Systems out-of-equilibrium: fluctuation relations

STEFANO RUFFO

SISSA, Trieste, Italy

IFPU Focus Week (Feb 6-10 2023); Dynamical complexity in astrophysical context

February 10, 2023

Bibliography

- Chris Jarzynski, Annu. Rev. Condens. *Matter Phys.* 2011.2:329-51
- S. Gupta, T. Dauxois and S. Ruffo, *Europhys. Lett.*, **113** 60008 (2016)

Hatano-Sasa, Jarzynski and Crooks

Protocol $\{\lambda(t)\}_{0\leq t\leq\tau}; \lambda(0)\equiv\lambda_1, \lambda(\tau)\equiv\lambda_2\}$

$$Y \equiv \int_0^\tau \mathrm{d}t \; \frac{\mathrm{d}\lambda(t)}{\mathrm{d}t}\frac{\partial\Phi}{\partial\lambda}(\mathcal{C}(t),\lambda(t)) \quad \Phi(\mathcal{C},\lambda)\equiv -\ln\rho_{\mathrm{ss}}(\mathcal{C};\lambda)$$

Y is dissipated work.

$$\left\langle e^{-Y}\right\rangle = 1.$$

$$\left\langle e^{-\beta W}\right\rangle = e^{-\beta\Delta F},$$

$$\frac{P_{\mathrm{F}}(W_{\mathrm{F}})}{P_{\mathrm{R}}(-W_{\mathrm{F}})} = e^{\beta(W_{\mathrm{F}}-\Delta F)}.$$

Fluctuation theorems: Nonequilibrium work relations

Gas-piston setup with $N \sim 10^{23}$ particle (Macroscopic). The piston is rapidly pushed into the gas and then pulled at the initial position (work is positive if done against the system)

$$W > 0$$

Microscopically (in a gas with few particles), we could observe $W < 0$, but, on average

$$\langle W \rangle > 0$$

The second principle can be formulated as an equality (Jarzynski)

$$\langle e^{-W/(k_B T)} \rangle = 1$$

If the piston is manipulated in a time symmetric manner (Crooks)

$$\frac{P(W)}{P(-W)} = e^{W/(k_B T)}$$

Protocol

$$t = 0\,[\lambda = A, T] \qquad \text{equilibrium} \;\; \rightarrow \;\; t = \tau\,\lambda = B\,\text{non equilibrium}$$
$$\rightarrow \;\; t = \tau^*\;[\lambda = B, T]\,\text{equilibrium}$$

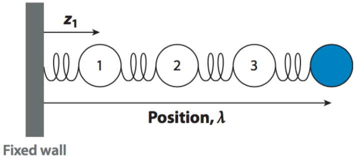
No external work is done on the system in the time interval $\tau < t < \tau^*$.
Clausius inequality (Second Law of Thermodynamics)

$$W \geq \Delta F = F_{B,T} - F_{A,T}$$

where F is the Helmholtz free energy. When the parameter λ is varied slowly (adiabatic transformation) $W = \Delta F$.

Important: Fluctuation theorems are valid also when the system is isolated after it is equilibrated at time $t = 0$.

Microscopic model



$$H(\mathbf{x};\lambda) = \sum_{i=1}^{3} \frac{p_i^2}{2m} + \sum_{i=0}^{3} U(z_{k+1} - z_k)$$

where $\mathbf{x} = (z_1, z_2, z_3, p_1, p_2, p_3)$ and the boundary conditions are $z_0 = 0,\ z_4 = \lambda(t)$

$$W = \int dW = \int_A^B \mathrm{d}\lambda \frac{\partial H}{\partial \lambda}(\mathbf{x}, \lambda) = \int_0^t \mathrm{d}t \dot{\lambda} \frac{\partial H}{\partial \lambda}(\mathbf{x}(\mathbf{t}), \lambda(t))$$

$$\mathcal{H}(\mathbf{x}, \mathbf{y}, \lambda) = H(\mathbf{x}; \lambda) + H_{env}(\mathbf{y}) + H_{int}(\mathbf{x}, \mathbf{y})$$

Boltzmann-Gibbs distributions

If the interaction with the bath H_{int} is sufficiently weak

$$p^{eq}_{\lambda,T}(\mathbf{x}) = \frac{1}{Z_{\lambda,T}} \exp\left[-H(\mathbf{x};\lambda)/(k_B T)\right] \ , \ Z_{\lambda,T} = \int \mathrm{d}\mathbf{x} \exp\left[-H(\mathbf{x};\lambda)/(k_B T)\right]$$

If H_{int} is instead "large"

$$p^{eq}_{\lambda,T} \propto \exp\left(-H^*/k_B T\right) \ , \ H^*\left(\mathbf{x};\lambda\right) = H\left(\mathbf{x};\lambda\right) + \phi(\mathbf{x},T)$$

where $\phi(\mathbf{x},T)$ is the free-energy cost of inserting the system into the thermostat. The free energy associated with the equilibrium state is

$$F_{\lambda,T} = -k_B T \ln Z_{\lambda,T}$$

For a "swarm" of independent trajectories $(\mathbf{x}_1(t), \mathbf{x}_2(t), \ldots, (0 < t < \tau)$ one can compute the corresponding work $W_1, W_2, \ldots,$ and determine the distribution $P(W)$, which must respect

$$\langle W \rangle = \int \mathrm{d}W P(W) W \geq \Delta F = F_{B,T} - F_{A,T}$$

Proof of Jarzynski for an isolated system

After preparing the system in the initial equilibrium state, we disconnect it from the environment and perform work by varying λ from A to B. The statistics of work is determined by the statistics over the initial state

$$\langle e^{-W/(k_B T)} \rangle = \int \mathrm{d}\mathbf{x}(0) p^{eq}_{A,T}(\mathbf{x}(0)) e^{-W/(k_B T)}$$

Since $\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\partial H}{\partial t}$, the work is given by

$$W = H(\mathbf{x}(\tau), B) - H(\mathbf{x}(0), A)$$

Changing variables from initial to final

$$\langle e^{-W/(k_B T)} \rangle = \frac{1}{Z_{A,T}} \int \mathrm{d}\mathbf{x}(\tau) |\partial \mathbf{x}(\tau)/\partial \mathbf{x}(0)|^{-1} \exp\left(-H(\mathbf{x}(\tau); B)/(k_B T)\right)$$

Using Liouville theorem $|\partial \mathbf{x}(\tau)/\partial \mathbf{x}(0)| = 1$, one finally gets

$$\langle e^{-W/(k_B T)} \rangle = \frac{Z_{B,T}}{Z_{A,T}} = e^{-(F_{B,T} - F_{A,T})/(k_B T)}$$

A stochastic model of long-range interacting particles

N interacting particles ($i = 1, 2, \ldots, N$) moving on a unit circle, with angles θ_1.

Microscopic configuration

$$\mathcal{C} = \{\theta_i; i = 1, 2, \ldots, N\}$$

The particles interact via the potential

$$\mathcal{V}(\mathcal{C}) = \frac{K}{2N} \sum_{i,j=1}^{N} [1 - \cos(\theta_i - \theta_j)]$$

$K = 1$ in the following. External fields h_i

$$\mathcal{V}_{\text{ext}}(\mathcal{C}) = \sum_{i=1}^{N} h_i \cos\theta_i$$

The fields h_i's may be considered as quenched random variables with a common distribution $P(h)$.

The net potential energy is therefore

$$V(\mathcal{C}) = \mathcal{V}(\mathcal{C}) + \mathcal{V}_{\text{ext}}(\mathcal{C})$$

The stochastic dynamics

All particles sequentially attempt to move backward (forward) on the circle

$$\theta_i \to \theta_i' = \theta_i + f_i \text{ with probability p}$$
$$\theta_i \to \theta_i' = \theta_i - f_i \text{ with probability q=1-p}$$

The f_i are quenched random variables, each particles carries its own f_i.
However, particles effectively take up the attempted position with probability $g(\Delta V(\mathcal{C}))\Delta t$

$$\Delta V(\mathcal{C}) = (1/N)\sum_{j=1}^{N}[-\cos(\theta_i' - \theta_j) + \cos(\theta_i - \theta_j)] - h_i[\cos\theta_i' - \cos\theta_i]$$

$$g(z) = (1/2)[1 - \tanh(\beta z/2)]$$

Overdamped motion of particles in contact with a heat-bath at inverse temperature β and in presence of an external field. For $p \neq q$ the particles move asymmetrically under the action of an external drive.

Master equation in continuous time

$P = P(\{\theta_i\}; t)$ be the probability to observe the configuration $\mathcal{C} = \{\theta_i\}$ at time t and take the limit $\Delta t \to 0$

$$
\begin{aligned}
\frac{\partial P}{\partial t} = \sum_{i=1}^{N} \Big[& \\
&+P(\ldots, \theta_i - f_i, \ldots; t) pg(\Delta V(\mathcal{C}[(\theta_i - f_i) \to \theta_i])) + \\
&+P(\ldots, \theta_i + f_i, \ldots; t) qg(\Delta V(\mathcal{C}[(\theta_i + f_i) \to \theta_i])) - \\
&-P(\ldots, \theta_i, \ldots; t) \Big\{ pg(\Delta V(\mathcal{C}[\theta_i \to (\theta_i + f_i)])) + qg(\Delta V(\mathcal{C}[(\theta_i) \to (\theta_i - f_i)])) \Big\} \Big]
\end{aligned}
$$

At long times, the system settles into a stationary state $P_{\mathrm{st}}(\{\theta_i\})$.

- Equilibrium: For $p = 1/2$, the particles move in a symmetric manner. The system has an equilibrium stationary state $P_{\mathrm{eq}}(\{\theta_i\}) \propto e^{-\beta V(\{\theta_i\})}$. Detailed balance is satisfied.
- Non Equilibrium: For $p \neq 1/2$, the particles have a preferred direction, The system at long times settles into a nonequilibrium stationary state, characterized. Detailed balance is violated leading to nonzero probability currents in phase space.

Fokker-Planck limit and Langevin equation

We assume that $f_i \ll 1 \; \forall \; i$. Taylor expanding in powers of f_i's and retaining terms up to second order

$$\frac{\partial P}{\partial t} = -\sum_{i=1}^{N} \frac{\partial J_i}{\partial \theta_i},$$

where the probability current J_i for the i-th particle is given by

$$J_i = \left[(2p-1)f_i + \frac{f_i^2 \beta}{2}\left(\frac{1}{N}\sum_{j=1}^{N} \sin \Delta\theta_{ji} + h_i \sin\theta_i\right)\right]P - \frac{f_i^2}{2}\frac{\partial P}{\partial \theta_i}.$$

The corresponding Langevin equation is

$$\dot{\theta}_i = (2p-1)f_i + \frac{f_i^2 \beta}{2}\left(\frac{1}{N}\sum_{j=1}^{N} \sin(\theta_j - \theta_i) + h_i \sin\theta_i\right) + f_i \eta_i(t),$$

where $\eta_i(t)$ is a random noise with

$$\langle \eta_i(t) \rangle = 0, \quad \langle \eta_i(t)\eta_j(t') \rangle = \delta_{ij}\delta(t-t').$$

Equilibrium vs. non equilibrium

- Equilibrium: For $p = 1/2$ the system settles into an equilibrium stationary state $P_{\mathrm{eq}}(\{\theta_i\})$ which makes $J_i = 0$ individually for each i.
- Non Equilibrium: For $p \neq 1/2$, the system reaches a non-equilibrium stationary state. However, in the special case when the jump length is the same for all the particles and there is no external field ($f_i = f$ and $h_i = 0 \,\forall\, i$), one may make a Galilean transformation, $\theta_i \to \theta_i + [(2p-1)f/2]t$, so that in the frame moving with the velocity $[(2p-1)f/2]$, the Langevin equation takes a form identical to the one for $p = 1/2$, and the stationary state has again the equilibrium measure $P_{\mathrm{eq}}(\{\theta_i\})$.

The $N \to \infty$ limit and the single-particle distribution

In the thermodynamic limit $N \to \infty$ with $h_i = h$, let us introduce the single-particle distribution $\rho(\theta; f, t)$, the density of particles with jump length f which are at location θ on the circle at time t. ρ is periodic $\rho(\theta; f, t) = \rho(\theta + 2\pi; f, t)$ and normalized

$$\int_0^{2\pi} d\theta \ \rho(\theta; f, t) = 1 \ \ \forall \ \ f.$$

In terms of $\rho(\theta; f, t)$, the Langevin equation reads

$$\dot{\theta} = (2p-1)f + \frac{f^2\beta}{2}\Big(m_y \cos\theta - m_x \sin\theta + h \sin\theta\Big) + f\eta(t),$$

where

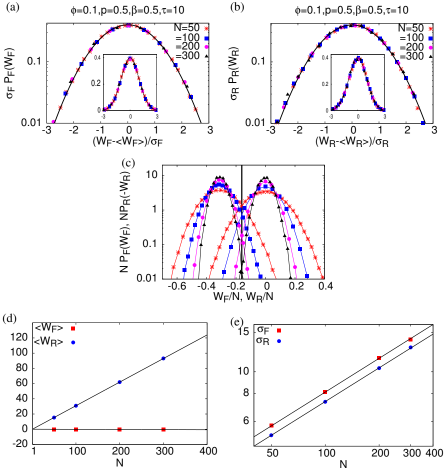
$$(m_x, m_y) = \int d\theta df \ (\cos\theta, \sin\theta)\rho(\theta; f, t)\mathcal{P}(f),$$

and

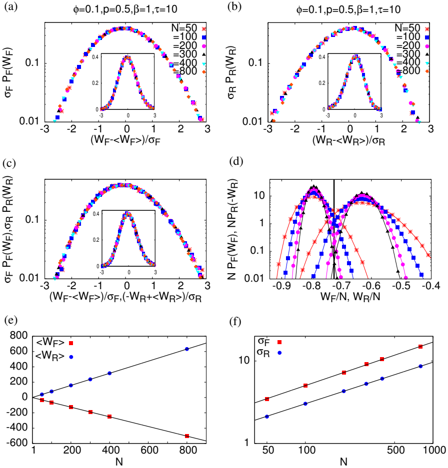
$$\langle \eta(t) \rangle = 0, \quad \langle \eta(t)\eta(t') \rangle = \delta(t - t').$$

This stochastic dynamics is very similar to the one of the Sakaguchi model.

Work distributions for homogeneous state



Work distributions for inhomogeneous state



$$P_{\mathrm{F,R}}(W_{\mathrm{F,R}}) \sim \frac{1}{\sigma_{\mathrm{F,R}}} g_{\mathrm{F,R}}\left(\frac{W_{\mathrm{F,R}} - \langle W_{\mathrm{F,R}} \rangle}{\sigma_{\mathrm{F,R}}}\right) \quad g_{\mathrm{F}}(x) = g_{\mathrm{R}}(-x)$$

Hatano-Sasa distribution