J STOCHASTIC DIFFERENTIAL EQUATIONS

Up to this point we considered mechanical Hamiltonian systems in thermal equilibrium and looked at the reversible addition of thermal energy, leading to adiabatic, i.e. entropy-conserving changes of state. But this picture is incomplete, as we should understand better how exactly the many microscopic degrees of freedom of a system provide thermal fluctuations and how the motion of a single degree of freedom is changed under the influence of random, stochastic forces, or better, how the distribution of amplitudes of a system with many degrees of freedom evolves with time, as every degree of freedom follows its own equation of motion.

An example of such a distribution could be the amplitude distribution $p(x)\mathrm{d}x$ of a harmonic oscillator: Going from $x = 0$ to x requires mechanical work $\delta\mathrm{W} = kx^2/2$ with the spring constant k. The energy needed is supplied as thermal energy from the interaction with all other degrees of freedom in the system, $\delta\mathrm{Q} = -\mathrm{ST}$. Energy conservation would then imply that $\mathrm{dE} = \delta\mathrm{W} + \delta\mathrm{Q}$ and therefore that entropy can be expressed as a function of amplitude of the oscillator, $\mathrm{S}(x) = kx^2/2/(k_\mathrm{B}\mathrm{T})$, if there is no overall change in energy, $\mathrm{dE} = 0$.

$$\mathrm{S}(x) \sim k_\mathrm{B} \ln p(x) \quad \rightarrow \quad p(x) = \frac{\exp\left(\frac{\mathrm{S}(x)}{k_\mathrm{B}}\right)}{\int \mathrm{d}x\, \exp\left(\frac{\mathrm{S}(x)}{k_\mathrm{B}}\right)} \sim \exp\left(-\frac{k}{k_\mathrm{B}\mathrm{T}}\frac{x^2}{2}\right) \tag{J.523}$$

i.e. a Gaussian with variance $k_\mathrm{B}\mathrm{T}/k$, which seems reasonable, as the amplitude of the random motion should increase with higher temperature and decrease for a higher spring constant: One should really imagine that there is a trembling of the pendulum due to thermal fluctuations corresponding to this variance. An observation of $\langle x^2\rangle$ would immediately determine k_B for a system with known spring constant k and temperature T, with the experimental challenge being the smallness of thermal fluctuations $k_\mathrm{B}\mathrm{T}$ for reasonable temperatures.

J.1 *Brownian motion*

Macroscopic objects suspended in a fluid perform a random motion, as first noticed by Robert Brown, who observed pollen in water under a microscope. Naturally, there are two types of forces acting on such an object: a frictional force and a random agitation due to collisions with atoms and molecules in the fluid. The two are not independent, as state by the fluctuation-dissipation theorem. Writing down an equation of motion with a friction coefficient D

$$m\ddot{x} = -\mathrm{D}\dot{x} \quad \text{leads to the solution} \quad \dot{x}(t) \propto \exp\left(-\frac{t}{\tau}\right) \tag{J.524}$$

with a time constant $\tau = m/\mathrm{D}$, under which all motion ceases. But what about the random impacting of atoms and molecules that provide fluctuations in energy of the amount $k_\mathrm{B}\mathrm{T}$ in thermal equilibrium?

J.1.1 Langevin-equation

The key point is to add an external, randomly fluctuation force $\eta(t)$, as realised by Paul Langevin:

$$m\ddot{x}(t) = -\mathrm{D}\dot{x}(t) + \sigma\eta(t) \tag{J.525}$$

with amplitude σ. This external force has the property that it vanishes on average, $\langle\eta(t)\rangle = 0$ and that its magnitude at different times is uncorrelated, $\langle\eta(t)\eta(t')\rangle = 2\cdot\delta_\mathrm{D}(t-t')$, expressed by the Dirac δ_D-function. As the equation of motion is still linear, the solution is given as a superposition of the friction term and the time-integrated effect of the random force:

$$\dot{x}(t) = \exp\left(-\frac{t}{\tau}\right)\cdot\left[\dot{x}(0) + \int_0^t \mathrm{d}t\,\exp\left(+\frac{t}{\tau}\right)\frac{\sigma}{m}\eta(t)\right] \tag{J.526}$$

While there is no macroscopic, ordered motion due to $\langle\eta(t)\rangle = 0$,

$$\langle\dot{x}(t)\rangle = \dot{x}\cdot\exp\left(-\frac{t}{\tau}\right) \tag{J.527}$$

there is a diffusive motion as can be seen from the variance

$$\begin{aligned}&\langle\dot{x}(t)\dot{x}(t')\rangle = \\ &\dot{x}(0)^2\exp\left(-\frac{t+t'}{\tau}\right) + \left(\frac{\sigma}{m}\right)^2\exp\left(-\frac{t+t'}{\tau}\right)\int_0^t \mathrm{d}t\int_0^{t'}\mathrm{d}t'\exp\left(\frac{t+t'}{\tau}\right)\cdot 2\delta_\mathrm{D}(t-t') = \\ &\underbrace{\exp\left(-\frac{t+t'}{\tau}\right)\left[\dot{x}(0)^2 - \frac{\sigma^2}{\mathrm{D}m}\right]}_{\to 0\text{ for }t,t'\gg\tau} + \frac{\sigma^2}{\mathrm{D}m}\exp\left(-\frac{t-t'}{\tau}\right)\end{aligned} \tag{J.528}$$

Therefore, random fluctuations keep the particle in motion with velocity variance:

$$\langle\dot{x}(t)^2\rangle = \frac{\sigma^2}{\mathrm{D}m}\quad\text{for } t = t' \tag{J.529}$$

Assuming equipartition between the kinetic and thermal energies then leads to

$$\frac{m}{2}\langle\dot{x}^2\rangle = \frac{1}{2}k_\mathrm{B}\mathrm{T}\quad\text{such that}\quad\sigma^2 = \mathrm{D}k_\mathrm{B}\mathrm{T} \tag{J.530}$$

i.e. the amplitude of thermal fluctuation is related to the friction coefficient: First of all, that seems to be a surprising result, as D was phenomenological and σ was a model of the agitation of the fluid due to thermal motion. That the two are related makes a lot of sense, though, because their microsopci origin is identical: The macroscopic motion of the object through a fluid causes a momentum transfer onto the atoms and molecules, and the thermal motion of the atoms and molecules give rise to a momentum transfer onto the object.

Fig. 38 illustrates the influence of a randomly fluctuating force term in a damped

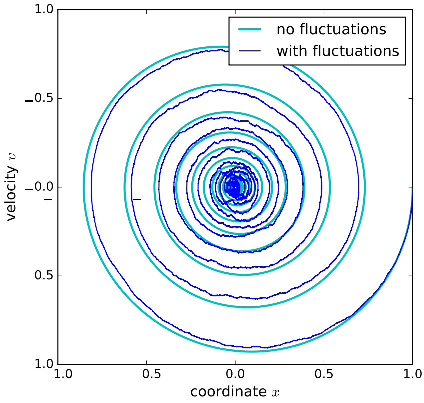

Figure 38: Solution to a damped harmonic oscillator in phase space (x, υ) with and without a fluctuating, Gaussian-distributed force.

harmonic oscillator.

J.1.2 Random walks

The object suspended in a fluid undergoes a random walk under the influence of the thermal, random force $\eta(t)$: We can repeat the above reasoning for the position $x(t)$ instead of the velocity $\dot{x}(t)$. The time constant τ^{-2} can be used to constraint $\ddot{x}$ to be very small at late times, so an object always slows down. Then, the equation of motion reads

$$D\dot{x}(t) = \sigma\eta(t) \quad \text{and is solved by} \quad x(t) = x_0 + \int\limits_0^t \mathrm{d}t\, \frac{\sigma}{D}\eta(t) \tag{J.531}$$

As before, we find that there is no net motion $\langle x(t)\rangle = 0$ but that the variance is nonzero

$$\langle x^2(t)\rangle = \frac{\sigma^2}{D^2}\int\limits_0^t \mathrm{d}t \int\limits_0^{t'} \mathrm{d}t'\, 2\delta_D(t-t') = 2\left(\frac{\sigma}{D}\right)^2 \cdot t \quad \rightarrow \quad \langle x(t)^2\rangle \propto t \tag{J.532}$$

such that the variance increases proportional to t, which is typical for diffusive processes. The diffusion constant Q is derived as

$$Q = \left(\frac{\sigma}{D}\right)^2 = \frac{k_B T}{D} \tag{J.533}$$

commonly known as Einstein's relation. Substitution of a Stokes-like friction law for a spherical object of radius r in a fluid with viscosity $\nu\rho$ yields the Stokes-Einstein-relation:

$$D = 6\pi(\nu\rho)\cdot r \quad \rightarrow \quad Q = \frac{k_B T}{b\pi(\nu\rho)\cdot r} \tag{J.534}$$

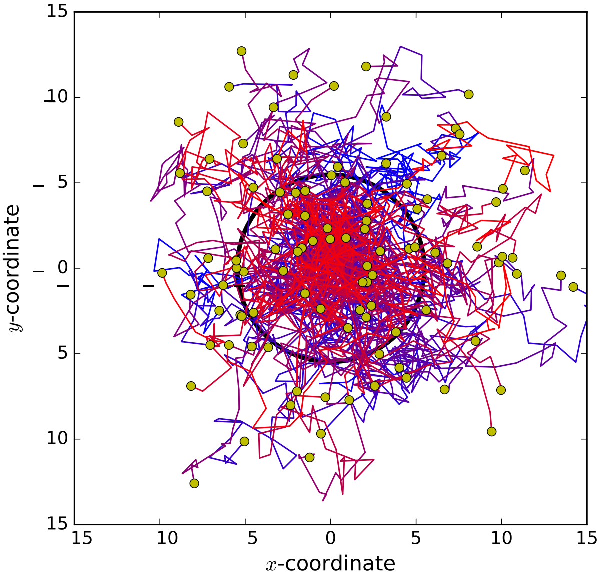

Figure 39: Discrete random walks in 2 dimensions with $n = 30$ steps each drawn isotropically from a Gaussian distribution with variance $\sigma^2 = 1$. The walks are initialised at the origin and the endpoints are marked with a yellow dot. The typical distance that the random walks are able to cover is $\sqrt{n}\sigma \simeq 5.47$, indicated by the circle.

linking viscosity and temperature, in the spirit of the fluctuation-dissipation-theorem. Fig. 39 gives an impression of discretised random walks in two dimensions, in particular of the diffusive process scaling $\propto \sqrt{t}$, or rather $\propto \sqrt{n}$ in the discrete case.

J.2 *Fokker-Planck-equation and evolution of distributions*

Up to this point, the Langevin-equation has described the motion of a damped system under the influence of a thermal fluctuating force. An interesting generalisation is that of an entire ensemble of particles, which represent a distribution, and where every particle itself follows its Langevin-dynamics $\ddot{x} = -D\dot{x} + \sigma\eta(t)$. On would expect that the distribution then widens and diffuses, and the time evolution of this distribution is given by the Fokker-Planck-equation.

If $\varphi(v, w)$ is the probability for a velocity change of a particle from υ to $\upsilon + w$ on a time scale τ, one would write for the velocity distribution

$$p(\upsilon, t+\tau) = \int_{-\infty}^{+\infty} \mathrm{d}w\; p(\upsilon - w, t)\varphi(\upsilon - w, w) \tag{J.535}$$

as a convolution integral or a Green-like propagator: How often one observes a velocity υ depends on how often the velocity $\upsilon - w$ appeared and how likely the transition from $\upsilon - w$ to υ was.

If τ is chosen to be infinitesimally small then $\varphi \neq 0$ only for $|w| \ll |\upsilon|$ and one observes only small changes in velocity, suggesting a Taylor-expansion:

$$p(\upsilon, t+\tau) = \int \mathrm{d}w \left(p(\upsilon, t) - \frac{\partial p}{\partial \upsilon}w + \frac{\partial^2 p}{\partial \upsilon^2}\frac{w^2}{2}\right)\left(\varphi(\upsilon, w) - \frac{\partial \varphi}{\partial \upsilon}w + \frac{\partial^2 \varphi}{\partial \upsilon^2}\frac{w^2}{2}\right) \tag{J.536}$$

Multiplying out this relation and keeping all terms up to order w^2 yields these terms:

1. $\int \mathrm{d}w\; \varphi(\upsilon, w) = 1$
2. $\int \mathrm{d}w\; w\varphi(\upsilon, w) = \langle w \rangle$
3. $\int \mathrm{d}w\; w\frac{\partial \varphi}{\partial \upsilon} = \left\langle \frac{\partial w}{\partial \upsilon} \right\rangle = \frac{\partial}{\partial \upsilon}\langle w \rangle$
4. $\int \mathrm{d}w\; w^2\varphi(\upsilon, w) = \langle w^2 \rangle$
5. $\int \mathrm{d}w\; w^2\frac{\partial \varphi}{\partial \upsilon} = \frac{\partial}{\partial \upsilon}\langle w^2 \rangle$
6. $\int \mathrm{d}w\; w^2\frac{\partial^2 \varphi}{\partial \upsilon^2} = \frac{\partial^2}{\partial \upsilon^2}\langle w^2 \rangle$

Collection of these results and resubstitution into the distribution $p(\upsilon, t+\tau)$ yields

$$p(\upsilon, t+\tau) =$$
$$\int \mathrm{d}w \left(p(\upsilon, t) \cdot \underbrace{\varphi(\upsilon, w)}_{1} - p \cdot \underbrace{w \cdot \frac{\partial \varphi}{\partial \upsilon}}_{3} + \underbrace{p\frac{w^2}{2}\frac{\partial^2 \varphi}{\partial \upsilon^2}}_{6} - \frac{\partial p}{\partial \upsilon}\underbrace{w\varphi}_{2} + \frac{\partial p}{\partial \upsilon}\underbrace{\frac{\partial \varphi}{\partial \upsilon}w^2}_{5} + \frac{\partial^2 p}{\partial \upsilon^2}\underbrace{x\frac{w^2}{2}}_{4} \right) \tag{J.537}$$

such that the evolution equation becomes

$$p(\upsilon, t+\tau) = p(\upsilon, t)\left(1 - \frac{\partial}{\partial \upsilon}\langle w \rangle + \frac{\partial^2}{\partial \upsilon^2}\langle w^2 \rangle - \langle w \rangle - \frac{\partial}{\partial \upsilon}\langle w^2 \rangle + \langle w^2 \rangle\right) \tag{J.538}$$

From the Langevin-equation one can obtain an expression for the average change in velocity: υ changes on the time scale τ, so $\dot{\upsilon} = w/\tau = -\mathrm{D}\upsilon$, such that

$$\frac{\partial}{\partial \upsilon}\langle w \rangle = -\mathrm{D}\tau. \tag{J.539}$$

The variance $\langle w^2\rangle = 2k_\mathrm{B}\mathrm{T}\frac{\mathrm{D}}{m}\tau$ is obtained from the Einstein-relation, which as well suggests that $\frac{\partial}{\partial v}\langle w^2\rangle = 0$. Therefore,

$$\frac{p(\upsilon, t+\tau) - p(\upsilon, t)}{\tau} = \mathrm{D}p + \mathrm{D}\upsilon\frac{\partial p}{\partial \upsilon} + k_\mathrm{B}\mathrm{T}\frac{\mathrm{D}}{m}\frac{\partial^2 p}{\partial \upsilon^2} \tag{J.540}$$

and in the limit τ → 0:

$$\frac{\partial}{\partial t}p(t,\upsilon) = \mathrm{D}\frac{\partial}{\partial \upsilon}\left[(p\upsilon) + \frac{k_\mathrm{B}\mathrm{T}}{m}\frac{\partial p}{\partial \upsilon}\right] \tag{J.541}$$

which is the sought-after Fokker-Planck-equation. It is a advection-diffusion equation for the probability distribution $p(t,\upsilon)$ and allows particular stationary solutions, for instance the Maxwell-Boltzmann-distribution

$$p \sim \exp\left(-\frac{m\upsilon^2}{2k_\mathrm{B}\mathrm{T}}\right) \tag{J.542}$$

for $\partial p/\partial t = 0$.

J.3 *Spectral decomposition of random forces* $\sigma\eta(t)$

The random force $\sigma\eta(t)$ is randomly fluctuating, and a Fourier-decomposition

$$\eta(t) = \frac{1}{2\pi}\int \mathrm{d}\omega\, \mathrm{C}(\omega)\cdot\exp(+\mathrm{i}\omega t) \quad\leftrightarrow\quad \mathrm{C}(\omega) = \int \mathrm{d}t\, \eta(t)\cdot\exp(-\mathrm{i}\omega t) \tag{J.543}$$

would be able to differentiate between fluctuations taking place on different time scales, by means of the Fourier-transform $\mathrm{C}(\omega)$. The ✈ Wiener-Khinchin-theorem states that the variances in real and Fourier-space are identical,

$$\langle \eta(t)^2\rangle = \int \mathrm{d}t\, \eta(t)^2 = \int \frac{\mathrm{d}\omega}{2\pi}|\mathrm{C}(\omega)|^2 \tag{J.544}$$

and tha tthe correlation function is the inverse Fourier-transform of the spectrum $|\mathrm{C}(\omega)|^2$,

$$\langle \eta(t)\eta(t+\tau)\rangle =$$

$$\frac{1}{(2\pi)^2}\int \mathrm{d}t \int \mathrm{d}\omega \int \mathrm{d}\omega'\, \mathrm{C}(\omega)\mathrm{C}^*(\omega')\cdot\exp(\mathrm{i}(\omega-\omega')t)\cdot\exp(-\mathrm{i}\omega'\tau) =$$

$$\int \mathrm{d}\omega\, |\mathrm{C}(\omega)|^2\exp(-\mathrm{i}\omega\tau) \tag{J.545}$$

With this idea, let's Fourier-decompose all terms in the Langevin-equation,

$$\dot{\upsilon} + D\upsilon = \sigma\eta(t) \tag{J.546}$$

including the time derivatives:

$$\upsilon(t) = \int \frac{d\omega}{2\pi}\upsilon(\omega)\exp(i\omega t) \quad \rightarrow \quad \frac{\partial}{\partial t}\upsilon(t) = \int \frac{d\omega}{2\pi} i\omega\upsilon(\omega)\exp(i\omega t) \tag{J.547}$$

and

$$\eta(t) = \int \frac{d\omega}{2\pi} C(\omega)\exp(i\omega t) \tag{J.548}$$

The, the Langevin-equation can be written as $(i\omega + D)\upsilon(\omega) = \sigma \cdot C(\omega)$ in Fourier-space, which can be solved for $\upsilon(\omega)$ as

$$\upsilon(t) = \int \frac{d\omega}{2\pi}\frac{\sigma C(\omega)}{i\omega + D}\exp(i\omega t) \tag{J.549}$$

with the corresponding variance

$$\langle \upsilon^2(t)\rangle = \int dt\, \upsilon^2(t) = \int \frac{d\omega}{2\pi}\frac{\sigma|C(\omega)|^2}{D^2 + \omega^2} = \frac{k_B T}{m} \tag{J.550}$$

using the Wiener-Khinchin-theorem in the second and equipartition in the last step. The result implies that the thermal energy is present in terms of kinetic energy in the system, and is assembled from fluctuations on all time scales, weighted by $1/\omega^2$ for large frequencies, but by D^2 for small frequencies, as clearly there is damping relevant for slow motion on large time scales.

J.4 *Irreversible processes*

J.4.1 Irreversibility in statistical physics

The fundamental physical laws are time reversible, and this is a true statement for the motion of particles or the dynamics of fields, in all branches of physics. For instance,

$$m\frac{d^2x^i}{dt^2} = -\partial^i\Phi \quad \text{Newton's equation of motion}$$

$$\partial_\alpha\partial^\alpha A^\mu = \frac{4\pi}{c}\jmath^\mu \quad \text{Maxwell's field equation (in Lorenz-gauge } \partial_\alpha A^\alpha = 0\text{)}$$

$$\frac{d^2x^\mu}{d\tau^2} = -\frac{q}{c}F^{\mu\nu}\frac{dx_\nu}{d\tau} \quad \text{Lorentz-equation of motion}$$

$$R_{\mu\nu} - \frac{R}{2}g_{\mu\nu} = -\frac{8\pi G}{c^4}T_{\mu\nu} - \Lambda g_{\mu\nu} \quad \text{gravitational field equation}$$

$$\frac{d^2x^\alpha}{d\tau^2} + \Gamma^\alpha_{\mu\nu}\frac{dx^\mu}{d\tau}\frac{dx^\nu}{d\tau} = 0 \quad \text{geodesic equation of motion}$$

In all of these examples, time reversibility is ensured by second derivatives (or squares of first derivatives), and the only case where a deeper explanation is necessary would be the Lorentz-equation of motion: The field tensor $F^{\mu\nu}$ is in fact a first derivative of the potential A^{μ}, so there is in fact a square of first derivatives as well.

Statistical systems with many degrees of freedom behave very different: While the dynamics of their fundamental constituents follows time-reversible laws like in the five examples, the Fokker-Planck equation as a diffusion equation is not time reversible. It is naturally to observe a widening distributions with time, but not the opposite. To understand this, let's have a look at a famous nonlinear equation:

$$\partial_t v^i + (v^j \partial_j) v^i = -\frac{\partial^i p}{\rho} - \partial^i \Phi + \nu \Delta v^i \quad \text{Navier-Stokes-equation} \tag{J.551}$$

for the evolution of the velocity v^i of a fluid element on which pressure p and gravity Φ is acting, for the particular case of incompressible fluids, $\partial_i v^i = 0$. ν is the coefficient of viscosity, which encapsulates the microscopic dynamics of the atoms the fluid is made of. Ignoring this term for a second and setting $\nu = 0$ recovers the Euler-equation

$$\partial_t v^i + (v^j \partial_j) v^i = -\frac{\partial^i p}{\rho} - \partial^i \Phi \quad \text{Euler-equation} \tag{J.552}$$

for the motion of ideal inviscid fluids which is perfectly time-reversible: Making the replacements

$$t \to t, \quad \partial_t \to -\partial_t, \quad v^i \to -v^i \tag{J.553}$$

does not change anything in the Euler-equation, but this invariance is broken if $\nu \neq 0$, as $\Delta v^i \to -\Delta v^i$. Clearly, this has to do with the dichotomy between the microscopic degrees of freedom and the macroscopic motion.

Reversible changes of state, in which the entropy stays constant, proceed over a sequence of equilibria (such that temperature is defined at every point and changes because of the change in internal energy), while irreversible changes in state take place spontaneously under entropy generation. The rate of change of entropy with time would be given by

$$\frac{\partial S}{\partial t} = \frac{\partial x}{\partial t}\frac{\partial S}{\partial x} \tag{J.554}$$

with a control parameter x of the system, such as the length of a pendulum as discussed in the section about adiabatic changes. In equilibrium the condition $\partial S/\partial x = 0$ would hold,

$$\dot{x} = C\frac{\partial S}{\partial x} = \frac{C}{2}\left.\frac{\partial^2 S}{\partial x^2}\right|_{x_0}(x - x_0) \tag{J.555}$$

with a suitable Taylor expansion around the equilibrium value x_0.

This result is a bit surprising when thinking about second-order equations of motion so typical for e.g. mechanical systems. There, a force $\partial\Phi/\partial x$ would provide the reason for acceleration

$$m\ddot{x} = m\dot{\upsilon} = -\frac{\partial}{\partial x}\Phi \tag{J.556}$$

very unlike thermodynamics, where a first order equation appears:

$$\dot{x} = C\frac{\partial S}{\partial x} \tag{J.557}$$

and the gradient of the thermodynamic potential such as the entropy determines velocity instead of acceleration. But when including dissipative forces into a mechanical system

$$m\dot{\upsilon} + \beta\upsilon = -\frac{\partial}{\partial x}\Phi \tag{J.558}$$

in the limit of strong damping, $\beta\upsilon \gg m\dot{\upsilon}$ one falls back onto a perfectly non-reversible equation of motion

$$\beta\upsilon = \beta\dot{x} = -\frac{\partial}{\partial x}\Phi \tag{J.559}$$

This would exactly be the limit in which the gradient of a potential is related to a velocity rather than an acceleration.

An example illustrating this idea might be the following: Imagine a ball submersed in a liquid, on which a spring is attached. The liquid provides both a heavy damping of the system as well as a source of thermal fluctuations. The potential $\Phi = kx^2/2$ under which the ball moves is provided by the spring with spring constant k. The kinetic energy E of the ball is coupled to the heat bath as the impacting molecules of the liquid can transfer kinetic energy. So we would write $E = E_0 - \Phi(x)$ and consequently for the entropy $S(x) = S(E_0 - \Phi(x), V, N)$, in the microcanonical sense. A Taylor-expansion of the entropy gives

$$S(x) = S_0 - \frac{\partial S}{\partial E_0}\Phi(x) + \ldots = S_0 - \frac{1}{k_B T}\Phi(x) + \ldots \tag{J.560}$$

where in the second equality we have substituted the definition of temperature with $\partial S/\partial E = 1/(k_B T)$. There is a gradient in entropy collinear with the gradient in the potential,

$$\frac{\partial S}{\partial x} = -\frac{1}{k_B T}\frac{\partial \Phi}{\partial x} = \frac{k}{k_B T}x \quad \rightarrow \quad \dot{x} = C\frac{\partial S}{\partial x} = -C\frac{k}{k_B T}x \tag{J.561}$$

with a similar proportionality between $\dot{x}$ and the entropy gradient as before. Therefore, the solution for the equation of motion of the system is

$$x(t) \propto \exp\left(-\frac{k}{k_B T}x\right) \tag{J.562}$$

which is a non-reversible process because of the appearance of a first derivative $\dot{x}$ instead of a second derivative $\ddot{x}$ typical for a single, microscopic degree of freedom.

A second example would be two bodies in thermal contact. The total energy is simply $E = E_1 + E_2$, and under a perturbation ϵ in one of the bodies the total energy would be conserved, $(E_1 + \epsilon) + (E_2 - \epsilon) = E$. Writing the entropy S as an additive function dependent on the energies of the two subsystems as $S(\epsilon) = S_1(E_1 + \epsilon) + S_2(E_2 - \epsilon)$ on can Taylor-expand the entropy as

$$S(\epsilon) = S_1(E_1) + \epsilon \underbrace{\frac{\partial S_1}{\partial E_1}}_{=\frac{1}{k_B T}} + \frac{\epsilon^2}{2}\frac{\partial^2 S_1}{\partial E_1^2} + S_2(E_2) - \epsilon \underbrace{\frac{\partial S_2}{\partial E_2}}_{=\frac{1}{k_B T}} + \frac{\epsilon^2}{2}\frac{\partial^2 S_2}{\partial E_2^2} \tag{J.563}$$

to second order: Then, the two terms $\partial S_1/\partial E_1 = 1/(k_B T) = \partial S_2/\partial E_2$ in thermal equilibrium, and the higher-order terms are controlled by the smallness of ϵ. Changing the energy with time leads to a corresponding change in entropy,

$$\frac{\partial S}{\partial t} = \epsilon\dot{\epsilon}\left(\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2}\right) \tag{J.564}$$

Contrarily, if there is no equilibrium,

$$\frac{1}{k_B T_1} = \frac{\partial S_1}{\partial E_1}(E_1 + \epsilon) = \frac{1}{k_B T} + \frac{\partial^2 S_1}{\partial E_1^2}$$

$$\frac{1}{k_B T_2} = \frac{\partial S_2}{\partial E_2}(E_2 - \epsilon) = \frac{1}{k_B T} + \frac{\partial^2 S_2}{\partial E_2^2}$$

and both temperature become equal if there is no perturbation in energy $\epsilon = 0$, inducing the temperature imbalance. Therefore, the time evolution of entropy

$$\frac{\partial S}{\partial t} = \dot{\epsilon}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{J.565}$$

is driven by the rate of change of energy, and aims at establishing an equilibrium.

J.4.2 Reversibility in classical mechanics

Classical mechanics is perfectly time-reversible, not only in the Newtonian equation of motion, but in the Hamiltonian description as well: The Hamilton-function and the corresponding equations of motion

$$\mathcal{H} = \frac{p^2}{2m} \quad\rightarrow\quad \frac{\partial \mathcal{H}}{\partial p} = \dot{x}, \quad \frac{\partial \mathcal{H}}{\partial x} = -\dot{p} \tag{J.566}$$

are inveriant under the transformation $t \longrightarrow -t$, because the canonical momentum transforms as

$$p = \frac{\partial \mathcal{L}}{\partial \dot{x}} \rightarrow -p \tag{J.567}$$

as a consequence of the sign change of $\dot{x}$, and keeping in mind that the time-derivative brings in another minus sign. While this is fundamentally true for any Hamiltonian system and while reversibility of the microscopic world is certainly given, observing reversible processes become very unlikely in the macroscopic world, where the system moves towards increasing its entropy in irreversible processes.

Coming back to the go-to example of the harmonic oscillator with spring constant k and invoking equipartition between potential and thermal energy

$$\frac{k}{2}\langle x^2\rangle = \frac{1}{2}k_B T, \quad \to \quad \langle x^2\rangle = \frac{k_B T}{k} \tag{J.568}$$

one can compute a typical amplitude for a fluctuation amounting to the thermal energy $k_B T$. The distribution of amplitudes of an ensemble of harmonic oscillators in thermal equilibrium is then given by the entropy, $S(x) = k_B T \ln p(x)$ and comes out as being Gaussian distributed in the amplitude x (which is only the case of the harmonic oscillator, as potential energy is $\propto x^2$)

$$p(x) = \frac{\exp\left(\frac{S}{k_B}\right)}{\int \mathrm{d}x\, \exp\left(\frac{S}{k_B}\right)} = \sqrt{\frac{k}{2\pi k_B T}} \exp\left(-\frac{k}{k_B T}\frac{x^2}{2}\right) \tag{J.569}$$

The probability of observing large amplitudes $|x| \gg \sqrt{\frac{k_B T}{k}}$ in a system with a typical spring constant k in thermal equilibrium with temperatures that we are used to are very, very unlikely, as

$$k_B T \sim 10^{-21}\mathrm{J} \tag{J.570}$$

at room temperature. Vice versa, observing 1J of thermal energy acquired as a fluctuation out of thermal equilibrium happens at the probability of $\exp(-10^{21})$, which is an incredibly small number.

In summary, it is absolutely the case that the microscopic laws of Nature are time-reversible, but macroscopic objects are, in a probabilistic way exempt from thermal fluctuations, as the energies involved are much, much higher than typical thermal energies provided at sensible temperatures.