Fluctuation-dissipation theorem for Brownian motion

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When a particle immersed in a dissipative environment and subject to thermal noise reaches an equilibrium state, a relation between the relative strength of friction and noise must hold. Such relations go under the name "fluctuation-dissipation theorem", and Brownian motion exemplifies one of the simplest cases.

Assume that a macroscopic particle resides in a medium in which it is subject to (*i*) random kicks by smaller particles and (*ii*) a friction force. Its momentum $\boldsymbol{p}$ may then be described by the following *stochastic differential equation*:

$$\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} \;=\; -\Gamma\boldsymbol{p} + \boldsymbol{f}(t)\ . \tag{1}$$

Here $\boldsymbol{f}(t)$ is a stochastic force or "noise", *i.e.*, a random variable, and Γ is a friction constant. It is easy to see that the Green function of the homogeneous differential equation is given by

$$\mathsf{p}_{\mathrm{G}}(t) \;=\; \mathbb{I}\,\mathrm{e}^{-\Gamma t}\,\Theta(t)\ . \tag{2}$$

A particular solution of Eqn. (1) results from the convolution of the stochastic force (*i.e.*, the inhomogeneity) with the Green function:

$$\begin{aligned}\boldsymbol{p}(t) \;&=\; [\mathsf{p}_{\mathrm{G}} * \boldsymbol{f}](t) \\ &=\; \int_{-\infty}^{\infty}\mathrm{d}t'\ \Theta(t')\mathrm{e}^{-\Gamma t}\,\mathbb{I}\boldsymbol{f}(t-t') \\ &=\; \int_{0}^{\infty}\mathrm{d}t'\ \mathrm{e}^{-\Gamma t'}\boldsymbol{f}(t-t')\ .\end{aligned} \tag{3}$$

Let the following two relations hold for the average and the covariance of the noise:

$$\langle \boldsymbol{f}(t)\rangle \;=\; 0\ , \tag{4a}$$

$$\langle \boldsymbol{f}(t_1)\cdot\boldsymbol{f}(t_2)\rangle \;=\; C(t_1-t_2)\ . \tag{4b}$$

Note in particular that we assume the covariance only to depend on the difference of the times t_1 and t_2.[1] Also, C must be an even function, since the left hand side of Eqn. (4b) is symmetric in t_1 and t_2. For the expectation value of the momentum we find:

$$\begin{aligned}\langle\boldsymbol{p}^2\rangle \;&=\; \left\langle\int_0^{\infty}\mathrm{d}t_1\,\mathrm{e}^{-\Gamma t_1}\boldsymbol{f}(t-t_1)\int_0^{\infty}\mathrm{d}t_2\,\mathrm{e}^{-\Gamma t_2}\boldsymbol{f}(t-t_2)\right\rangle \\ &=\; \int_0^{\infty}\mathrm{d}t_1\int_0^{\infty}\mathrm{d}t_2\ \mathrm{e}^{-\Gamma(t_1+t_2)}\,C(t_1-t_2)\ .\end{aligned} \tag{5}$$

The form of the integrand suggests that it is useful to transform to the following new time-variables:

$$\begin{aligned}t_- \;&=\; t_1-t_2 \\ t_+ \;&=\; \tfrac{1}{2}(t_1+t_2)\end{aligned} \quad\Rightarrow\quad \frac{\partial(t_-,t_+)}{\partial(t_1,t_2)} = \begin{vmatrix} 1 & -1 \\ \frac{1}{2} & \frac{1}{2}\end{vmatrix} = 1\ . \tag{6}$$

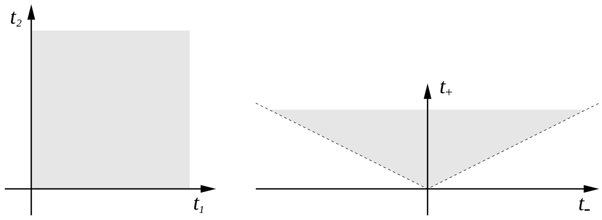

FIG. 1: Transformation of the range of integration under the substitution from Eqn. (6): The region $t_1, t_2 \geq 0$ is mapped onto the region $t_+ \geq \frac{1}{2}|t_-|$.

It is important to note that the range of integration for t_+ and t_- is different from the range for t_1 and t_2. This is illustrated in Fig. 1. The integral in Eqn. (5) now becomes

$$\begin{aligned}\langle\boldsymbol{p}^2\rangle \;&=\; \int_{-\infty}^{\infty}\mathrm{d}t_-\ C(t_-)\int_{|t_-|/2}^{\infty}\mathrm{d}t_+\ \mathrm{e}^{-2\Gamma t_+} \\ &=\; \frac{1}{2\Gamma}\int_{-\infty}^{\infty}\mathrm{d}t_-\ C(t_-)\,\mathrm{e}^{-\Gamma|t_-|} \\ &=\; \frac{1}{\Gamma}\int_0^{\infty}\mathrm{d}t_-\ C(t_-)\,\mathrm{e}^{-\Gamma t_-}\ .\end{aligned} \tag{7}$$

In the last step we used the fact that C is even. If we denote the Laplace-transform of C with C^*, Eqn. (7) is briefly written as

$$\langle\boldsymbol{p}^2\rangle \;=\; \frac{C^*(\Gamma)}{\Gamma}\ . \tag{8}$$

If the random kicks and the friction are to model a canonical thermal heat bath, the equipartition theorem must hold, which implies

$$\frac{\langle\boldsymbol{p}^2\rangle}{2m} = \frac{d}{2}\,k_{\mathrm{B}}T, \tag{9}$$

where d is the dimension of space. Inserting this into Eqn. (8) yields

$$\Gamma \;=\; \frac{C^*(\Gamma)}{dmk_{\mathrm{B}}T}. \tag{10}$$

This is the relation that we were looking for, and it is an example of a *fluctuation-dissipation-theorem*: The correlation function of the fluctuating force is related to the friction coefficient, *i.e.*, to the dissipation.

In many cases the time for the fluctuation function $C(t)$ to decay is much smaller than the typical relaxation time $1/\Gamma$.[2] When computing the Laplace-integral, $C(t)$ has decayed to zero long before $\mathrm{e}^{-\Gamma t}$ has significantly changed from 1. Hence, one may evaluate the Laplace-transform at $\Gamma = 0$:

$$\Gamma \;\approx\; \frac{C^*(0)}{dmk_\mathrm{B}T} \;=\; \frac{1}{2dmk_\mathrm{B}T}\int_{-\infty}^{\infty} \mathrm{d}t\, C(t) \tag{11}$$

Special case: For δ-correlated stochastic forces[3] Eqn. (11) can be simplified even further. Assuming that the correlator can be written as

$$C(t) = C_0\, \delta(t), \tag{12}$$

an evaluation of the integral gives

$$\Gamma \;=\; \frac{C_0}{2dmk_\mathrm{B}T} \qquad \Rightarrow \quad C_0 \;=\; 2d\Gamma mk_\mathrm{B}T. \tag{13}$$

In molecular dynamics simulations this relation is sometimes used to thermostat the system. If a stochastic force and a friction coefficient are introduced which satisfy Eqn. (13), the system will converge toward the canonical state with temperature T.

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[1] One says that the stochastic process is "homogeneous".

[2] This is *e.g.* true if the mass of the Brownian particle is much larger than the mass of the little molecules that push it.

[3] This is sometimes called "white noise".