Stochastic thermodynamics

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Abstract

The formulation of thermodynamics at a level of a single stochastic trajectory is shown to be consistent with the ensemble laws. Both theory and experiment are presented by studying the paradigmatic colloidal particle. The theory is built upon studying the Langevin equation and identifying work and heat along a trajectory. Similarly, using the corresponding Fokker-Planck equation, the trajectory dependent entropy is constructed. This enables one to formulate a general fluctuation theorem. Lastly, experimental evidence for the developed theory is presented.

January 15, 2017

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1 Introduction

The main idea behind stochastic thermodynamics [1, 2] is to provide a robust framework, which allows the description of general nonequilibrium stochastic systems. It generalizes the phenomenological formulations of nonequilibrium thermodynamics developed for systems locally close to equilibrium. It is possible to show [1, 2] the validity of consistently formulating the laws of thermodynamics not only for ensemble averages but at the level of a single fluctuating trajectory. Such a framework allows studying small systems subjected to measurable fluctuations. This paper begins with the formulation of stochastic thermodynamics using a simple model system consisting of a colloidal particle, confined to one dimension, which serves as the paradigm in the field. A definition of entropy for a single trajectory is given together with the first and the second law. The fluctuation theorems, which generalize these laws are discussed next and it is shown that they can be described as a manifestation of a general fluctuation theorem. Lastly, although perhaps most importantly, an experiment is reviewed where the developed theory allows for a successful interpretation of the measured results. A polystyrene brownian particle was driven by a nonharmonic time-dependent potential. By accurately measuring the position of the particle and the use of relations, derived for the Langevin equation, strong agreement between theory and experiment was shown. The first law of thermodynamics, the Jarzynsky relation and a detailed fluctuation theorem were verified.

2 Classical thermodynamics vs. statistical mechanics

Classical thermodynamics describes systems in equilibrium states with a set of state variables such as volume V, number of particles N, internal energy E, ... The energy of the system can be changed by external perturbations which we distinguish as either work W, which is macroscopically controllable, or heat Q, which is not. We have, for small changes, the first law of thermodynamics - conservation of energy:

$$\mathrm{d}E = \mathrm{d}W + \mathrm{d}Q\,. \tag{1}$$

With the formulation of the second law of thermodynamics, an important state variable, the entropy of the system S, is introduced. The seconds law states that the total entropy change of an isolated system between the initial and final equilibrium can never be negative:

$$\Delta S_{\mathrm{tot}} \geq 0\,. \tag{2}$$

Standard thermodynamics does not, nor does it intend to, describe the dynamics of the evolution of systems.

Statistical mechanics gives an explanation of the thermodynamic properties of systems at the microscopic level. The mechanical laws governing in this microscopic picture do not contain the concepts of heat, work or entropy. However, through the introduction of statistical ensembles, it provides insight into and deeper understanding of macroscopic state variables. Even more, statistical mechanics allows us to extend the description of systems to those away from equilibrium. Especially, for near-equilibrium, very slightly perturbed systems, many results have been obtained, such as the fluctuation-dissipation theorem. These fit into the linear response theory. The goal is to describe general transitions that occur arbitrarily far from equilibrium. One of the most important results is the Crooks fluctuation theorem [3, 4], which relates the work done on a system during a non-equilibrium transformation to the free energy difference between the initial and final states. It reads

$$\frac{p(W)}{\tilde{p}(-W)} = \exp\left(\beta(W - \Delta\mathcal{F})\right), \tag{3}$$

where W is work and $\Delta\mathcal{F}$ is the free energy difference between two states. The theorem implies the Jarzynski equality:

$$\exp\left(-\Delta\mathcal{F}/k_{\mathrm{B}}T\right) = \langle\exp\left(-W/k_BT\right)\rangle, \tag{4}$$

with T being the temperature. The Jarzynski relation reduces to the second law of thermodynamics (2).

3 Colloidal particle - trajectory thermodynamics

Let us introduce the main concepts of stochastic thermodynamics [1, 2] through the paradigmatic colloidal particle in a medium, confined to one dimension. The overdamped motion $x(t)$ of a Brownian particle is described by removing the inertial term from the Langevin equation, which results in

$$\begin{aligned}
\dot{x} &= \mu F(x, \lambda) + \zeta \\
&= \mu\left[-\partial_x V(x, \lambda) + f(x, \lambda)\right] + \zeta,
\end{aligned} \tag{5}$$

where $F(x, \lambda)$ is a force that arises from a conservative potential $V(x, \lambda)$ or a directly applied force $f(x, \lambda)$ and ζ is thermal white noise with zero mean value $\langle \zeta(t) \rangle = 0$ and the autocorrelation equal to the delta function $\langle \zeta(\tau)\zeta(\tau') \rangle = 2D\delta(\tau - \tau')$. D is the diffusion constant and μ is the mobility. In equilibrium D and μ are related by the Einstein relation $D = k_\mathrm{B}T\mu$, where T denotes the temperature of the surrounding medium. The external time-dependent parameter $\lambda(\tau)$ is changing in a known, controllable way. Before we begin with the formulation of thermodynamics for this system, we note a crucial assumption in stochastic thermodynamic: the strength of noise is not affected by the time dependent force.

3.1 First law of thermodynamics

The first successful suggestion of an application of the first law of thermodynamics to an individual trajectory solution of the Langevin equation is due to Sekimoto [5] with his stochastic energetics:

$$\mathrm{d}w = \mathrm{d}V + \mathrm{d}q \,, \tag{6}$$

where $\mathrm{d}w$, $\mathrm{d}V$ and $\mathrm{d}q$ are the differentials of work, internal energy and heat per trajectory, respectively. The goal is to identify individual contributions to the first law balance. Let us first consider the case of a particle in equilibrium, for $f = 0$ and $\lambda = \mathrm{const.}$. Here, no work is done on the system or extracted from it, hence any increase in internal energy $\mathrm{d}V$ should be identified with the heat, received from the reservoir:

$$\mathrm{d}V = \mathrm{d}q \,.$$

In order to identify the contribution to internal energy of the system from both work and heat transfer, we multiply the Langevin equation by the position increment $\mathrm{d}x$ and subsequently completing the total differential of energy by adding $\partial_\lambda V(x, \lambda)\, \mathrm{d}\lambda$:

$$0 = -\big[-\dot{x} + \zeta(t) + \mu f(x, \lambda) \big]\, \mathrm{d}x + \mu \partial_x V(x, \lambda)\, \mathrm{d}x \,,$$
$$\partial_\lambda V(x, \lambda)\, \mathrm{d}\lambda + f(x, \lambda)\, \mathrm{d}x = F(x, \lambda)\, \mathrm{d}x + \mathrm{d}V(x, \lambda) \,. \tag{7}$$

Because applying work to the system (particle) requires either a time-dependent potential $V(x, \lambda(t))$ or an external force $f(x, \lambda(t))$, we assign to the work differential the following expression:

$$\mathrm{d}w = \partial_\lambda V(x, \lambda)\, \mathrm{d}\lambda + f\, \mathrm{d}x \,. \tag{8}$$

Thus we have for the heat exchanged with the heat bath

$$\mathrm{d}q = \mathrm{d}w - \mathrm{d}V = F\, \mathrm{d}x \,. \tag{9}$$

Integrating the left-hand side of eq. (8) over a time interval t yields

$$w[x(\tau)] = \int_0^t \Big((\partial V/\partial \lambda)\dot{\lambda} + f\dot{x} \Big)\, \mathrm{d}\tau \tag{10}$$

and similarly

$$q[x(\tau)] = \int_0^t F\dot{x}\, \mathrm{d}\tau \,. \tag{11}$$

The first law integrated along an individual trajectory thus reads

$$w[x(\tau)] = q[x(\tau)] + \Delta V \,. \tag{12}$$

3.2 The Second law

Having expressed the first law along a trajectory, we now consider the second law and entropy. For this we need to include into consideration the statistical properties of the system. The time propagation of the probability distribution of the particle position $p(x(t), t)$ is given by the Fokker-Planck equation

$$
\begin{aligned}
\partial_t p(x, t) &= -\partial_x j(x, t) \\
&= -\partial_x [\mu F(x, \lambda) p(x, t) - D \partial_x p(x, t)],
\end{aligned}
\tag{13}
$$

where $j(x, t)$ stands for the probability current. In nonequilibrium, the solution is a distribution

$$
p(x, \lambda) = \exp\left(-\phi(x, \lambda)\right)
\tag{14}
$$

with ϕ the nonequilibrium potential. For a time-independent parameter λ and $f = 0$ any initial distribution will reach the thermal equilibrium

$$
p_{\text{eq}}(x, \lambda) = \exp\left(-[V(x, \lambda) - \mathcal{F}(\lambda)]/k_B T\right),
\tag{15}
$$

where the free energy $\mathcal{F}$ is

$$
\mathcal{F}(\lambda) = -k_B T \ln \int \exp\left(-V(x, \lambda)/T\right) \mathrm{d}x.
\tag{16}
$$

We define the stochastic, trajectory dependent entropy of the system:

$$
s(t) = -\ln p(x(t), t).
\tag{17}
$$

The time-dependent probability distribution $p(x, t)$ is obtained from the Fokker-Planck equation (13). The introduced stochastic entropy is trajectory as well as ensemble dependent, since a change in the initial condition $p_0(x, 0)$ of the ensemble results in a different probability for the same trajectory and therefore a different entropy s. A change in entropy of the medium due to heat transfer along the trajectory is defined as follows:

$$
\Delta s_{\text{m}}[x(t)] = \frac{q[x(t)]}{T}.
\tag{18}
$$

We see that upon averaging the newly introduced entropy along a trajectory over the given ensemble, the familiar ensemble entropy of non-equilibrium thermodynamics is recovered:

$$
S(t) = -\int p(x, t) \ln p(x, t) \, \mathrm{d}x = \langle s(t) \rangle.
\tag{19}
$$

Most importantly, the total change in entropy along a trajectory $x(t)$

$$
\Delta s_{\text{tot}} = \Delta s_{\text{m}} + \Delta s
\tag{20}
$$

satisfies the integral fluctuation theorem

$$
\langle \exp(-\Delta s_{\text{tot}}) \rangle = 1
\tag{21}
$$

from which the second law follows

$$
\langle \Delta s_{\text{tot}} \rangle \geq 1.
\tag{22}
$$

4

4   Fluctuation theorems

Fluctuation theorems (FTs) [1, 6] state universal properties of the probability distribution $p(\Omega)$ for functionals $\Omega[x(\tau)]$, which are usually work, heat and entropy change, evaluated along single trajectories taken from ensembles with specified initial distributions $p_0(x_0)$. They can be phenomenologically classified into integral FTs and detailed FTs, which are somewhat stronger and also imply the corresponding integral FTs. The latter are of the form

$$\langle \exp(-\Omega) \rangle = \int p(\Omega) \exp(-\Omega) \, \mathrm{d}\Omega = 1 \tag{23}$$

and imply the inequality

$$\langle \Omega \rangle \geq 0 \,. \tag{24}$$

A detailed FT is a relation of the form

$$p(-\Omega)/p(\Omega) = \exp(-\Omega) \,. \tag{25}$$

Lastly, the generalized Crooks FT compare the $p(\Omega)$ of the original process with $p^\dagger(\Omega)$ of the 'conjugate' (mostly time reversed) process for the same physical quantity:

$$p^\dagger(-\Omega) = p(\Omega) \exp(-\Omega) \,. \tag{26}$$

4.1   Unification of fluctuation theorems

The aforementioned FTs were found individually, case by case. Due to the resemblance amongst them, a unified framework which reduced to these particular cases has been sought. It turned out that comparing the systems dynamics with its 'conjugate' one was a step towards the unification [1]. The conjugate dynamics is related to the actual process by a one-to-one mapping

$$\{x(\tau), \lambda(\tau), F, \mu, T\} \quad \to \quad \{x^\dagger(\tau), \lambda^\dagger(\tau), F^\dagger, \mu^\dagger, T^\dagger\} \tag{27}$$

so it here obeys the Langevin equation

$$\dot{x}^\dagger = \mu^\dagger F^\dagger(x^\dagger, \lambda^\dagger) + \zeta^\dagger \,. \tag{28}$$

We introduce the following functional

$$R[x(\tau)] = \ln \frac{p[x(\tau)]}{p^\dagger[x^\dagger(\tau)]} = \ln \frac{p_0[x_0]}{p_0^\dagger[x_0^\dagger]} + \ln \frac{p[x(\tau)|x_0]}{p^\dagger[x^\dagger(\tau)|x_0^\dagger]}$$
$$= R_0 + R_1 \,, \tag{29}$$

which is a logarithm of the original and conjugate trajectory probabilities ratio. We shall restrict the choice of conjugate dynamics to time reversed dynamics since it allows one to express all of the previously mentioned FTs. The mapping reads

$$x^\dagger(\tau) = x(t-\tau), \quad \lambda^\dagger(\tau) = \lambda(t-\tau) \tag{30}$$

and $F^\dagger(x^\dagger, \lambda^\dagger) = F(x^\dagger, \lambda^\dagger)$, $T^\dagger = T$, $\mu^\dagger = \mu$. Using eq. (29) we write the time dependent part of the functional R as

$$R_1 = \Delta s^{\mathrm{m}} = \frac{q}{T} \,, \tag{31}$$

which bears the meaning that the logarithmic ratio of probabilities of a trajectory and its time reverse is proportional to the heat, dissipated along the path. The following general FT holds

for functionals $S_\alpha[x(\tau)]$ of the original dynamics that map with a definite parity $\epsilon = \pm 1$ to the conjugate one as

$$S_\alpha^\dagger([x^\dagger(\tau)], \lambda^\dagger, F^\dagger) = \epsilon_\alpha S_\alpha([x(\tau)], \lambda, F) \,. \tag{32}$$

$S_\alpha^\dagger[x^\dagger(\tau)]$ represent the same physical quantity in the conjugate picture as $S_\alpha[x(\tau)]$ in the original. For example, in time reversed dynamics, both heat and work map with $\epsilon_\alpha = -1$. At this point we can finally derive the FT for any function g depending on an arbitrary number of functionals S_α:

$$\langle g(\{\epsilon_\alpha S_\alpha^\dagger[x^\dagger(\tau)]\})\rangle^\dagger = \int \mathrm{d}x_0^\dagger \int \mathrm{d}[x^\dagger(\tau)] p_0^\dagger(x_0^\dagger) p[x^\dagger(\tau)|x_0^\dagger] g(\epsilon_\alpha S_\alpha^\dagger) \tag{33}$$

$$= \int \mathrm{d}x_0^\dagger \int \mathrm{d}[x^\dagger(\tau)] p_0(x_0) p[x(\tau)|x_0] \exp[-R] g(S_\alpha) \tag{34}$$

$$= \int \mathrm{d}x_0 \int \mathrm{d}[x(\tau)] p_0(x_0) p[x(\tau)|x_0] \exp[-R] g(S_\alpha) \tag{35}$$

$$= \langle g(\{S_\alpha[x(\tau)]\}) \exp\big(-R[x(\tau)]\big)\rangle \,. \tag{36}$$

At the second equality, relations (29) and (32) were used. For the third equality, we recognized that summing over all reversed trajectories is equivalent to summing over all forward ones.

4.1.1 FT derived from time reversal

Using the time reversal conjugate dynamics (30) we can obtain the FTs discussed in previous sections. If one opts to choose for g the characteristic function, the following family of FTs is obtained:

$$\frac{p^\dagger(S_\alpha^\dagger = \epsilon_\alpha s_\alpha)}{p(S_\alpha = s_\alpha)} = \langle \exp(-R)|S_\alpha = s_\alpha\rangle \,. \tag{37}$$

By starting the original and time reversed dynamics in the respective stationary state, the functional R becomes

$$R = \Delta\phi + \Delta s_\mathrm{m} \,. \tag{38}$$

By taking work w for S_α, one gets

$$p^\dagger(-w) = p(w)\langle \exp(-\Delta\phi + \Delta s^\mathrm{m})|w\rangle \tag{39}$$

from which the Crooks FT (3) follows for a time-dependent $V(x, \lambda(\tau))$ and $f = 0$ if both dynamics start off in their respective equilibrium states. For then we have $\Delta\phi = \Delta(V - \mathcal{F})/T$, hence $R = (w - \Delta\mathcal{F})/T$. Moreover, if we choose simply $g = 1$, we immediately retrieve a most general integral FT:

$$\langle \exp(-R)\rangle = 1 \,. \tag{40}$$

5 Experiments

5.1 Thermodynamics of a particle in nonharmonic time-dependent potential

In the experiment exp. [7] the motion of an overdamped colloidal particle in a time-dependent nonharmonic potential was studied. The goal was to demonstrate the first law-like balance between applied work, exchanged heat and internal energy at the level of a single trajectory. Also, both the detail fluctuation theorem and the Jarzynski relation were verified with good accuracy. As colloids highly charged polystyrene beads with radius $R = 2\,\mu\mathrm{m}$, suspended in

water, were used. The suspension was contained in a glass cell. The bead concentration was sufficiently low as to not allow for assembled clusters. A focused laser beam ($\lambda = 1064\,\text{nm}$, $P = 2\,\text{mW}$), directed vertically from the top, confined the motion of a particle to an one dimensional trajectory along the z axis. With the use of additional optical tweezers ($\lambda = 532\,\text{nm}$, $P \leq 60\,\text{mW}$), positioned at the bottom, a particle was driven between two equilibrium states. The setup of the laser beams is shown in the upper left inset in fig.1a. The laser intensity was periodically modulated according to a time symmetric protocol $I(\tau) = I(t_\text{s} - \tau)$ with pulse duration $t_\text{s} = 120\,\text{ms}$, which had to be shorter than the particle relaxation time $t_\tau = 480\,\text{ms}$ to ensure that the system is out of equilibrium. Figure 1b shows the positions of a particle responding to laser pulses. Of course the time between pulses $t_\text{p} = 700\,\text{ms}$ had to be longer than t_τ. The total time-dependent potential for a particle at a distance z can thus be written [7]:

$$V(z, \tau) = A_0 \exp(-\kappa z) + B_0 z + C_0 I(\tau) z\,, \tag{41}$$

where the first term accounts for the electrostatic interaction of the particle, wall and water, the second term accounts for the particle weight and upper tweezer's light pressure and the last term represents the lower tweezer's contribution. Figure 1a shows the measured nonharmonic potential for different intensities of the lower optical tweezers. The motion of the bead is described by the Langevin equation (5) and the work and heat changes are, in accordance with (8, 9), given by

$$\mathrm{d}w = \frac{\partial V}{\partial \tau}\,\mathrm{d}\tau\,, \quad \mathrm{d}q = -\frac{\partial V}{\partial z}\,\mathrm{d}z\,. \tag{42}$$

Integration along a particle trajectory $z(\tau)$ yields the work functional

$$W[z(\tau)] = \int_0^{t_\text{s}} \frac{\partial V}{\partial \tau}\,\mathrm{d}\tau = \frac{C_0}{\nu} \sum_i \dot{I}(\tau_i) z(\tau_i)\,, \tag{43}$$

where the sum is allowed by the discrete sampling of the particle position at times $\tau_i = i\delta t$ (the rate is denoted by $\nu = 2\,\text{kHz}$). The heat exchange along a trajectory is obtained similarly:

$$Q[z(\tau)] = \int_0^{t_\text{s}} \frac{\partial V}{\partial z} \dot{z}(\tau)\,\mathrm{d}z = -\frac{1}{\nu} \sum_i \frac{\partial V}{\partial z} \dot{z}(\tau_i)\,. \tag{44}$$

The replacement of the particle velocity with an average

$$\dot{z}(\tau_i) = \nu \int_{\tau_i}^{\tau_{i+1}} \dot{z}(\tau)\,\mathrm{d}\tau \tag{45}$$

is justified by the fact that $\partial V/\partial z$ is varying on a time scale much larger than δt, despite the velocity autocorrelation decay time being shorter. One must be able to, of course, measure the potential $V(z)$ which is experimentally done by simply measuring the distance probability distribution $p(z)$ of a colloid. This is because in thermal equilibrium one has $V(z) \propto -\text{k}_\text{B}T \ln p(z)$. Therefore the measurement somehow reduces to the exact determination of the particles positions. The latter were determined using total internal reflection microscopy, where the colloid was illuminated under an evanescent field. This was created by reflecting a laser beam at a glass-water interface and the scattered light intensity from a bead was measured which allowed a vertical spatial resolution of $5\,\text{nm}$. The acquired data of work, heat and internal energy is plotted in fig. 2c. The measured work distribution over several thousands trajectories allowed checking the validity of the Jarzynski relation (4). The data yielded $\langle \exp(-W/\text{k}_\text{B}T) \rangle \approx 1.03$ which was in agreement with $\Delta\mathcal{F} = 0$ for the applied symmetric protocol $I(\tau)$. Secondly, a

stronger detailed fluctuation theorem (3) was tested, which also showed good agreement of the measured histogram with the calculated probability distribution (fig. 2d).
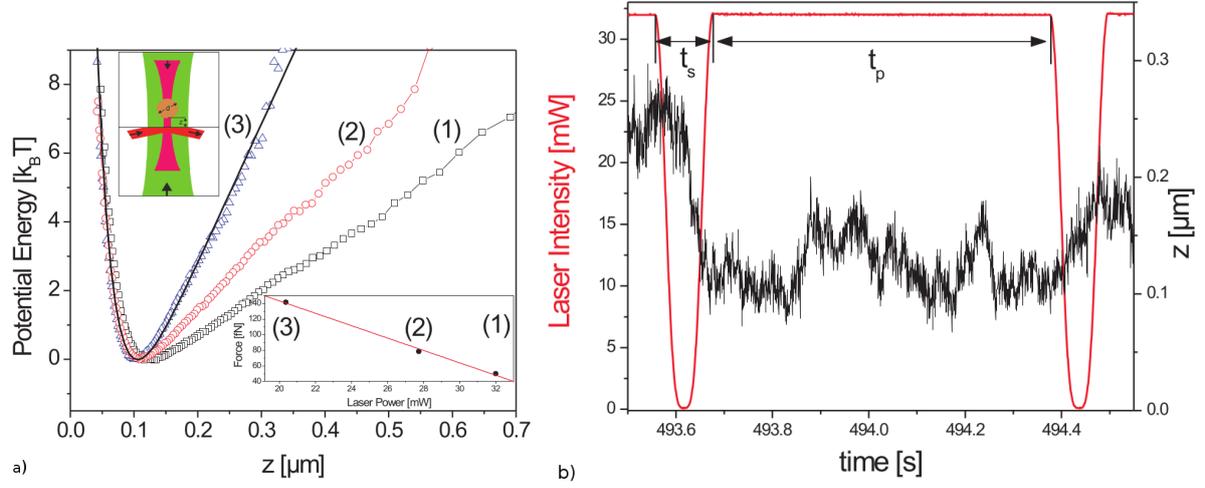

Figure 1: a): particle wall interaction potential $V(z)$ for different intensities of the lower optical tweezers [decresing form (1) to (3)]. Bottom right inset: light pressure is linearly dependent on the intensity. Upper left inset: schematics of the colloid near the wall subjected to three laser sources. b): particle positions (trajectory) and laser pulses. During the first pulse the particle is pressed towards the surface. During the second pulse thermal fluctuations in the water carry the particle away from the surface. The applied work is hence positive for the first pulse and negative for the second. Reproduced from [7].
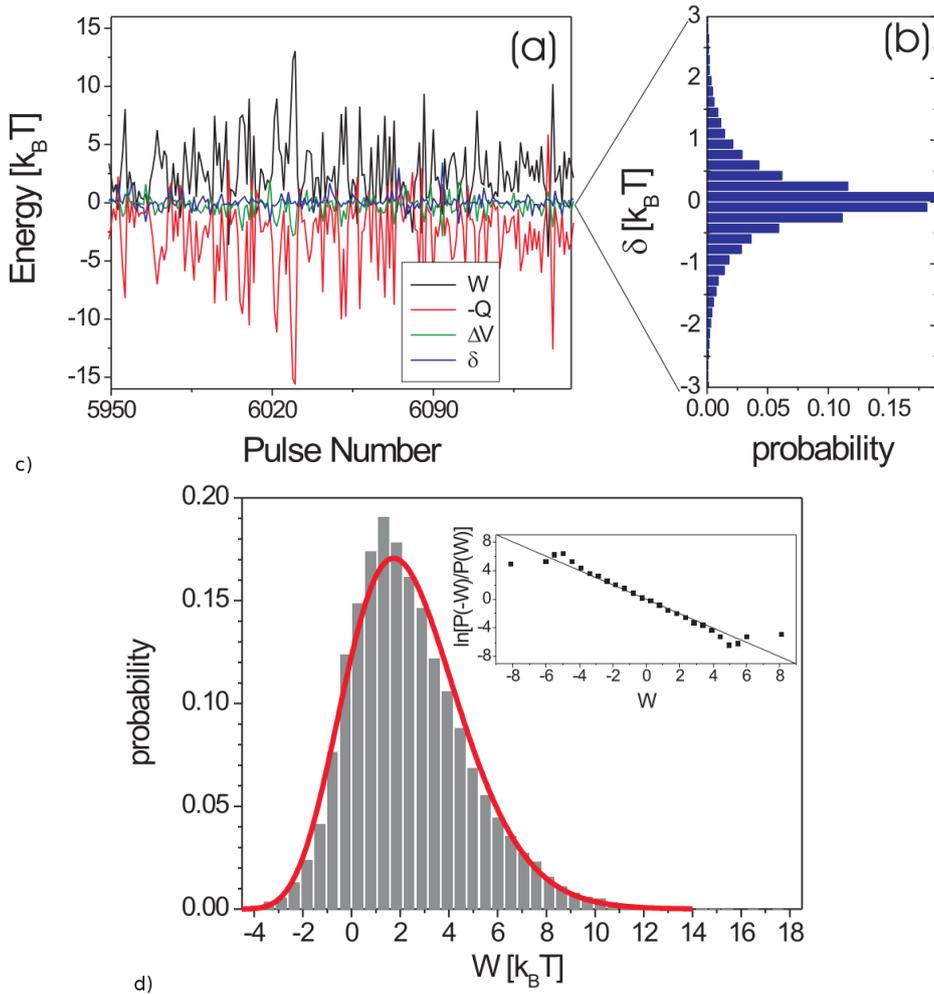
Figure 2: c): (a) quantities $-Q$, W, ΔV for consecutive drivings of the bead. (b) distribution of deviations from the first law $\delta = W - Q - \Delta V$. d): non-Gaussian work distribution of about 16 000 trajectories with the theoretical curve. Inset: logarithm of the ratio of the probabilities to find trajectories with work $-W$ and W. The deviation from a linear relationship is due to poor statistics of large negative work trajectories. Reproduced from [7].

6   Conclusion

We have introduced stochastic thermodynamic and within this framework expressed the most important concepts from thermodynamics through the paradigmatic colloidal particle. The assignment of entropy to a trajectory opened the gate towards formulating general fluctuation theorems. An experiment was presented where the newly introduced ideas were successfully tested. It is important to note however, that we were dealing with quite a simple model and generalizations to master equation dynamics, hamiltonian systems, biomolecular systems, etc. have already been made and that research is very much active.

References

[1] U. Seifert, *Stochastic thermodynamics, fluctuation theorems and molecular machines*, Rep. Prog. Phys. **75**, 126001 (2012).

[2] C. Van Den Broeck, *Stochastic thermodynamics: A brief introduction* in C. Bechinger, F. Sciortino and P. Ziherl (ed.), *Physics of Complex Colloids* (105 Press, Amsterdam, 2013).

[3] G. Crooks *Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences*, Phys. Rev. E **60**, 2721 (1999).

[4] D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr. and C. Bustamante, *Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies*, Nature **437**, 231 (2005).

[5] K. Sekimoto, *Langevin equation and thermodynamics*, Prog. Theor. Phys. Supp. **130**, 17 (1998).

[6] M. Esposito and C. Van den Broeck, *Three Detailed Fluctuation Theorems*, Phys. Rev. Lett. **104**, 090601 (2010).

[7] V. Blickle, T. Speck, L. Helden, U. Seifert and C. Bechinger, *Thermodynamics of a Colloidal Particle in a Time-Dependent Non-Harmonic Potential*, Phys. Rev. Lett. **96**, 070603 (2006).