Simulation of small systems: II

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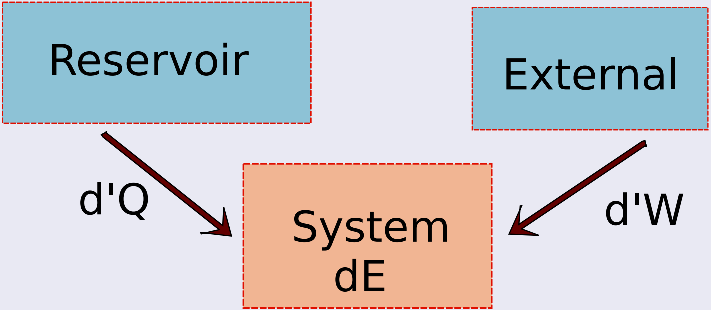

As for macroscopic systems, when the system receives heat from the reservoir (thermal environment), it is considered as positive.

Stochastic thermodynamics

For an infinitesimal timestep dt. The force exerced by the thermal environment is

$$-\gamma\frac{dx}{dt}+\xi(t)$$

and the heat received is $d'Q$

$$\delta' Q=\left(-\gamma\frac{dx}{dt}+\xi(t)\right)\circ dx(t)$$

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Underdamped motion

the heat is given by $-\gamma \frac{dp}{dt} + \xi(t)$ times the displacement. Equation of motion,

$$\frac{dp}{dt} = -\frac{\partial U(x,\lambda)}{\partial x} - \gamma \frac{dx}{dt} + \xi(t)$$

Underdamped motion

the heat can be written as

$$d'Q = \left(\frac{dp}{dt} + \frac{\partial U(x,\lambda)}{\partial x}\right) \circ dx(t)$$

Stochastic thermodynamics

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The work brought to the system corresponds to a change performed by the external operator, one has

$$d'W = \frac{\partial U(x,\lambda)}{\partial \lambda} \circ d\lambda(t)$$

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First law of thermodynamics

One uses two identities: the first one

$$\frac{dp}{dt} \circ dx(t) = \frac{dp}{dt} \circ \frac{p}{m} dt = d\left(\frac{p^2}{2m}\right)$$

which gives

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$$\frac{\partial U(x,\lambda)}{\partial x} \circ dx(t) = dU(x,\lambda) - \frac{\partial U(x,\lambda)}{\partial \lambda} \circ d\lambda$$

which gives

$$dE = d'Q + d'W$$

where E is the total energy of the system

$$E = \left(\frac{p^2}{2m} + U(x,\lambda)\right)$$

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Conservation of the energy of the system.

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Equation of motion

$$\gamma \frac{dx}{dt} = -\frac{\partial U(x,\lambda)}{\partial x} + \xi(t)$$

The heat is given by

$$d'Q = \frac{\partial U(x,\lambda)}{\partial x} \circ dx(t)$$

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and finally

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for an overdamped motion, the mean kinetic energy stays at equilibrium and only the internal energy is modified by work and/or heat.

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for an overdamped motion, the mean kinetic energy stays at equilibrium and only the internal energy is modified by work and/or heat.
The thermodynamics quantities have been defined for a single trajectory, and it is also interesting to calculate an ensemble average of these fluctuating observables. It is convenient to use the Fokker-Planck and/or Kramers equations.

Underdamped motion

For a underdamped motion, the mean heat variation can be rewritten as

$$\begin{aligned}\langle d'Q\rangle &= \int\int\left(\frac{dp}{dt}+\frac{\partial U(x,\lambda)}{\partial x}\right)\circ\frac{dx(t)}{dt}P(x,p)dxdpdt & (1)\\ &= \int\int\left(\frac{p}{m}\circ\frac{dp}{dt}+\frac{\partial U(x,\lambda)}{\partial x}\circ\frac{dx(t)}{dt}\right)P(x,p)dtdxdp & (2)\end{aligned}$$

$$\langle d'Q\rangle = \int\left(\frac{\partial E}{\partial x}J_x+\frac{\partial E}{\partial p}J_p\right)dxdpdt$$

$\vec{J}=\left(\frac{dx}{dt}P(x,p),\frac{dp}{dt}P(x,p)\right)$ is the flux of probability in the phase space.

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For a underdamped motion, the mean heat variation can be rewritten as

$$\langle d'Q \rangle = \int\int \left(\frac{dp}{dt} + \frac{\partial U(x,\lambda)}{\partial x}\right) \circ \frac{dx(t)}{dt} P(x,p) dxdpdt \tag{1}$$

$$= \int\int \left(\frac{p}{m} \circ \frac{dp}{dt} + \frac{\partial U(x,\lambda)}{\partial x} \circ \frac{dx(t)}{dt}\right) P(x,p) dtdxdp \tag{2}$$

$$\langle d'Q \rangle = \int \left(\frac{\partial E}{\partial x} J_x + \frac{\partial E}{\partial p} J_p\right) dxdpdt$$

$\vec{J} = \left(\frac{dx}{dt} P(x,p), \frac{dp}{dt} P(x,p)\right)$ is the flux of probability in the phase space.

$$\langle d'Q \rangle = \int \vec{\nabla} E \vec{J} dxdpdt$$

Overdamped motion

The mean heat variation can be rewritten as

$$\langle d'Q\rangle = \int\int \left(\frac{\partial U(x,\lambda)}{\partial x}\right) \circ \frac{dx(t)}{dt} P(x) dxdt \tag{3}$$

$$= \int\int \left(\frac{\partial U(x,\lambda)}{\partial x} \circ \frac{dx(t)}{dt}\right) P(x,) dtdx \tag{4}$$

$$\langle d'Q\rangle = \int \frac{\partial E}{\partial x} J_x dxdt$$

Overdamped motion

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$$\langle d'Q\rangle = \int\vec{\nabla}E\vec{J}dxdt$$

Entropy and second law of thermodynamics

One defines a stochastic entropy coming from the particle trajectory. For an overdamped motion

$$s(t) = -\ln(P((x(t,\lambda),t))) \tag{5}$$

where $P((x(t,\lambda)),t)$ is is the probability provided by the Fokker-Planck equation associated with the Langevin equation and calculated along the particle trajectory x_t.

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The stochastic entropy depends both on the trajectory and on the ensemble.

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The stochastic entropy depends both on the trajectory and on the ensemble.

Taking the time derivative of the stochastic entropy, one has

$$\frac{ds(t)}{dt} = -\frac{1}{P(x,t)}\left(\frac{\partial P(x,t)}{\partial t} + \frac{\partial P(x,t)}{\partial x}\frac{dx}{dt}\right)$$

Entropy and second law of thermodynamics

The flux of the Fokker-Planck equation is given by

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial J}{\partial x}$$

with

$$J = -\frac{1}{\gamma}\left(\frac{\partial U(x,\lambda)}{\partial x} + \frac{1}{\beta}\frac{\partial}{\partial x}\right) P(x,t)$$

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which gives

$$\frac{\partial P(x,t)}{\partial x} = -\beta\left(\gamma J(x,t) + \frac{\partial U(x,t)}{\partial x}P(x,t)\right)$$

Entropy and second law of thermodynamics

Let us recall that the time derivative of the entropy is given by

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$$\frac{ds(t)}{dt} = -\frac{\partial_t P(x,t)}{P(x,t)} + \left(\frac{\beta\gamma J(x,t)}{P(x,t)} + \beta\partial_x U(x,\lambda)\right)_{x_t}\frac{dx}{dt}$$

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Entropy coming from the environment

The heat released in the environnement is equal to the opposite heat received by the system and the entropy rate is given by

$$\frac{ds_m(x(t))}{dt} = \beta\frac{-dq(x(t))}{dt}$$

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By using the définition of the heat

$$\frac{ds_m(x(t))}{dt} = -\beta\partial_x U(x,\lambda)\frac{dx}{dt} \qquad (6)$$

Entropy coming from the environment

By summing the two contributions to the total entropy, one obtains the total entropy

$$\frac{ds_{tot}(t)}{dt} = -\frac{\partial_t P(x,t)}{P(x,t)} + \left(\frac{J(x,t)}{DP(x,t)}\right)_{x_t} \frac{dx}{dt}$$

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Average of the total entropy

For a given function $f(x)$, the brackets denote

$$\langle f(x) \rangle = \int dx f(x) P(x,t)$$

Consequently, one has

$$\left\langle g(x) \frac{dx}{dt} \right\rangle = \int dx g(x) J(x,t)$$

where $J(x,t)$ is the flux.

Average of the total entropy

The mean rate of the total entropy is then given by

$$\frac{dS_{tot}(t)}{dt} = \left\langle \frac{ds_{tot}(t)}{dt} \right\rangle$$
$$= -\int dx \frac{\partial p(x,t)}{\partial t} + \int dx \frac{J^2(x,t)}{Dp(x,t)} \tag{7}$$

Due to the conservation of the probability, one has $\int dx \frac{\partial p(x,t)}{\partial t} = 0$ and finally the mean rate of the total entropy is

$$\frac{dS_{tot}(t)}{dt} = \int dx \frac{J^2(x,t)}{Dp(x,t)} \geq 0 \tag{8}$$

because the integrand $\frac{J^2(x,t)}{Dp(x,t)}$ is positive.

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The total entropy increases with time as expected by the second law of the thermodynamics.

Large deviation functions

For a random variables A_n parameterized by n which is an increasing index, the theory of large deviations gives that the probability $P(A_n = a)$ behaves as $\approx e^{-I(a)n}$ for large n. $I(a)$ is called the rate function. In other words, the leading behavior can be expressed as

$$\lim_{n\to\infty} -\frac{\ln(P(A_n))}{n} = I(a) \tag{9}$$

This theory encompasses various situations occurring in statistical physics, stochastic processes, probability theory.

Independent and Identically Distributed variables

Let us consider a probability distribution $p(x)$, and let us define the mean value of n variables

$$S_n = \frac{1}{n}\sum_{i=1}^{n} x_i$$

where x_i are random variables chosen with the probability distribution $p(x)$.

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where x_i are random variables chosen with the probability distribution $p(x)$. The probability of having $S_n = s$ is given by

$$P(S_n = s) = \int dx_1 \int dx_2 \cdots \int dx_n p(x_1)p(x_2)\cdots p(x_n)\delta(x_1 + x_2 + \cdots + x_n - sn)$$

where δ is the Dirac function.

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where δ is the Dirac function.
By introducing the Laplace transform of P and the change of variable $s \to ns$

$$\tilde{P}(u) = \int_0^\infty e^{-us} P(s) ds$$

one obtains

$$\tilde{P}(u) = \tilde{p}^n(u/n)$$

Independent and Identically Distributed variables

With an exponential distribution $p(x) = \lambda \exp(-\lambda x)$, one obtains

$$\tilde{P}(u) = \frac{\lambda^n}{(\lambda + u/n)^n}$$

which gives

$$P(s) = \frac{\lambda^n (ns)^n}{n!} e^{-\lambda ns}$$

By using the Stirling formula ,$n! \sim n^n e^{-n} \sqrt{2\pi n}$, $P(s)$ goes at large n as

$$P(s) \approx \exp(-I(s)n)$$

where $I(s)$ is the rate function is given by

$$I(x) = \lambda x - \ln(\lambda x) - 1$$

Independent and Identically Distributed variables

The rate function $I(x)$ is maximum and cancels when $\lambda x = 1$, which corresponds to the mean value $\lambda s = 1$. Expanding to second-order at the maximum of the function, one obtains

$$I(x) = \frac{1}{2}(\lambda x - 1)^2 \tag{10}$$

This corresponds to the law of large numbers.

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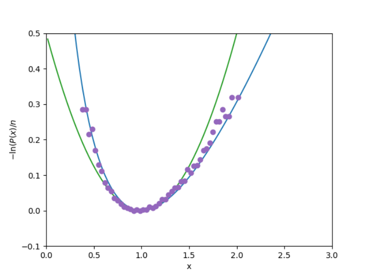

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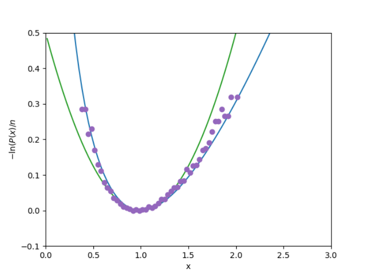

The rate function is a difficult task to obtain in simulations, because the large values of the rate function corresponds to rare events.

Gartner-Ellis theorem

For a random variable A_n where n is a positive integer, one defines the scaled cumulant generating function

$$\lambda(k) = \lim_{n\to\infty} \frac{1}{n} \ln\langle e^{nkA_n}\rangle$$

If $\lambda(k)$ exists and is differentiable for all real values k then the probability $P(A_n)$ is given as a large deviation function

$$P(a) \approx e^{-nI(a)}$$

which gives

$$\langle e^{nkA_n}\rangle \approx \int da e^{n(ka-I(a))}$$

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By using the saddle-point method (or Laplace's method), one obtains that

$$\lambda(k)) = \sup_{a\in R}(ka - I(a)) \tag{11}$$

where sup means "supremum of".

Gartner-Ellis theorem

The Legendre-Fenchel transform of the rate function gives the scaled cumulant generating function. If $\lambda(k)$ is a differentiable function, the inverse transform holds and the rate function is then given by

$$I(a) = \sup_{k \in R}(ka - \lambda(k)) \tag{12}$$

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Application in Statistical Mechanics

The thermodynamic potentials satisfy a large deviation principle. The partition functions associated with the different ensembles: for the microcanonical ensemble, the partition function has a large deviation principle, where the rate function is the opposite of the mean entropy per particle (or per lattice site)

$$Z(E, V, N) \approx e^{Ns(e,\rho)} \tag{13}$$

The canonical partition function has a large deviation principle

$$Z(V, N, T) \approx e^{-N\beta f(\rho,\beta)} \tag{14}$$

where $\beta = 1/k_B T$ is the inverse temperature and f is the free energy per particle.

Application in Statistical Mechanics

For concave entropy, the free energy can be obtained from a Legendre-Fenchel transform

$$\beta(f(\rho,\beta) = \sup_{e\in R}(\beta e - s(e,\rho)) \tag{15}$$

Conversely, if the free energy is differentiable for all temperatures, one can obtain the entropy as

$$s(e,\rho) = \inf_{\beta\in R^+}(\beta e - f(\rho,\beta)) \tag{16}$$

where *inf* is the "infimum of".

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Fluctuation theorems

The different fluctuation theorems express the universal properties of the probability distribution of the thermodynamic quantities. This corresponds to a generalisation of thermodynamics by including the fluctuations. Three classes of properties have been proved under specific assumptions. Let us introduce a variable $\Lambda(x,t)$ which depends on x and t.

Integral fluctuation theorem

If $\Lambda(x,t)$ is a non dimensional functional, one says that Λ obeys the integral fluctuation theorem iff

$$\langle \exp(-\Lambda) \rangle = \int d\Lambda p(\Lambda) \exp(-\Lambda) = 1 \tag{17}$$

where $p(\Lambda)$ is the distribution probability.
Many conséquences:

- $$\langle \Lambda \rangle \geq 0$$

  Because $\exp(-x) < 1 - x$, one has

  $$-\langle \Lambda \rangle \leq 0$$

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- The integral being equal to 1, there are trajectories where Λ is negative. apparent violation of the second law of thermodynamics?.

  In fact, this corresponds to fluctuations which can lead to negative values of Λ.

Integral fluctuation theorem

- $$P(\Lambda < -\lambda) \leq \int_{-\infty}^{-\lambda} d\Lambda p(\Lambda) e^{-\lambda-\Lambda} \leq e^{-\lambda}$$

  To prove the inequality, one writes

$$\begin{aligned} P(\Lambda < -\lambda) &= \int_{-\infty}^{-\lambda} d\Lambda p(\Lambda) \\ &\leq \int_{-\infty}^{-\lambda} d\Lambda p(\Lambda) e^{-\lambda-\Lambda} \\ &\leq \int_{-\infty}^{\infty} d\Lambda p(\Lambda) e^{-\lambda} e^{-\Lambda} \\ &\leq e^{-\lambda} \end{aligned}$$

Integral fluctuation theorem

- IFT imposes a constraint between the variance and the mean of Λ when the distribution $p(\Lambda)$ is gaussian

$$\langle(\Lambda - \langle\Lambda\rangle)^2\rangle = 2\langle\Lambda\rangle$$

if $p(\Lambda) = \frac{1}{\sqrt{2\pi}\sigma} exp(-\frac{(\Lambda-\langle\Lambda\rangle)^2)}{2\sigma^2}$ with $\sigma^2 = \langle(\Lambda - \langle\Lambda\rangle)^2\rangle$ one has

$$\int e^{-\Lambda} p(\Lambda) = e^{\sigma^2/2-\langle\Lambda\rangle}$$

Detailed fluctuation theorem

The detailed fluctuation theorem provides a relationship between the probability of obtaining the quantity Λ and the opposite $-\Lambda$:

$$\frac{p(-\Lambda)}{p(\Lambda)} = \exp(-\Lambda) \tag{18}$$

When a quantity Λ satisfies this relation, the IFT is also satisfied.

$$\int d\Lambda \exp(-\Lambda) p(\Lambda) = \int d\Lambda p(-\Lambda) \tag{19}$$

$$= \int d\Lambda p(\Lambda) = 1 \tag{20}$$

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Generalized Crooks fluctuation theorem

Comparing the probability distribution function $p(\Lambda)$ with the probability $p^{\dagger}(\Lambda)$ of the same quantity Λ for a "conjugate" process (generally one considers a time-reversed process)

$$\frac{p^{\dagger}(-\Lambda)}{p(\Lambda)} = \exp(-\Lambda) \tag{21}$$

Work fluctuation theorems

We first consider work fluctuations when the initial configuration is in equilibrium whereas the final configuration is not necessarily in equilibrium. The system evolves between the two states due to a driving force.

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Jarzynski relation

Jarzynski showed the work which allows to drive the system from the initial equilibrium state by using a time-dependent potential $U(x, \lambda)$ for a time t satisfies the relation

$$\left\langle \exp\left(-\frac{w}{T}\right)\right\rangle = \exp\left(-\frac{\Delta\mathcal{F}}{T}\right) \qquad (22)$$

where $\Delta\mathcal{F}$ is the difference of the free energy between the final state where the control parameter is equal to λ_t and the initial state with a control parameter λ_0. This can be viewed as a IFT relation for the dimensionless dissipated work.

$$w_d = \frac{w - \Delta\mathcal{F}}{T} \qquad (23)$$

Jarzynski relation

Therefore, experimentally and/or in simulation, it becomes possible to obtain the free energy difference $\Delta\mathcal{F} = \mathcal{F}(\lambda_t) - \mathcal{F}(\lambda_0)$, namely a equilibrium property, from non equilibrium measurements.

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Crooks fluctuation theorem

The Crooks fluctuation theorem states that the probability distribution $p(w)$ for work spent in the process is related to the probability distribution $\tilde{p}$ for work in the reverse process. The control parameter of the reversed process is given by $\tilde{\lambda}(\tau) = \lambda(t - \tau)$ and the initial state of the reversed process is an equilibrium state where $\tilde{\lambda}(0) = \lambda(t)$.

$$\frac{\tilde{p}(w)}{p(w)} = \exp\left(-\frac{w - \Delta\mathcal{F}}{T}\right) \tag{24}$$

Note that for a system where the Crooks relation holds, the Jarzynski theorem is satisfied. Indeed, knowing that $\tilde{p}(w)$ is normalized, one immediately infers that the JR holds.

Jarzynski relation

Therefore, experimentally and/or in simulation, it becomes possible to obtain the free energy difference $\Delta\mathcal{F} = \mathcal{F}(\lambda_t) - \mathcal{F}(\lambda_0)$, namely a equilibrium property, from non equilibrium measurements.

Jarzynski relation

Therefore, experimentally and/or in simulation, it becomes possible to obtain the free energy difference $\Delta\mathcal{F} = \mathcal{F}(\lambda_t) - \mathcal{F}(\lambda_0)$, namely a equilibrium property, from non equilibrium measurements.

Entropy production

The entropy production along a trajectory is the sum of two terms as previously seen

$$\Delta s_{tot} = \Delta s_m + \Delta s \tag{25}$$

with

$$\Delta s = -\ln(p(x_t, \lambda_t)) + \ln(p(x_0, \lambda_0)) \tag{26}$$

The total entropy obeys the IFT

$$\langle \exp\left(-\Delta s_{tot}\right)\rangle = 1 \tag{27}$$

By using the convexity of the exponential function, one infers that $\langle \Delta s_{tot}\rangle \geq 0$ wich shows that the entropy production is obviously compatible with the second law of thermodynamics.