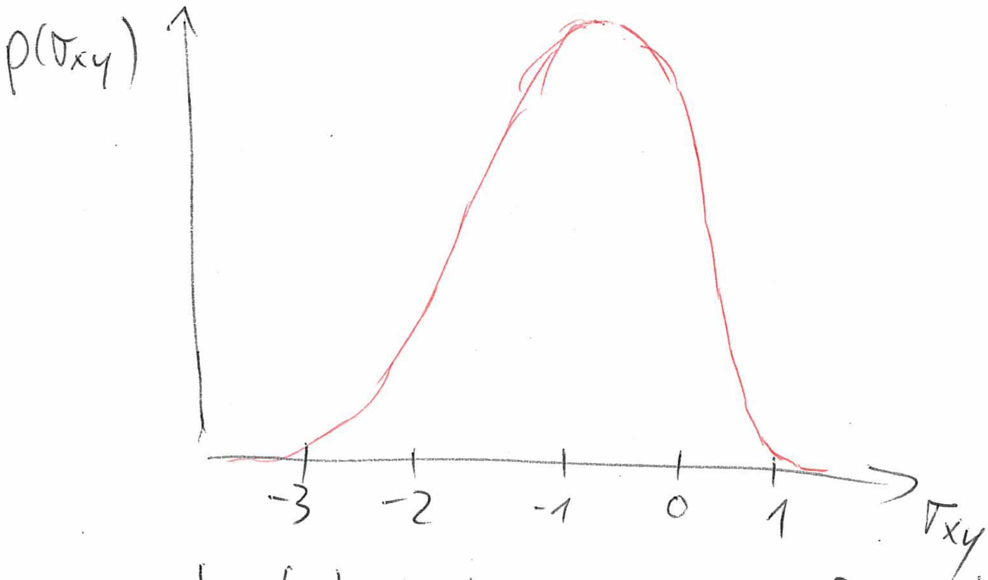
Nonequilibrium Fluctuation Relations

The condition that a physical system be in thermal equilibrium imposes considerable constraints on its possible. If the system is (as commonly assumed) in contact with a heat bath, we know that the state of the system follows the canonical distribution $P_{eq} \sim e^{-\beta \mathcal{H}}$ E.g. velocities are always normally distributed irrespectively of the interaction potential. Moreover, we have the second law of thermodynamics, telling us that entropy will always increase, $\Delta S \geq 0$, and the Fluctuation-Dissipation Theorem that universally connects the correlations of equilibrium fluctuations to the linear response functions of small external perturbations.

It was believed for a long time that out of equilibrium no such general statements, independent of the details of the system could be made. In the 1990ies, though, a whole zoo of very general statements about exactly such nonequilibrium processes were published that later became known as <u>Fluctuation Relations</u>

One of the starting points was the paper DJ Evans, EGD Cohen, and GP Morriss, PRL 71, 2401 (1993). The authors analyzed a small 2d system of 56 thermostatted disks which

they exposed to a finite shear rate $\dot{\gamma}$.
They recorded the distribution of $p(\sigma_{xy})$
the shear stress σ_{xy} after some fixed
time t



more notably, there is a finite probability for the shear stress to have the "wrong" sign. More importantly, they derived a formula to calculate the probability of these events that oppose the relaxation to the steady state

$$\boxed{\frac{p(\sigma_{xy})}{p(-\sigma_{xy})} = \exp\left[\frac{N\sigma_{xy}\dot{\gamma}t}{k_B T}\right]}$$

I.e., although these events occur with a finite probability, they are exponentiall suppressed.

This formula was proven more formally soon after by

G. Gallavotti, and EGD Cohen, PRL 74, 2694 (1995)

who showed that it should hold much more generally.

In

C. Jarzynski, PRL 78, 2690 (1997)

He considered a system, initially in thermal equilibrium, at a certain value of an external control parameter λ_0. Now this control parameter shall be changed to another value λ_1 with a finite switching rate. This finite switching rate will bring the system temporarily out of equilibrium although it will eventually reach a new equilibrium at $\lambda = \lambda_1$. The initial- and the final equilibrium states will have a well defined free energy difference ΔF. Due to the finite switching rate, the work W necessary to get from λ_0 to λ_1 will depend on the microscopic initial conditions and over many realizations of the experiment one will find a distribution $p(W)$. Jarzynski realized that this measurable distribution can tell us something about the free energy difference ΔF. In particular,

$$\boxed{\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F)}$$

where the average $\langle \cdot \rangle$ is with respect to $p(W)$

The Jarzynski-relation is sometimes seen as an improvement of the second law inequality which can be written as

$$\langle W \rangle \geq \Delta F$$

The former immediately implies the latter through the convexity

$$\langle e^{-x} \rangle \leq e^{-\langle x \rangle}$$

but on the other hand thermodynamics only deals with $\langle W \rangle$ and never attempts a description of $p(W)$.

In

GE Crooks, PRE 61, 2361 (2000)

the author considered the probability distribution $p[\underline{x}(t) | \underline{x}(0)]$ of trajectories $\underline{x}(t)$ which evolve from the initial conditions $\underline{x}(0)$ via some Markovian stochastic dynamics

We will discuss in more detail below his result that this trajectory-probability is related to the probability $\hat{p}[\hat{x}(t)|\hat{x}(0)]$ for the time-reversed dynamics

$$\boxed{\frac{p[x(t)|x(0)]}{\hat{p}[\hat{x}(t)|\hat{x}(0)]} = \exp(-\beta Q[x])}$$

via a quantity $Q[x]$ that is a natural definition of a trajectory-dependent dissipated heat.

Only after the work by Crooks it started to become clear under which conditions these Fluctuation-Relations hold and that, as we will see below, they are all related.

In the mean time it was discovered that one more Fluctuation-Relation had been discovered earlier in the Soviet Union

GN Bochkov, and YE Kuzovlev, JETP 45, 125 (1977)

A system initially in thermal equilibrium shall be subjected to a varying external force. Averaging over the work distribution they found

$$\langle \exp(-\beta W) \rangle = 1$$

Let us understand these relations in more detail. To be precise let's consider a one-dimensional over-damped dynamics

$$\partial_t x(t) = \mu\left[-\partial_x V(x,\lambda) + f(x,\lambda)\right] + \xi(t)$$

where μ is a given mobility and the particle is subjected to an conservative potential V, an external force f and stochastic noise ξ. Both the potential and the force can be changed by the control parameter λ. Initially, the system shall be in thermal equilibrium such that the intial conditions of trajectories $x(t)$ are distributed according to

$$p_0(x_0) = \frac{1}{Z} e^{-\beta \mathcal{H}(x_0)} = e^{\beta F - \beta \mathcal{H}(x_0)}$$

where $F = F(\beta, \lambda)$ is the free energy. We now consider trajectories $x(\tau)$ between time 0 and t.

We introduce trajectory dependent work-, $w[x(\tau)]$, and heat-functionals $q[x(\tau)]$ to formulate a generalized first law of thermodynamics

$$dV = \delta w - \delta q$$

There has been considerable discussion in the literature about the proper definition of the work functional. Adopting the definition

$$\delta w := \frac{\partial V}{\partial \lambda} d\lambda + f dx$$

yields

$$\delta q = \delta w - dV = (-\partial_x V + f) dx$$

which seems plausible given that in the overdamped system, mechanical work has to be dissipated into heat.

Other definitions like

$$\delta \tilde{w} := (-\partial_x V + f) dx$$

are equally valid but a lot of confusion has arisen over inconsistent use of these definitions.

Using technical results from the theory of stochastic differential equations one can show that the probability of a trajectory

$$p[x(\tau)] \sim \exp(-A[x(\tau)])$$

can be given in terms of the so called action

$$A[x(\tau)] := \int_0^t d\tau \left[(\partial_t x + \mu \partial_x V - \mu f)^2/4D - \frac{1}{2}\mu \partial_x^2 V + \frac{1}{2}\mu \partial_x f \right]$$

where D is the variance of the noise

$$\langle \xi(t)\xi(t') \rangle = 2D\delta(t-t')$$

Moreover, the heat can be calculated as

$$q[x(t)] = -T\{ A[x(\tau), \lambda(\tau)] - A[x(t-\tau), \lambda(t-\tau)] \}$$

We can now interpret

$$A[x(t-\tau), \lambda(t-\tau)] \equiv A[\hat{x}(\tau), \hat{\lambda}(\tau)]$$

as the action of the time reversed dynamics $\hat{x}(\tau) = x(t-\tau)$ and $\hat{\lambda}(\tau) = \lambda(t-\tau)$. Then

$$q[x(\tau)] = T \ln \frac{p[x(\tau), \lambda(\tau)]}{\hat{p}[\hat{x}(\tau), \hat{\lambda}(\tau)]}$$

and it is natural to identify

$$\Delta s\,[x(\tau)] := q/T$$

with a change in entropy

Considering an arbitrary functional $B[x(\tau)]$ of the trajectory, we can define its forward average

$$\langle B \rangle_F := \int dx_0 \int \mathcal{D}[x(\tau)]\, p_0(x_0)\, p[x(\tau)|x_0]\, B[x(\tau)]$$

Noting that the initial distribution $\hat{p}_0(\hat{x}_0)$ of the time reversed dynamics is the canonical distribution of the final state of the original dynamics we have

$$\frac{p_0(x_0)\, p[x(\tau)|x_0]}{\hat{p}_0(\hat{x}_0)\, \hat{p}[\hat{x}(\tau)|\hat{x}_0]} = e^{+\beta\Delta E - \beta\Delta F - \beta q[x(\tau)]}$$

$$= e^{\beta w[x(\tau)] - \beta\Delta F}$$

using the trajectory version of the first law of thermodynamics

sometimes $w[x(\tau)] - \Delta F$ is called dissipative work.

With this we find the following relation between the forward and backward trajectory averages

$$\boxed{\langle B[x(\tau)]\rangle_F = \langle B[\hat{x}(\tau)]\, e^{-\beta w[\hat{x}(\tau)] + \beta\Delta F}\rangle_R}$$

or, equivallently

$$\boxed{\langle B[x(\tau)]\, e^{-\beta w[x(\tau)] + \beta\Delta F}\rangle_F = \langle B[\hat{x}(\tau)]\rangle_R}$$

Setting $B[x(\tau)] \equiv 1$, we recover the Jarzynski Relation

$$\langle e^{-\beta W[x(\tau)]} \rangle_F = e^{-\beta \Delta F}$$

which is therefor just a consequence of the Crooks-Relation between forward and backward trajectory probabilities.