IV.2.2. Fluctuating Dissipative Forces

The above random-walk model is not purely academic, or for illustrative purposes and simplicity only. There are actually many processes in nature that have random-walk-like features. The folding of large organic molecules (proteins) is an example of a problem in modern chemistry that is addressed in terms of (self-avoiding) random-walk processes. ***Brownian Motion*** is a good physical example for a random-walk process in three dimensions. This term describes the erratic motion of a relatively heavy particle moving in a thermally agitated medium, like pollen particles in warm air. In the following, some of the important characteristics of Brownian motion, which are entirely due to molecular interactions, will be discussed.

Collisions of the gas molecules with the Brownian particle can be modeled with a randomly fluctuating "***Langevin force***" ***F(t)***, which has a chaotic time dependence. For simplicity, only one degree of freedom (x) will be considered here for the Brownian particle of mass M. Then, the equation of motion of the Brownian particle for this degree of freedom can be expressed as (see Equ. II.33)

$$M\ddot{x} = F(t) \qquad \text{(IV.52)}$$

Like all quantities related to the chaotic motion of microscopic gas particles in thermal motion, the stochastic force due to molecular interactions has a probability distribution defining an average smooth force and its fluctuating part, the latter including possible higher moments. Therefore, it is reasonable to decompose the random force into at least these two components, such that the equation of motion for the Brownian particle reads

$$M\ddot{x} = \langle F(t) \rangle + L(t) \qquad \text{(IV.52a)}$$

It is the fluctuating part ***L(t)*** that is commonly called ***Langevin force***. Since the average has been separated out, the Langevin force has no average, i.e.,

$$\langle L(t) \rangle = 0 \qquad \text{(IV.52b)}$$

Therefore, the equation of motion for the average position and velocity is simply

$$M\langle \ddot{x} \rangle = \langle F(t) \rangle \qquad \text{(IV.52c)}$$

Because of this feature, the fluctuating part does not lead to a significant deviation of the Brownian particle from its average trajectory. This force just induces fluctuations around the average path. Before discussing further the effects of the Langevin force ***L(t)***, the average force $\langle F(t) \rangle$component will be considered. It turns out that there is a significant average molecular effect on the Brownian particle. This effect leads to ***dissipation, friction and viscosity*** that the particle experiences on its path through the medium.

Consider a disc, or piston, representing schematically a massive Brownian body moving with velocity $\vec{u}$ through a gas at temperature T. The velocity of the body should be small in comparison with typical velocities of the gas particles. Otherwise, more complicated effects like compression of the gas, leading to sound waves, and wake turbulence have to be taken into account. The disc receives a recoil momentum in each collision with a gas molecule. Obviously, the disc collides with more particles on its front face than on its back. Since the collision rate is

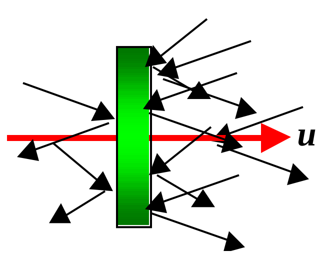


Figure IV-9: Origin of friction

proportional to the relative velocity of disc and gas particles (see Sect. III.4), the forward velocity $\boldsymbol{u} = \boldsymbol{u_x}$ of the Brownian disc causes a boost to this rate. A fast-moving disc has little chance to be hit from the back. Therefore, the combined effect of all collisions results in a ***net frictional drag***, at least in this approximation. As will be shown next, this basic asymmetry is responsible for the generation of dissipative forces.

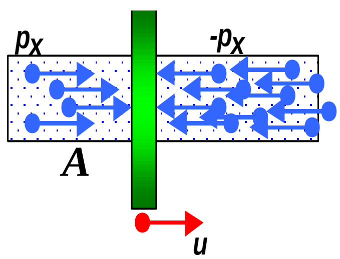


Figure IV-10

As illustrated in the figure, particles with velocities v_x hit the disc of area $\boldsymbol{A}$ from front and back, and impart each a momentum, approximately equal to $-2p_x$ or $+2p_x$ on it, respectively. Differences in momentum transfers will give rise to higher-order effects, which are neglected in the ***present first-order approximation***. The gas particles of mass m have a uniform, isotropic Boltzmann-type probability distribution $f(\vec{r},\vec{p}) = \rho(\vec{r})\, f(\vec{p})$. This is a joint distribution for position and momentum, given by a product of particle density ρ and momentum distribution f. It is assumed that this joint probability distribution is not disturbed by the motion of the disc. This implies ***slow motion of the disc in comparison to the gas particles***.

Under these idealistic conditions, one calculates for the number of particles colliding with the disc on its back within time interval Δt,

$$dN_B = d^3\vec{p}\, f(\vec{r},\vec{p})\left[\left|v_x\right| - u\right] A dt \qquad \text{(IV.53a)}$$

Similarly, one has for the number of particles colliding with the front side of the disc,

$$dN_F = d^3\vec{p}\, f(\vec{r},-\vec{p})\left[\left|v_x\right| + u\right] A dt \qquad \text{(IV.53b)}$$

For a Boltzmann distribution, $f(\vec{r},-\vec{p}) = f(\vec{r},+\vec{p})$. Then, the net force on the disc due to collisions from either side is given by

$$\begin{aligned} \langle F_x \rangle &= \frac{\Delta p_x}{\Delta t} = \int \frac{dN_B}{\Delta t} 2p_x - \int \frac{dN_F}{\Delta t} 2p_x = \\ &= 2A \int d\vec{p}^3 \; f(\vec{r},\vec{p}) \cdot m|v_x| \left\{ \left[|v_x| - u \right] - \left[|v_x| + u \right] \right\} dt \\ &= -[4Am \int d\vec{p}^3 \; f(\vec{r},\vec{p}) \cdot |v_x|] \cdot u = -\gamma u \end{aligned} \qquad \text{(IV.54)}$$

This average of the fluctuating force,

$$\langle F_x \rangle = -\gamma u_x \quad with \quad \gamma = 4A\rho m \langle |v_x| \rangle \qquad \text{(IV.55)}$$

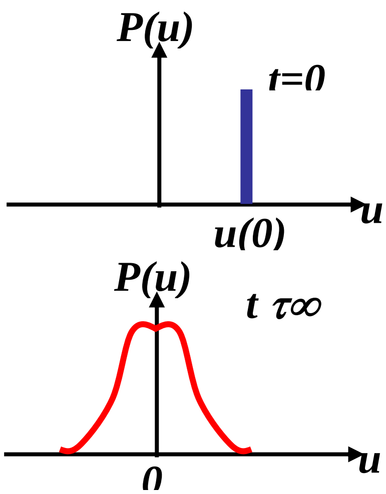
is a ***frictional force***. It is proportional to the velocity of the Brownian body (higher-orders do not appear in the present first-order approximation). Its direction is opposite to the velocity of the disc. Hence, the force tends to slow the motion of the disc down. The constant γ is the ***frictional coefficient*** with the ***dimension of momentum/length***. Hence, the force has the proper dimension of energy/length. The main dependence of the magnitude of the friction coefficient is via the momentum transfer $\langle \Delta q \rangle = 2m \langle |v_x| \rangle$ from the gas particles to the Brownian particle and the "area of attack" *A* exposed to collisions. This dependence is the reason why deformable particles assume a streamlined shape when passing through a viscous medium.

The above considerations provide a simple solution for the equation of motion (cf. Equ. IV. 52c) of the average position $\langle x \rangle = u_x$,

$$\langle \dot{x}(t) \rangle = \langle \dot{x}(t=0) \rangle \cdot e^{-\frac{\gamma}{M} \cdot t} \qquad \text{(IV.55a)}$$

This frictional process leads, hence, to an exponential decay of the average velocity of the Brownian particle to zero! The typical ***relaxation time for the average velocity*** of linear motion is

$$t_{u,relax} \approx \frac{M}{\gamma} \qquad \text{(IV.55b)}$$



The velocity $\langle \dot{x} \rangle = u_x$ decreases rapidly, if the frictional coefficient γ is very large, and it decreases very slowly for a heavy Brownian particle. Once the average velocity of the Brownian particles is close to zero, the Brownian particle exhibits a random trajectory with no preferred direction, like the gas particles. This is a necessary result of the random collisions with the gas particles. The Brownian particle then has a velocity distribution that is very different from the initial distribution, which had just one value ***u(0)*** an no velocity fluctuations, as shown in the figure. ***The dissipation process is associated with increasing fluctuations*** (***Fluctuation-Dissipation Theorem***).

The above derivation can easily be generalized, leading to the friction force

$$\langle \vec{F} \rangle = -\gamma \vec{u} \quad with \quad \gamma = 4A\rho m \langle |v_x| \rangle \qquad \text{(IV.56a)}$$

V-11

Inserting the average speed of the gas particles, as calculated in Equ. III.115c, one predicts a frictional coefficient of

$$\gamma = 4A\rho m \langle |v_x| \rangle = A\rho\sqrt{32mk_BT} \qquad \text{(IV.56b)}$$

Of interest for applications is also that the friction strength depends on the geometrical cross section area ***A*** (*"area of attack"*) of the Brownian particle mentioned previously.

In summary, the random, thermal motion of the gas particles has on ***average a slowing-down effect on the motion of a heavy and slow Brownian particle***. The kinetic energy lost by the Brownian body is mostly transferred to the gas particles and leads to a temperature increase (heating) of the gas. This effect can be described reasonably well by the action of a ***velocity-proportional frictional force***. The strength of the friction force, represented by the friction coefficient γ, increases with the particle density, the mass and the speed of the particles of the gaseous medium, which in turn depends on the temperature of the medium. It is somewhat counterintuitive that a ***higher temperature leads to higher frictional drag*** exerted by combined effect of the particles in a gas. Dissipation leads also to increased fluctuations, which will be dealt with further below.

Friction of the type discussed above is naturally also experienced by the particles of a gas (or a liquid) themselves, when there is an overall mismatch of velocities. This occurs, for example, when there are layers of particles streaming past each other with different overall velocities, i.e., when a velocity gradient du/dx exists.

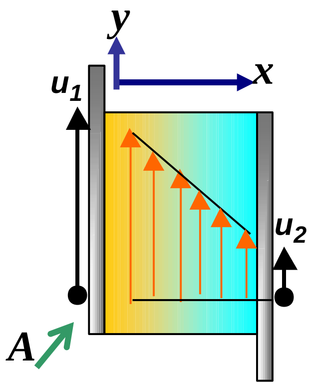


Figure IV-12: Viscosity in liquids

Consider two equal plates moving parallel to each other with velocities ***u_1*** and ***u_2*** in ***y direction***. The plates are separated by a layer of liquid or gas of thickness ***Δx***, wetting an area of ***A*** on the inside of both plates. The fluid or gas films directly at the plate surfaces have velocities very nearly equal to the respective plate velocities, a behavior enforced by friction. Because of the difference ***$\Delta u = u_1 - u_2$*** in plate velocities, a velocity gradient will eventually be established in the fluid or gas layer between the plates, as indicated in the figure. In moving the plates, adjacent gas/liquid layers move against each other and experience friction (viscosity). As a consequence, moving the plates parallel to each other with a constant relative velocity requires a force and costs energy, which is dissipated within the gas/liquid layer between the plates. This dissipative process is termed ***viscosity***. It can be described by the viscous friction force

$$F_y = -\eta A \cdot \frac{\Delta u}{\Delta x} \qquad \text{(IV.57)}$$

That is, the frictional force between the plates retards the motion in *y* direction. It is proportional to the velocity gradient ***Δu/Δx*** perpendicular to the plates and proportional to the wetted area ***A***. The proportionality factor is called ***viscosity coefficient η***. This coefficient is measured in units of ***Poise (****1 p = 1g/cm s****)***. Some typical values for liquids and gases are quoted in the table. Note the different orders of magnitude and the different behavior with increasing temperature.

Table IV-2: Viscosity Coefficients

Liquids	**η/mp (0°C)**	**η/mp (20 °C)**	**η/mp (30 °C)**	**η/mp (50 °C)**
Water	17.921	10.050	8.007	5.494
Acetone	4.013	3.311		2.561
Glycerol	42200 (2.8 °C)	10690		
Gases	**η/μp (200K)**	**η/μp (300K)**	**η/μp (1000K)**	
Nitrogen	129.5	178.6	401.1	
Oxygen	147.6	207.1	472.0	
Argon	159.4	227.0	530.2	

Having evaluated the ***average behavior of fluctuating forces***, the discussion returns now to the fluctuating Langevin term. The equation of motion (Equ. IV-52) for the fluctuating force can now more specifically be expressed as

$$M\ddot{x} = -\gamma \cdot \dot{x} + L(t) \qquad \text{(IV.58)}$$

with a Langevin force that has zero average, $\langle L(t) \rangle = 0$, calculated with respect to all interactions with gas particles. Although the average fluctuating force is zero, its higher order moments have effects. They lead notably to a dispersion of the trajectories about the average path. The general treatment of the fluctuating part of the force can be rather involved. However, the important effects can already be gleaned from the consideration of a schematic model force.

This model of a Langevin force is constructed from a random succession of short "kicks" of the Brownian particle from all sides. Such a force can be approximated by a superposition of delta-function-***like pulses***, such as illustrated in the figure. Such a pulse can be constructed in a number of ways. A simple method illustrated in the code (MATHCAD_252\Rand_Force.mcd) constructs a rectangular pulse by subtracting two Heaviside step functions, $\Theta(t)$, shifted with respect to one another by the bin width Δt:

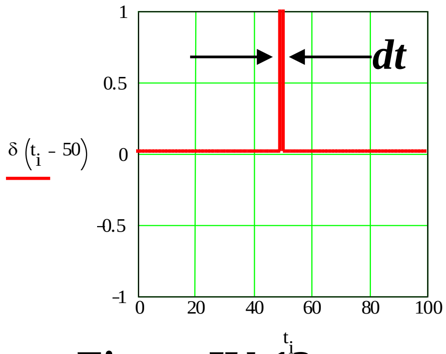


Figure IV-13: Delta function

$$\delta(t) = \frac{1}{\Delta t}\left[\Theta(t+\frac{\Delta t}{2}) - \Theta(t-\frac{\Delta t}{2})\right] \qquad \text{(IV.59)}$$

This function describes a unipolar pulse of unit height and a width of Δt, which is centered at time t. It is an obvious property of this function that, when folded with a function $f(t)$, it projects out the value of this function at the position of the delta function:

$$f(t_0) = \int d\tau\, f(\tau)\cdot\delta(\tau - t_0) \qquad \text{(IV.60)}$$

Using this approximation of the delta function, a series of brief kicks can be simulated by a sum of N identical force pulses, except that positive and negative directions occur with equal statistical weights, such that there is not net effect by the train of pulses. This superposition

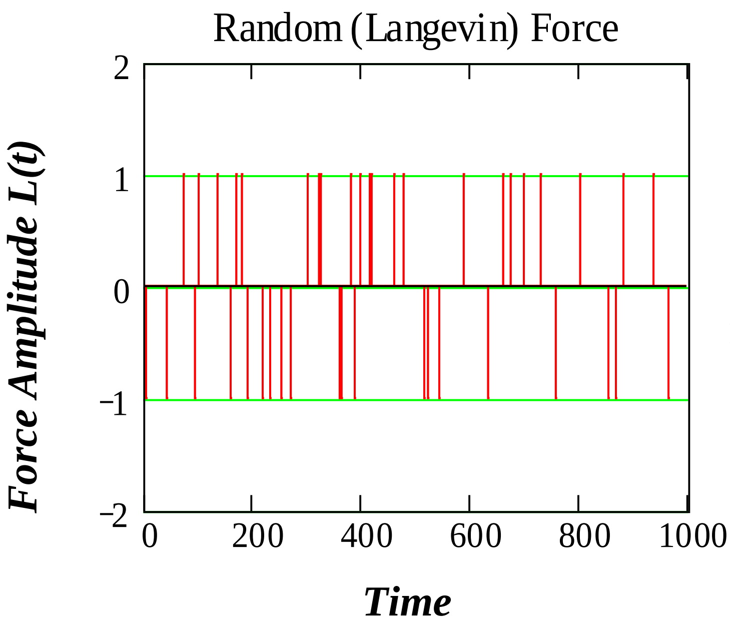


Figure IV-14: Random force

$$L(t) = \varphi \sum_{n=0}^{N} (-1)^n \times$$
$$\times \delta(t - rnd(1000) \cdot \Delta t)$$
(IV.61)

is, therefore, an appropriate representation of a Langevin force. The Langevin force of Equ. IV.61 has the general form of

$$L(t) = \varphi \sum_{n=0}^{N} (\pm 1)_n \cdot \delta(t - t_n)$$
(IV.62)

In Equ. IV.61, the positions for the large, ideally infinite number ($N \to \infty$) of total pulses are distributed by a random-number generator (***rnd(…)***) in a very large time interval $0 \le t_i \le 1000 \cdot \Delta t$. The factor φ is the common amplitude of all force kicks. The direction of each force kick is decided by the sign factor *(-1)^n* . Both directions appear with equal probabilities. In the expression of Equ. IV.62, the sign factor $(\pm 1)_n$ is a random sign factor, changing randomly from *+1* to *-1* for the different times t_i .

The average of the fluctuating force *L(t)* is defined as an average over an arbitrary time interval $-T/2 \le t \le +T/2$. For example, one calculates for he average of the force of Equ. IV.62:

$$\langle L(t) \rangle = \left\langle \varphi \sum_{n=0}^{N} (\pm 1)_n \cdot \delta(t - t_n) \right\rangle = \varphi \sum_{n=0}^{N} (\pm 1)_n \cdot \langle \delta(t - t_n) \rangle$$
$$= \varphi \sum_{n=0}^{N} (\pm 1)_n \frac{1}{T} \int_{-T/2}^{+T/2} dt\, \delta(t - t_n) = \frac{\varphi}{T} \sum_{n=0}^{N} (\pm 1)_n \approx 0$$
(IV.63)

The integral in this equation, divided by the length of the integration interval defines the time average in an intuitive way. The averaging interval should be chosen long enough to cover many individual pulses represented by the delta functions at the different times t_i. Each of the integral is then equal to *1/T*. Obviously, the forces of Equs. IV.61 and 62 have no net average over time, as is required by construction (see Equ. IV.52b). This is insured by the alternating signs of the individual random force pulses.

In addition, because of the random distribution in time of the force pulses, there is ***no memory of the past*** contained in these kicks. This latter behavior is typically expressed in terms of the ***time-correlation function C***,

$$C(\tau) = \langle L(t) \cdot L(t+\tau) \rangle \qquad \text{(IV.62)}$$

which is defined as the time average of the product of the fluctuating force *L(t)* with itself but shifted by some time τ. Only for $\tau = 0$ can one expect a non-zero average. In the latter case, one gets again a single delta-function-like pulse, such that the fluctuating force fulfills the requirements

$$\langle L(t) \rangle = 0 \quad and \quad \langle L(t) \cdot L(t+\tau) \rangle = 2K \cdot \delta(\tau) \qquad \text{(IV.63)}$$

Here, *K* is the amplitude of the average pulse, divided by the time interval *T*.

The solution of the equation of motion (see Equ. IV.58) can now be given:

$$u(t) = \dot{x}(t) = \dot{x}(t) \cdot e^{-\frac{\gamma}{M} \cdot t} + \frac{1}{M} \int_0^t d\tau \, e^{-\frac{\gamma}{M} \cdot (t-\tau)} L(\tau) \qquad \text{(IV.64)}$$

One proves by differentiation, that this function does in fact fulfill the equation of motion for the Brownian particle. In Equ. IV.64, the first term disappears fairly rapidly, as time passes, while the second term does not. As discussed previously (cf. Equ. 55a), the former term represents the frictional slowing-down process, the loss of the average velocity. One may neglect this term, except for times of the order of the slowing-down time ($t_{u,relax}$).

The above expression for the velocity $u = u_x$ actually defines a ***velocity distribution at each time t, since L(t) represents such a distribution***. This distribution has a zero average, but not necessarily zero higher moments. For larger times, one can neglect the first term in Equ. IV.64 and calculate the mean-square velocity:

$$\left\langle u^2(t) \right\rangle = \frac{1}{M^2} \left\langle \int_0^t d\tau\, e^{-\frac{\gamma}{M}\cdot(t-\tau)} L(\tau) \int_0^t d\tau'\, e^{-\frac{\gamma}{M}\cdot(t-\tau')} L(\tau') \right\rangle \qquad \text{(IV.65)}$$

The integrals over τ and τ' represent the functional dependence of the velocity as defined by the equation of motion for any force and does, by itself, not lead to any fluctuations in *u*. The only fluctuating entities in Equ. IV.65 are the terms $L(\tau)$ and $L(\tau')$. Hence, the integrals are not affected by the averaging process and can be taken out of the angle brackets,

$$\begin{aligned} \left\langle u^2(t) \right\rangle &= \frac{1}{M^2} \int_0^t d\tau\, d\tau'\, e^{-\frac{\gamma}{M}\cdot(2t-\tau-\tau')} \left\langle L(\tau)\cdot L(\tau') \right\rangle \\ &= \frac{2K}{M^2} \int_0^t d\tau\, d\tau'\, e^{-\frac{\gamma}{M}\cdot(2t-\tau-\tau')} \delta(\tau-\tau') \end{aligned} \qquad \text{IV.66)}$$

The integration over τ' is trivial because of the delta function, yielding

$$\left\langle u^2(t)\right\rangle = \frac{2K}{M^2}\int_0^t d\tau\, e^{-\frac{2\gamma}{M}\cdot(t-\tau)} = \frac{K}{M^2}\frac{M}{\gamma}\left(1-e^{-\frac{2\gamma}{M}t}\right) \quad \text{(IV.67)}$$

This equation shows that fluctuations in the velocity due to random collisions with the gas particles, absent at *t=0*, build up over times of the order of

$$t_{relax} \approx M/2\gamma \quad \text{(IV.68)}$$

This is a relaxation time which is slightly shorter than the slowing-down time $t_{u,relax}$ but of the same order. Therefore, fluctuations develop on the same time scale as the Brownian particle is slowed down, as they should. In the long-time limit, the velocity fluctuations become stationary, the second moment of the velocity distribution no longer changes. Then, the Brownian particle has reached equilibrium with the gas particles and

$$\left\langle u^2\right\rangle \cong \frac{K}{\gamma M} \quad \text{(IV.69)}$$

On the other hand, for this equilibrium situation, it is also known that the energy of random motion has to comply with the equipartition law, according to which

$$\frac{M}{2}\left\langle u^2\right\rangle \cong \frac{M}{2}\frac{K}{\gamma M} = \frac{1}{2}\frac{K}{\gamma} = \frac{1}{2}k_B T \quad \text{(IV.70)}$$

This relation implies that there is a close relation between the time correlation function and the friction coefficient:

$$K = \gamma k_B T \quad \text{(IV.71)}$$

This is an example of a very common relation, the ***Fluctuation-Dissipation Theorem***. It asserts that the moments of a probability distribution for an observable caused by the same random processes are dependent of each other. ***The magnitude of the fluctuations, represented by the constant K, is proportional to the friction coefficient and increases with increasing temperature***.