shown that it is possible to solve explicitly the differential equations governing the evolution of the PDF for the work and heat exchanged by a dragged brownian particle, and that the resulting predictions are vindicated by experiment. In particular one observes a non negligible probability for the "transient violations" of the second law of thermodynamics, i.e., positive values of the exchanged heat Q.

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