Figure 1: The robust appearance of Robert Brown (1773–1858)

1 Brownian motion and the Langevin equation

In 1827, while examining pollen grains and the spores of mosses suspended in water under a microscope, Brown observed minute particles within vacuoles in the pollen grains executing a jittery motion. He then observed the same motion in particles of dust, enabling him to rule out the hypothesis that the motion was due to pollen being alive. Although he did not himself provide a theory to explain the motion, the phenomenon is now known as Brownian motion in his honour.

1.1 Derivation

The Langevin equation is Newtons second law for a Brownian particle, where the forces include both the viscous drag due to the surrounding fluid and the fluctuations caused by the individual collisions with the fluid molecules.

In order to describe the statistical nature of the force fluctuations we state the Central limit theorem, which we have already proved in the special case of a random walk:

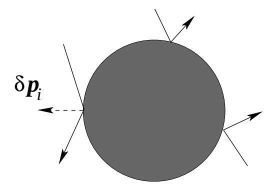

Figure 2: Fluid molecules hitting a suspended particle

When a variable ΔP is a sum of independent increments,δp_i, like a random walk

$$\Delta P = \sum_{i=1}^{N} \delta p_i \tag{1}$$

where $\langle \delta p_i \rangle = 0$ and $\langle \delta p_i^2 \rangle = \sigma$, then, when N is large, the random variable ΔP has a Gaussian distribution with $\langle \Delta P^2 \rangle = N\sigma$.

Now, take δp_i to be the x-component of the momentum transfer to the Brownian particle from a molecular collision, and let N be the number of collisions during the time Δt. Then ΔP is the x-component of the momentum received by the Brownian particle during the time Δt, and $\langle \Delta P^2 \rangle \propto \Delta t$. The corresponding force $\Delta P / \Delta t$ will have a variance

$$\langle \tilde{F}_x^2 \rangle = \frac{\langle \Delta P^2 \rangle}{\Delta t^2} \propto \frac{1}{\Delta t} \ . \tag{2}$$

In a computer simulation of a Brownian particle one would have to integrate Newtons second law for the particle picking a random force $\tilde{F}(t)$ from a Gaussian distribution at every timestep Δt. Will this force be correlated from time step to time step? No, not as long as Δt is larger than the correlation time of the forces from the molecules which is of the order a few mean free times of the molecules.

When this requirement is fullfilled we may hence write the correlation function as

$$\langle \tilde{F}_x(t)\tilde{F}_x(0)\rangle = \begin{cases} \frac{a}{\Delta t} & \text{when} \quad |t| < \Delta t/2 \\ 0 & \text{when} \quad |t| > \Delta t/2 \end{cases} \tag{3}$$

where the constant a could in principle be determined from the variance of Δp_i. In stead we will determine it from the equipartition principle. In the $\Delta t \to 0$ limit the above equation becomes

$$\langle \tilde{F}_x(t)\tilde{F}_x(0)\rangle = a\delta(t) \ , \tag{4}$$

and likewise for the other spatial comnponents of the force which will all be independent of each other.

The regression hypothesis requires that on the average a particle velocity fluctuation will decay as a macroscopic velocity perturbation. Since $\langle \tilde{F}\rangle = 0$ the fluctuating force by itself will cause no average decay of the velocity. The macroscopic decay we need is the one caused by viscosity, i.e. $m\dot{v} = -\alpha v$ where m is the particle mass, v is the velocity relative to the surrounding fluid, and α is a constant coefficient, which for a sphere which is small (but larger than a Brownian particle), has the exact form $\alpha = 6\pi\eta r$, where η is the viscosity, r is the spheres radius. This friction law is known as Stokes law, and it is valid when the sphere moves at moderate speeds relative to a viscous fluid.

A version of Newtons 2. law which is consistent with the regression hypothesis, and at the same time takes the fluctations into account is the Langevin equation

$$m\frac{d\mathbf{v}}{dt} = -\alpha\mathbf{v} + \tilde{\mathbf{F}} \tag{5}$$

where each component of $\tilde{\mathbf{F}}$ has a Gaussian distribution of magnitudes, and a correlation function given by Eq. (4). Both forces on the right hand side above come from the molecular fluid. The drag force $-\alpha\mathbf{v}$ represents the velocity dependence, and it is therefore reasonable to postulate that $\tilde{\mathbf{F}}$ is velocity-independent, and therfore

$$\langle \tilde{F}_i v_j\rangle = 0 \tag{6}$$

where i and j are Cartesian indices.

1.2 Velocity auto-correlation function

The first thing we compute from Eq. (5) is the velocity autocorrelation function. For simplicity we will start out in one dimension, since the generalization to higher dimensions is straightforward. Multiplying Eq. (5) by $e^{\alpha t/m}/m$ we can then write it as

$$\frac{d}{dt}\left(v(t)e^{\frac{\alpha t}{m}}\right) = e^{\frac{\alpha t}{m}}\frac{\tilde{F}(t)}{m} \tag{7}$$

which can be intergrated from $t = -\infty$ to give

$$v(t) = \int_{-\infty}^{t} dt' e^{\frac{-\alpha(t-t')}{m}}\frac{\tilde{F}(t')}{m} \tag{8}$$

where $e^{\frac{-\alpha t}{m}}$ plays the role of a response function. The velocity auto-correlation function now follows directly as

$$\begin{aligned}
\langle v(t)v(0)\rangle &= \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt'' e^{\frac{-\alpha(t-t'-t'')}{m}} \frac{\langle \tilde{F}(t')\tilde{F}(t'')\rangle}{m^2} && (9)\\
&= \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt'' e^{\frac{-\alpha(t-t'-t'')}{m}} \frac{a\delta(t'-t'')}{m^2} && (10)\\
&= \int_{-\infty}^{0} dt'' e^{\frac{-\alpha(t-2t'')}{m}} \frac{a}{m^2} = \frac{a}{2m\alpha}e^{\frac{-\alpha t}{m}} && (11)
\end{aligned}$$

where we have used Eq. (4) and the fact that the average $\langle ...\rangle$ commutes with the integration. Note that the first integration above is over t'. Assuming $t > 0$ this guarantees that the $t' = t''$ at some point during the integration and the a non-zero value of the δ-function is sampled. The above result is in agreement with the regression hypothesis since a macroscopic perturbation $\overline{v}$, which is governed by $d\overline{v}/dt = -\alpha\overline{v}$, decays as $\overline{v}(t) = e^{-\alpha t/m}\overline{v}(0)$.

We may combine Eq. (11) with the equipartition principle to fix a. Since

$$\frac{1}{2}m\langle v^2\rangle = \frac{kT}{2} \tag{12}$$

we get

$$a = 2\alpha kT\ . \tag{13}$$

In other words, the magnitude of the fluctuations increase both with temperature and friction.

1.3 The Langevin equation and diffusion

We may integrate the velocity over time to get the displacement $x(t)$, and the diffusive behavior linked to the variance $\langle x^2(t)\rangle$. Note that this is a refinement of the random walker, since now the step length is governed by the integration of Newtons 2. law.

Starting from Eq. (8) and using Eq. (4) we get

$$\begin{aligned}\langle x^2(t)\rangle &= \int_0^t dt' \int_0^t d\bar{t}' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{\bar{t}'} d\bar{t}'' e^{\frac{-\alpha(t'-t''+\bar{t}'-\bar{t}'')}{m}} \frac{2\alpha kT\delta(t''-\bar{t}'')}{m^2} && (14)\\ &= \frac{2\alpha kT}{m^2}\int_0^t dt' \int_0^t d\bar{t}' \int_{-\infty}^{t'} dt'' \Theta(\bar{t}'-t'') e^{\frac{-\alpha(t'+\bar{t}'-2t'')}{m}} && (15)\end{aligned}$$

where the Heaviside function $\Theta(t)$, which is 1 for $t > 0$ and zero otherwise, appeared because the integration over the δ-function is nonzero only if its argument passes 0. The Θ-function will be 0, however, only if $\bar{t}' < t'$, so we get

$$\langle x^2(t)\rangle = \frac{2\alpha kT}{m^2}\int_0^t dt' \int_0^t d\bar{t}' \int_{-\infty}^{\min(t',\bar{t}')} dt'' e^{\frac{-\alpha(t'+\bar{t}'-2t'')}{m}} \ . \quad (16)$$

The three remaining integrals are straightforward and gives

$$\langle x^2(t)\rangle = \frac{2\ kT}{\alpha}\left(t - \frac{m}{\alpha}\left(1-e^{\frac{-\alpha t}{m}}\right)\right) \ . \quad (17)$$

When $t \gg m/\alpha$ only the t-term survives and $\langle x^2(t)\rangle = 2Dt$ with

$$D = \frac{kT}{\alpha} \ . \quad (18)$$

This relation is known as the Einstein relation. Like the fluctuation-disspation theorem it relates quantities related to spontaneous fluctuations, D and kT, with a quantitt that describe macroscopic decay, α. We could also have derived the Einstein relation directly from the Green-Kubo relation between D and the integral over the velocity autocorrelation function.

When $t \ll m/\alpha$ we Taylor expand the exponential to second order to get

$$\langle x^2(t)\rangle = \frac{kT}{m}t^2 \ , \quad (19)$$

that is $\sqrt{\langle x^2(t)\rangle} = v_{th}t$ where $v_{th}^2 = kT/m$ is exactly the thermal velocity that follows from the equipartition principle. Having a finite correlation time m/α

for the velocity the Langevin equation thus describes the crossover between the ballistic regime $\sqrt{\langle x^2(t)\rangle} \propto t$ to the diffusive regime $\sqrt{\langle x^2(t)\rangle} \propto \sqrt{t}$.

The Langevin equation is based on the approximation that the friction force has the instantaneous value $-\alpha\mathbf{v}$ and does not depend on the history of the motion. However, the amount of momentum given off by the Brownian particle does depend on the motion-history, and this momentum will change the velocity of the surrounding fluid, which in turn changes the force on the Brownian particle. A correct description then does take the history dependence of the force into account, and this changes the velocity correlation function: In the long time limit the correlation function changes from the $e^{-\alpha t}$ behavior to an $1/t^{d/2}$ behavior, where d is the dimension. This was discovered in the late 1960's, first through computer simulations, then analytically.

Langevin equations show up also outside physics. Stock prises for instance are often described by a Langevin equation.