Contents

Langevin Equation

0.1 Langevin equation

The Einstein's theory of Brownian motion is not a dynamical theory in the Newton's sense since there is no notion either of velocity or acceleration. A more elaborate model that takes into account the inertial effects of the Brownian particles was introduced by P. Langevin in 1908. According to classical mechanics, the motion of a mesoscopic particle in a fluid of microscopic particles would be described by the Netwon's second law:

$$m\frac{d\vec{v}}{dt} = \vec{F}_E + \vec{F}_T \tag{1}$$

where

- $\vec{F}_E$ is the sum of the external forces (gravitational field, electric field etc etc).
- $\vec{F}_T$ is the sum of the forces that each molecule of the fluid exerts on the mesoscopic particle:

$$\vec{F}_T = \sum_i \vec{f}_i. \tag{2}$$

To have a complete description one should consider, in addition to eq. (1), the evolution equations for the fluid particles and the solution of the full problem would correspond to solve $N+1$ coupled differential equations with N comparable to the Avogradro's number. Clearly this is an unsolvable problem and one must rely on simplifications based on physically reasonable assumptions. This is, for example, Langevin's approach to the problem, a phenomenological classical approach, in which the effect of the surrounding fluid on the motion of the mesoscopic particle is described as follows:

Note. If the Brownian particle were a macroscopic object, the hydrodynamic (Stokes law) would tell us that a good (approximate though) description of the interaction particle-fluid is given by considering a viscous force

$$\vec{F}_v = -\alpha\vec{v} \tag{3}$$

where α is the damping coefficient that, for a spherical particle of radius a is given by

$$\boxed{\alpha = 6\pi a\eta} \tag{4}$$

with η being the fluid viscosity. This classical result can be obtained by considering the effect of a uniform flow on a sphere at rest (Navier-Stokes in the Stokes regime with BC).

This is, however, a macroscopic description that cannot explain the never-ending and irregular motion of the Brownian particle since, for $\vec{F}_E = 0$ an exponentially decreasing (and regular) behaviour of the velocity is expected. The Langevin's idea was then to consider *two contributions* for $\vec{F}_T$.

1. The deterministic damping (Stokes) term

$$-\alpha\vec{v} \tag{5}$$

2. A fluctuating term $\vec{F}(t)$ who represents the contributions of the continuous collisions of the fluid molecules with the mesoscopic particle in the reference frame in which the particle is at rest. This force is considered to be independent on the particle velocity but depends on time.

With these hypothesis the equation of motion (Langevin equation) becomes:

$$\boxed{m\frac{d\vec{v}}{dt} = -\alpha\vec{v} + \vec{F}(t), \qquad \vec{v} = \frac{d\vec{r}}{dt}.} \tag{6}$$

The Langevin equation is historically the first example of a $s$tochastic differential equation, that is a differential equation with a random term $\vec{F}(t)$. For this reason the solution itself would be a random function of time, i.e. a stochastic process.

0.2 Hypothesis on the Langevin force

Since the Langevin force $\vec{F}(t)$ is a random variable it is necessary to define its statistics. Let us suppose that we have N different realization of the force $\vec{F}(t)$, $\{\vec{F}_1(t), \vec{F}_2(t), \cdots, \vec{F}_N(t)\}$. For a given realization the Langevin equations are integrable giving a particular solution that depends on the initial conditions. Suppose to consider the same initial condition for all the N realization $v(t=0) = v_0$. In this case the N equations of motions will differ from one another by the term $F_i(t)$. For fixed i the Cauchy problem ((eq. 6) + initial conditions) admit a unique solution and for N realizations of F there would be N distinct solutions $\{\vec{v}_1(t), \vec{v}_2(t), \cdots, \vec{v}_N(t)\}$. This form N realizations of the ensemble of solutions that can be used to perform ensemble averages. It is then important to define the statistical properties of $\vec{F}(t)$.

Hypothesis 0.2.1. Since the friction effect has been already taken into account and that $\vec{F}(t)$ considers just the random effects of the collisions of the fluid molecules with the particle at rest i.e. in a isotropic and homogeneous space, the average of $\vec{F}$ over the realizations must be zero:

$$\boxed{\langle\vec{F}(t)\rangle = \frac{1}{N}\sum_{i=1}^{N}\vec{F}_i(t) = 0 \qquad \forall t \quad \text{and} \quad N >> 1} \tag{7}$$

As a consequence, the effects of the collisions, described by $\vec{F}(t)$ are, in average, zero and the only systematic force acting on the particle would be the friction one.

Note. This hypothesis is necessary to get that, at equilibrium, the average velocity of the particle is zero, as it must be in the case in which no external forces are present.

The correlation function of the force $\vec{F}(t)$ between the times t_1 and t_2 is defined operatively as

$$C_F(t1, t2) \equiv \langle\vec{F}(t_1)\vec{F}(t_2)\rangle = \frac{1}{N}\sum_{i=1}^{N}\vec{F}_i(t_1)\vec{F}_i(t_2). \tag{8}$$

Since the fluid (or thermal bath) is supposed to be in a *stationary state* (actually most of the time it is supposed to be in thermodynamic equilibrium) the average taken at two different times $\langle\vec{F}(t_1)\vec{F}(t_2)\rangle$ depends only on the difference $t_1 - t_2$ and one can write

$$C_F(\tau) = \langle\vec{F}(t)\vec{F}(t+\tau)\rangle. \tag{9}$$

The function $C_F(\tau)$ is even with respect to τ ($C_F(\tau) = C_F(-\tau)$) and in general it decreases with $|\tau|$ with a characteristic time τ_c (*characteristic collision time*).

Hypothesis 0.2.2. We know that in general

$$C_F(\tau) \sim \exp(-t/\tau_c) \tag{10}$$

where τ_c is the correlation time of the Langevin force F related to the collisions with the surrounding fluid. In other words for $\Delta t >> \tau_c$ collision events occurring around t can be considered statistically independent from the ones occurring around $t + \Delta t$. The second assumption is the so called *t*wo time scales hypothesis, i.e. that the collision times τ_c are much smaller that the evolution time of the velocity $\vec{v}$. In other words the time at which a collision occurs is much smaller that all the other characteristic times of the problem such as, for example, the relaxation time m/α of the average of the velocity $\vec{v}$,

$$\boxed{\tau_c << m/\alpha.} \tag{11}$$

One can also say that $\vec{F}(t_1)$ and $\vec{F}(t_2)$ are independent random variables for $|t_1 - t_2| >> \tau_c$. We can then formally write

$$\langle \vec{F}(t_1)\vec{F}(t_2)\rangle = A\delta(t_1 - t_2) \tag{12}$$

where $A \in \mathbb{R}$ is a constant. We have then a δ-correlated random force. One can also say that the random force considered follows the statistics of a *w*hite noise.

Note. Actually the delta function is not a function (but a distribution) and what we have formally written above must be reconsidered in a more careful way. Will we do it later.

Hypothesis 0.2.3. Often, for simplicity, one supposes that $\vec{F}(t)$ is a *Gaussian process.* In this case, given eq. (7), all the statistical properties of $\vec{F}(t)$ are simply obtained by knowing the two points correlation function. This hypothesis can be justified starting from the *central limit theorem*, if one considers that due to the big numbers of fluid molecules surrounding the mesoscopic particle the force $\vec{F}(t)$ can be considered as a sum of a big number of elementary collisions. If $\vec{F}(t)$ is Gaussian process then the constant A is determined by the variance $\langle \vec{F}(t)^2\rangle \equiv \sigma^2$ of the Gaussian distribution and we get

$$\boxed{\langle \vec{F}(t_1)\vec{F}(t_2)\rangle = \sigma^2\delta(t_1 - t_2)} \tag{13}$$

Remark. From the theory of the stochastic processes we know that an uncorrelated Gaussian process is also independent. Hence, on the time scale of the evolution of v the process $F(t)$ is a completely random process.

0.3 Ornstein-Uhlenbeck's integration method

This is a simple and elegant method to find the solution of the Langevin equation [2]. It works nicely in the case of zero external force ($\vec{F}_E = 0$) and for other few cases. For general cases the approach based on the Fokker-Planck equation turns out to be more appropriate. Let us focus for simplicity to the 1D case. The idea is to integrate the Langevin equation of motion for the velocity

$$\frac{dv(t)}{dt} = -\gamma v(t) + A(t) \tag{14}$$

with the initial condition $v(t = 0) = v_0$ and where $\gamma = \alpha/m$ and $A(t) = F(t)/m$ is the fluctuating force per unit mass (fluctuating acceleration). This gives formally

$$v(t) = v_0 e^{-\gamma t} + \int_0^t e^{-\gamma(t-s)} A(s) ds. \tag{15}$$

If we now average over several independent realizations of the stochastic force F keeping the same initial condition $v(0) = v_0$, since $\langle A(t)\rangle_{v_0} = 0$ by hypothesis, we get

$$\boxed{\langle v(t)\rangle_{v_0} = v_0 e^{-\gamma t}.} \tag{16}$$

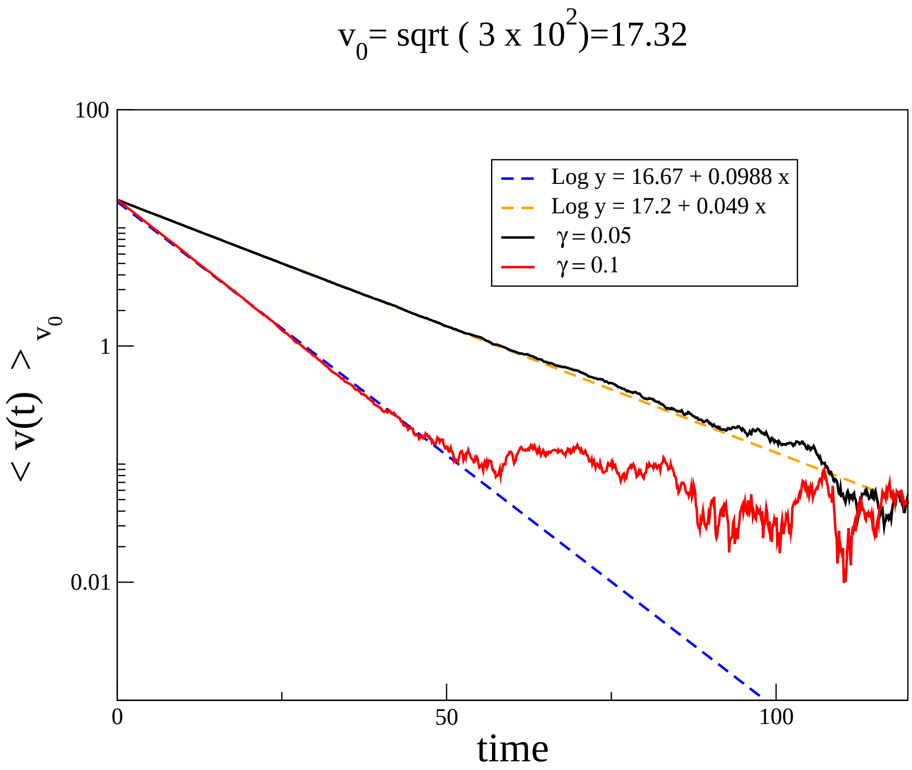

Figure 1: Log-linear plots of the time dependence of the averaged velocity for a Brownian motion in $d = 3$. The velocity has been averaged over 1000 configurations and the two curves correspond to two different values the γ.

The average velocity decreases exponentially to zero due to the damping term $-\gamma v$. Figure 1 shows the time dependence of the velocity averaged over 1000 configurations and for two different values of γ. The model considered is a $d = 3$ Brownian motion. The plot is linear in x and logarithmic in y. The linear behaviour clearly indicates an exponential decay of the average velocity from the initial condition $v_0 = \sqrt{v_{0x}^2 + v_{0y}^2 + v_{0z}^2} = \sqrt{10^2 + 10^2 + 10^2} = 10\sqrt{(}3)$. The estimate of the slopes agrees quite nicely with the real values of the γ parameter.

One can also easily compute the velocity-velocity correlation function

$$\langle v(t_1)v(t_2)\rangle_{v_0} = v_0^2 e^{-\gamma(t_1+t_2)} + \int_0^{t_1} ds_1 \int_0^{t_2} ds_2 e^{-\gamma(t_1-s_1)} e^{-\gamma(t_2-s_2)} \underbrace{\langle A(s_1)A(s_2)\rangle}_{=\frac{\sigma^2}{m^2}\delta(s_1-s_2)} \qquad (17)$$

The term with the double integral can be simplified as follows

$$\begin{aligned}\int_0^{t_1} ds_1 \int_0^{t_2} ds_2 e^{\gamma(s_1+s_2)}\delta(s_1-s_2) &= \\ &= \int_0^{\infty} ds_1 \int_0^{\infty} ds_2 e^{\gamma(s_1+s_2)}\theta(t_1-s_1)\theta(t_2-s_2)\delta(s_1-s_2) \\ &= \int_0^{\infty} ds_1 e^{2\gamma s_1} \underbrace{\theta(t_1-s_1)\theta(t_2-s_1)}_{\theta(\min(t_1,t_2)-s_1)} \\ &= \int_0^{\min(t_1,t_2)} ds_1 e^{2\gamma s_1} \\ &= \frac{1}{2\gamma}\left(e^{2\gamma\min(t_1,t_2)}-1\right). \qquad (18)\end{aligned}$$

By inserting eq. (18) in (17) and by using the identity $t_1+t_2-2\min(t_1,t_2)=|t_1-t_2|$ one obtains

$$\boxed{\langle v(t_1)v(t_2)\rangle_{v_0} = v_0^2 e^{-\gamma(t_1+t_2)} + \frac{\sigma^2}{2m^2\gamma}\left(e^{-\gamma|t_1-t_2|} - e^{-\gamma(t_1+t_2)}\right).} \qquad (19)$$

In particular, for $t_1 = t_2 = t$, one obtains the behaviour of the mean squared velocity:

$$\boxed{\left\langle v^2(t)\right\rangle_{v_0} = v_0^2 e^{-2\gamma t} + \frac{\sigma^2}{2m^2\gamma}\left(1-e^{-2\gamma t}\right).} \qquad (20)$$

Note. The subscript v_0 reminds us that the initial velocity is not a random variable but is a fixed value.

For short time scales the process $v(t)$ is not stationary since its two point correlation function is not simply a function of $t_1 - t_2$. To look for the stationary state one has to consider the limit of long time scales, i.e., for t_1, t_2 very large. In this case one can assume $\gamma t_1 >> 1$ and $\gamma t_2 >> 1$ giving

$$\boxed{\langle v(t_1)v(t_2)\rangle_{v_0} \simeq \frac{\sigma^2}{2m^2\gamma} e^{-\gamma|t_1-t_2|}.} \qquad (21)$$

Relations (16) and (21) indicate that for time scales longer than the characteristic time $1/\gamma$, $v(t)$ is a stationary stochastic process in the weak sense. Note that in this regime the correlation velocity-velocity correlation function does not depend on the initial condition v_0 but only on the time interval $|t_1 - t_2|$. By looking again at the particular case $t_1 = t_2$ we get, for the stationary state,

$$\lim_{t\to\infty} \langle v^2(t)\rangle_{v_0} = \frac{\sigma^2}{2m^2\gamma} \qquad (22)$$

In the large time scale ($t \to \infty$), where the particle reaches a stationary state its average kinetic energy is given by

$$\langle K\rangle_{v_0} = \frac{1}{2}m\langle v^2(t)\rangle_{v_0} = \frac{1}{2}m\frac{\sigma^2}{2m^2\gamma}. \qquad (23)$$

If we now suppose that the stationary state coincides with the state of thermodynamic equilibrium (particle in a thermal bath of temperature T) one can determine the constant σ^2 by assuming that at equilibrium the equipartition of the energy holds that is (we are in $d = 1$):

$$\langle E\rangle = \frac{1}{2}\kappa_B T. \qquad (24)$$

We then have

$$\lim_{t\to\infty} \frac{1}{2}m\langle v^2(t)\rangle = \frac{1}{2}\kappa_B T, \qquad (25)$$

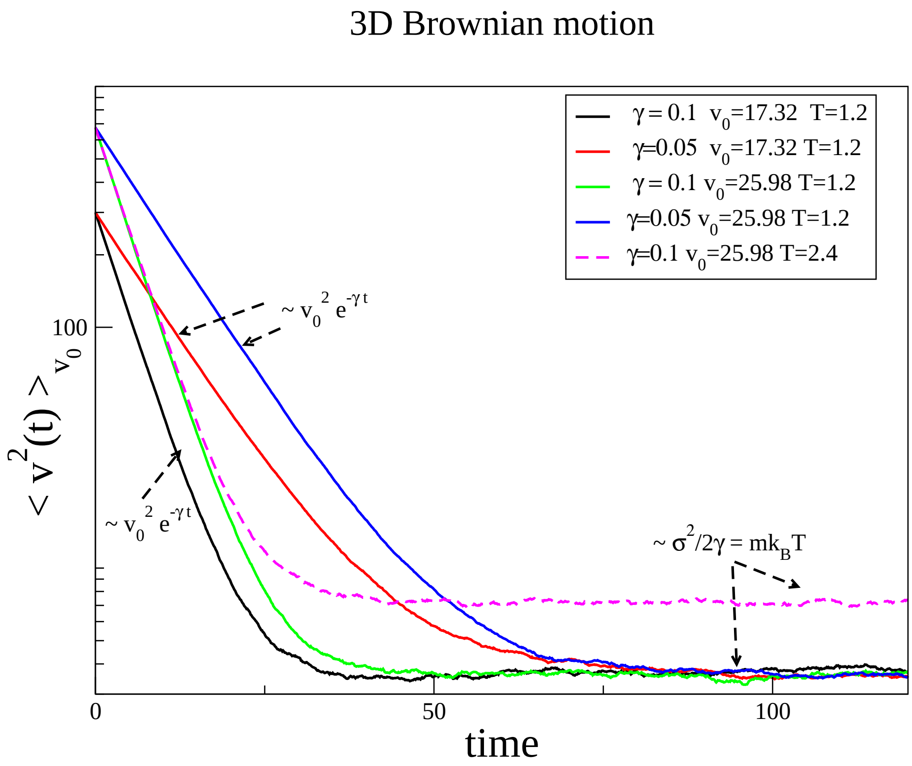

Figure 2: Log-linear plots of the time dependence of the averaged squared velocity for a d=3 Brownian motion. The curves are obtained by averaging over 1000 independent configurations. The two curves correspond to two different values of γ.

giving

$$\boxed{\sigma^2 = 2m\gamma\kappa_B T.} \tag{26}$$

With this value of σ^2 the Langevin equation for $v(t)$ can be written as

$$\boxed{\frac{d}{dt}v(t) = -\gamma v(t) + \sqrt{2m\gamma\kappa_B T}\hat{A}(t),} \tag{27}$$

with $\langle \hat{A}(t_1)\hat{A}(t_2)\rangle = \delta(t_1 - t_2)$. In this respect the Langevin equation describes the thermalization of a particle in a thermal bath at temperature T and with initial velocity v_0.

Note. Remembering that

$$\int_{\mathbb{R}} \langle A(0)A(t)\rangle dt = \int_{\mathbb{R}} \sigma^2\delta(t)dt = \sigma^2 = 2m\gamma k_B T \tag{28}$$

eq. (26) gives

$$\boxed{\gamma = \frac{1}{2m\kappa_B T}\int_{\mathbb{R}} \langle A(0)A(t)\rangle dt.} \tag{29}$$

Eq. (29) says that the deterministic (dissipative) force is expressed in terms of the autocorrelation function of the fluctuating (stochastic) force. This relation is known as the *second theorem of* **fluctuation-dissipation**. Given the importance of this theorems let us formulate it in a more canonical form.

0.3.1 Fluctuation-dissipation theorem for Langevin equation of motion

Suppose we consider a mesoscopic particle moving within a heat bath at temperature T. If an external force $F_E(t)$, is switched on the time evolution of the particle velocity will follow the Langevin equation

$$\frac{dv(t)}{dt} = -\gamma v(t) + \frac{F_E(t)}{m} + \sqrt{2m\gamma k_B T}\hat{A}(t) \tag{30}$$

with

$$\langle \hat{A}(t_1)\hat{A}(t_2)\rangle = \delta(t_1 - t_2). \tag{31}$$

From the theory of linear response we know that due to the presence of an external force $F_E(t)$, the system will respond with a variation of the average velocity field given by

$$\langle v(t)\rangle = \int_{\mathbb{R}} \chi(t-t')F_E(t')dt' = \int_{\mathbb{R}} \chi(t')F_E(t-t')dt' \tag{32}$$

where $\chi(t)$ is the *response function* (or mobility in this case) of the mesoscopic particle. Since the response function must be casual (the response cannot precede the force which causes it), $\chi(t-t') = 0$ if $t - t' < 0$. From the Lagevin equation one has

$$\frac{d}{dt}\langle v(t)\rangle = -\gamma\langle v(t)\rangle + \frac{1}{m}F_E(t) \tag{33}$$

that in Fourier space becomes

$$-i\omega\tilde{\langle v\rangle}(\omega) = -\gamma\tilde{\langle v\rangle}(\omega) + \frac{\tilde{F}_E(\omega)}{m} \tag{34}$$

and since

$$\tilde{\langle v\rangle}(\omega) = \tilde{\chi}(\omega)\tilde{F}_E(\omega) \tag{35}$$

one gets the result

$$\boxed{\tilde{\chi}(\omega) = \frac{1}{m}\frac{1}{\gamma - i\omega}.} \tag{36}$$

On the other hand we have shown that the velocity-velocity correlation function in the stationary state behaves as

$$\langle v(t)v(0)\rangle_s \sim \frac{k_B T}{m} e^{-\gamma|t|} \tag{37}$$

that in Fourier space becomes

$$\tilde{C}_v(\omega) = \int_{\mathbb{R}} e^{i\omega t}\langle v(t)v(0)\rangle_s dt = \frac{2k_B T}{m}\frac{\gamma}{\gamma^2+\omega^2}. \tag{38}$$

From eq. (36) and eq. (38) one obtains

$$\begin{aligned} Im\left(\tilde{\chi}(\omega)\right) \equiv \tilde{\chi}''(\omega) &= \frac{1}{m} Im\left(\frac{1}{\gamma - i\omega}\right) \\ &= \frac{1}{m}\frac{\omega}{\gamma^2+\omega^2} \\ &= \frac{\omega}{2k_B T}\tilde{C}_v(\omega). \end{aligned} \tag{39}$$

Hence,

$$\boxed{\tilde{\chi}''(\omega) = \frac{\omega}{2k_B T}\tilde{C}_v(\omega),} \tag{40}$$

that is the fluctuation-dissipation theorem given in its canonical form [4]. To see that the imaginary part of the response function is related to the energy dissipated by the system let us look for the power absorbed by the system in presence of an external force $F_E(t)$.

0.3.2 Power absorption

The work done by an external force F_E to change the observable v (in this case) by an amount dv is

$$\delta W = -F_E dv. \tag{41}$$

This is the work done on the medium. On the other hand the average rate at which work is done on the medium is just the power $dW(t)/dt$ absorbed by the medium, i.e.

$$\frac{dW}{dt} = -F_E(t)\frac{dv}{dt} \tag{42}$$

Since the above relation depends on the realization it is useful to consider the average over all the realization with the external force F_E fixed. This gives

$$\left\langle \frac{dW}{dt} \right\rangle = -F_E(t)\langle \frac{dv}{dt}\rangle. \tag{43}$$

On the other hand, by the linear response theory (eq. 32) we have

$$\left\langle \frac{dW}{dt} \right\rangle = -F_E(t)\frac{d}{dt}\int_{\mathbb{R}} \chi_v(t-t')F_E(t')dt'. \tag{44}$$

By writing the right-hand side in terms of the Fourier transforms $\tilde{\chi}_v(\omega)$ and $\tilde{F_{E}}_v(\omega)$ one gets

$$\left\langle \frac{dW}{dt} \right\rangle = i(2\pi)^{-2}\int_{\mathbb{R}^2} d\omega d\omega' \omega' \tilde{F_{E}}_v(\omega)\tilde{\chi}_v(\omega')\tilde{F_{E}}_v(\omega')e^{-i(\omega+\omega')t}. \tag{45}$$

Given an expression for $F_E(t)$ one can then compute the power adsorbed by the medium.

Example. Suppose that at time $t = 0$ a delta function force is applied i.e. $F_E(t) = F_0\delta(t)$. This gives $\tilde{F}_{Ev}(\omega) = F_0$ and by plugging it in equation (45) one gets

$$\left\langle \frac{dW}{dt} \right\rangle = i(2\pi)^{-2} \int_{\mathbb{R}^2} d\omega d\omega' \omega' \tilde{\chi}_v(\omega') F_0^2 e^{-i(\omega+\omega')t}. \tag{46}$$

The total energy absorbed is then obtained by integrating over all times

$$W = \int_{\mathbb{R}} \left\langle \frac{dW}{dt} \right\rangle dt = -(2\pi)^{-2} \int_{\mathbb{R}} d\omega \omega \tilde{\chi''}_v(\omega) F_0^2. \tag{47}$$

Note that only the imaginary part of $\tilde{\chi}_v(\omega)$ is kept since the total absorbed energy is a real quantity.

Example. Suppose to consider now a monochromatic force of the form

$$F_E(t) = F_0 \cos \omega t = \frac{1}{2} F_0 \left(e^{i\omega_0 t} + e^{-i\omega_0 t} \right). \tag{48}$$

In this case

$$\tilde{F}_{Ev}(\omega) = \pi F_0 \left(\delta(\omega + \omega_0) + \delta(\omega - \omega_0) \right) \tag{49}$$

and from eq. (45) one obtains

$$\left\langle \frac{dW}{dt} \right\rangle = -\frac{F_0^2}{4} \left[(-i\omega_0) \left(e^{-i2\omega_0 t} + 1 \right) \tilde{\chi}_v(\omega_0) + (i\omega_0) \left(e^{i2\omega_0 t} + 1 \right) \tilde{\chi}_v(-\omega_0) \right] \tag{50}$$

Clearly the istantaneous power absorption oscillates in time and one can compute the absorbed power by taking the time average of the above equation over one period of oscillation:

$$\overline{W(t)} = \frac{\omega_0}{\pi} \int_0^{\pi/\omega_0} dt \left\langle \frac{dW}{dt} \right\rangle = \frac{i\omega_0 F_0^2}{4} \left[\tilde{\chi}_v(\omega_0) - \tilde{\chi}_v(-\omega_0) \right] = \frac{\omega_0 F_0^2}{2} \tilde{\chi}''_v(\omega_0) \tag{51}$$

0.3.3 Velocity distribution function

It is possible to show that the random variable

$$u(t) \equiv v(t) - v_0 e^{-\gamma t} \tag{52}$$

follows the normal distribution, i.e., $v \in \mathbb{N}(0, var)$ where

$$Var \equiv \langle u^2(t) \rangle = \langle \left(v(t) - v_0 e^{-\gamma t} \right)^2 \rangle = \frac{\sigma^2}{2m^2\gamma} \left(1 - e^{-2\gamma t} \right) = \frac{k_B T}{m} \left(1 - e^{-2\gamma t} \right). \tag{53}$$

In other words the velocity $v(t)$ follows the distribution law

$$p(v,t)_{v_0} = \left(\frac{m}{2\pi\kappa_B T(1 - e^{-\gamma t})} \right)^{1/2} \exp \left\{ \frac{m}{2\kappa_B T} \frac{\left(v(t) - v_0 e^{-\gamma t} \right)^2}{1 - e^{-2\gamma t}} \right\} \tag{54}$$

Notice that in the limit $t \to \infty$, the distribution (54) approaches the well known Maxwell distribution

Remark. The proof that the random variable $u(t)$ follows a Normal distribution is easy but cumbersome. It reduces to show that for the moments $\langle u(t)^m \rangle_{v_0}$ the following relations hold (Uhlenbeck and Ornstein, Phys. Rev. **36**):

$$\langle u(t)^{2m+1} \rangle_{v_0} = 0 \tag{55}$$

$$\langle u(t)^{2m} \rangle_{v_0} = (2m-1)! \langle u(t)^2 \rangle_{v_0}. \tag{56}$$

In other words one has to show that all the odd moments are zero and that all the even moments can be expressed by the moment of order 2. This can be easily accomplished if the random force $F(t)$ follows itself a Normal distribution, namely $F \in \mathbb{N}(0, \sigma^2) = N(0, 2\gamma k_B T/m)$.

0.3.4 Velocity autocorrelation function and diffusion coefficient

From kinematics we know that, for sufficiently long times ($t >> \tau_v$) the system is in the diffusive regime, i.e.

$$\langle x^2 \rangle \simeq 2Dt \tag{57}$$

with

$$D = \int_0^\infty \langle v(0)v(t)\rangle dt. \tag{58}$$

On the other hand, from the solution of the Langevin equation we now know

$$\langle v(t_1)v(t_2)\rangle_{v_0} = v_0^2 e^{-\gamma(t_1+t_2)} + \frac{\sigma^2}{2m^2\gamma}\left(e^{-\gamma|t_1-t_2|} - e^{-\gamma(t_1+t_2)}\right) \tag{59}$$

that, for $\gamma t_1 >> 1$, $\gamma t_2 >> 1$ simplifies to

$$\langle v(t_1)v(t_2)\rangle_{v_0} \simeq \frac{\sigma^2}{2m^2\gamma} e^{-\gamma|t_1-t_2|}. \tag{60}$$

By putting $\tau = t_1 - t_2$ we then have

$$\langle v(t)v(t+\tau)\rangle_{v_0} \simeq \frac{\sigma^2}{2\gamma} e^{-\gamma|\tau|} \tag{61}$$

giving

$$\boxed{\tau_v = \gamma^{-1}}. \tag{62}$$

This relation shows that the average interval beyond which the velocities of the Brownian particle are essentially uncorrelated coincides with the inverse of the damping parameter. Moreover

$$\begin{aligned} D &= \int_0^\infty \langle v(0)v(t)\rangle dt \\ &= \int_0^\infty \frac{\sigma^2}{2m^2\gamma} e^{-\gamma t} dt = \frac{\sigma^2}{2m^2\gamma}\left[-\frac{e^{-\gamma t}}{\gamma}\right]_0^\infty \\ &= \frac{\sigma^2}{2m^2\gamma^2} \end{aligned} \tag{63}$$

and remembering that $\sigma^2 = 2m\gamma\kappa_B T$ we get the Einstein's relation

$$\boxed{D = \frac{\kappa_B T}{m\gamma} = \frac{\kappa_B T}{\alpha} \equiv \mu\kappa_B T}, \tag{64}$$

where $\mu = (\alpha)^{-1}$ is called *mobility* of the particle.

0.3.5 Simple applications of Einstein's relation

As an application we can compute the diffusion coefficient of a colloidal particle in water. We assume for simplicity a spherical particle of radius $a = 1\mu m$. The viscosity of the water is roughly $\eta = 10^{-3} Pas$. Since the Boltzmann constant is 1.38×10^{-23} Joule per degree at the room temperature we may have

$$\boxed{k_B T = 4.1 \times 10^{-21} J = 4.1 pNnm.} \tag{65}$$

By plugging all the values in eq. (64) we have

$$D \sim \frac{4.1 pNnm}{6\pi 10^{-3} Pas \times 10^3 nm} = 2 \times 10^6 nm^2/s \tag{66}$$

where we have used the definition of Pascal

$$1Pa = \frac{1N}{1m^2} = \frac{10^{12}pN}{10^{18}nm^2} = 10^{-6}pN/nm^2. \tag{67}$$

It is interesting to notice that the diffusion coefficient is inversely proportional to the linear size of the particle: smaller particle will have a larger diffusion coefficient. For example if we replace the colloidal particle with a protein of typical linear size $a = 5nm$ we get a diffusion coefficient (still in water)

$$D \sim 10^8 nm^2/s. \tag{68}$$

From the relation $\langle x^2 \rangle \simeq Dt$ we can see that, on average, a protein (in water) will travel $10\mu m$ in one second.

Suppose now to consider the case of a bacterium such as the E.Coli. Despite the E. Coli is a spherocylinder with dimensions $\sim 5-\mu m \times 0.8\mu m$ we can assume for simplicity he has a spherical shape with radius $1\mu m$. Since it is known that this bacterium tumbles every $\Delta t \simeq 1s$ after having travelled linearly for $\Delta x \simeq 30\mu m$, a simple estimate of its diffusion coefficient is $\frac{\Delta x^2}{6\Delta t} \simeq 150\mu m^2 s^{-1}$ i.e. two orders of magnitude larger than the corresponding "close-to-equilibrium" colloidal particle. Suppose that the bacterium is in equilibrium and that the fluctuation-dissipation theorem holds. In particular we can start from the Einstein's relation $D = \frac{k_B T}{\alpha}$ and find for the D_{bact} estimated above which it would be the corresponding equilibrium T. By plugging the values above this would give a fictitious temperature of the order of $90.000K$!!!

This is a clear indication that a bacterium such E. Coli in suspension with water is not an equilibrium system.

0.3.6 Fluctuations of the positions

We can now consider the fluctuations of the positions. From the integration of the velocity

$$v(t) = v_0 e^{-\gamma t} + e^{-\gamma t} \int_0^t e^{\gamma s} A(s) ds \tag{69}$$

one obtains for the position $x(t)$

$$\begin{aligned} x(t) &= x_0 + \int_0^t v(s)ds = x_0 + \frac{v_0}{\gamma}\left(1 - e^{-\gamma t}\right) \\ &+ \int_0^t ds e^{-\gamma s} \int_0^s e^{\gamma q} A(q) dq. \end{aligned} \tag{70}$$

By taking the average values and remembering the statistics of $F(t)$ we get

$$\boxed{\langle x(t) \rangle_{v_0} = x_0 + \frac{v_0}{\gamma}\left(1 - e^{-\gamma t}\right).} \tag{71}$$

In particular the average distance covered in the time interval t, with average velocity $\langle v(t) \rangle$ is given by:

$$\langle s(t) \rangle_{v_0} \equiv \langle x(t) \rangle_{v_0} - x_0 = \frac{v_0}{\gamma}\left(1 - e^{-\gamma t}\right) = \frac{1}{\gamma}\left(v_0 - \langle v(t) \rangle_{v_0}\right). \tag{72}$$

In figure 3 the time dependence of the x coordinate of a $d = 3$ Brownian particle is plotted for two different values of γ. One can easily see that the curves behave indeed as in Eq. (71).

By using the expression for $\langle x(t) \rangle_{v_0}$ we can write the law for the position $x(t)$ as

$$x(t) = \langle x(t) \rangle_{v_0} + \int_0^t ds e^{-\gamma s} \int_0^s e^{\gamma q} A(q) dq. \tag{73}$$

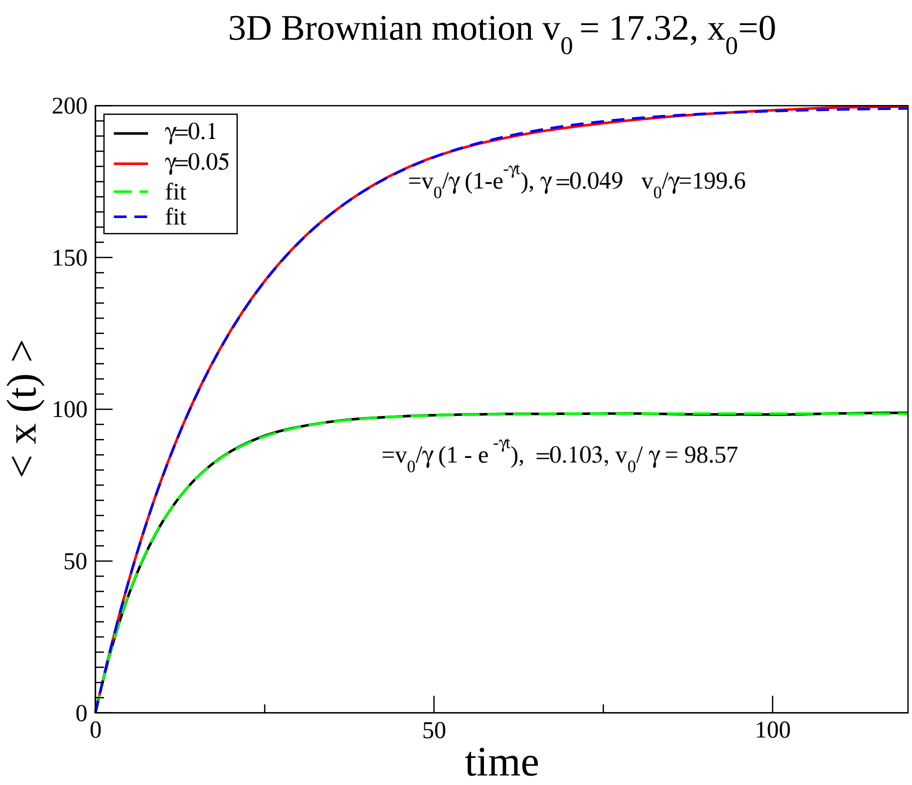

Figure 3: Time dependence of the averaged x-coordinate of a d=3 Brownian motion. The two curves are obtained by averaging over 1000 independent configurations and correspond to two different values of γ.

Integrating by part, where

$$f(s) = \int_0^s dq e^{\gamma q} A(q), \qquad g'(s) = e^{-\gamma s}, \tag{74}$$

one obtains

$$\begin{aligned}
\int_0^t ds \left[e^{-\gamma s} \int_0^s dq e^{\gamma q} A(q) \right] &= \left[-\frac{1}{\gamma} e^{-\gamma s} \int_0^s dq e^{\gamma q} A(q) \right]_0^t - \int_0^t ds \left(-\frac{e^{-\gamma s}}{\gamma} \right) e^{\gamma s} A(s) \\
&= -\frac{e^{-\gamma t}}{\gamma} \int_0^t dq e^{\gamma q} A(q) + \int_0^t ds \frac{A(s)}{\gamma}.
\end{aligned} \tag{75}$$

Hence,

$$\boxed{x(t) = \langle x(t) \rangle_{v_0} - \frac{e^{-\gamma t}}{\gamma} \int_0^t e^{\gamma s} A(s) ds + \frac{1}{\gamma} \int_0^t A(s) ds.} \tag{76}$$

The mean square for the fluctuations of the distance covered in time t can be obtaining by using its relation with the autocorrelation function of the velocities (see kinematics). Indeed if one assumes the initial conditions $x(0) = x_0$ and $v(0) = v_0$ the variance of the distance s is:

$$\begin{aligned}
\langle s^2(t) \rangle_{v_0} &\equiv \langle (x(t) - x_0)^2 \rangle_{v_0} \\
&= \left\langle \left[\int_0^t v(t_1) dt_1 \right]^2 \right\rangle_{v_0} \\
&= \left\langle \int_0^t v(t_1) dt_1 \int_0^t v(t_2) dt_2 \right\rangle_{v_0} = \int_0^t \int_0^t \langle v(t_1) v(t_2) \rangle_{v_0} dt_1 dt_2.
\end{aligned} \tag{77}$$

By using eq. (19) one gets

$$\begin{aligned}
\langle s^2(t) \rangle_{v_0} &= \int_0^t dt_1 \int_0^t dt_2 \langle v(t_1) v(t_2) \rangle_{v_0} \\
&= \frac{\sigma^2}{2m^2\gamma} \left[\underbrace{\int_0^t dt_1 \int_0^t dt_2 e^{-\gamma |t_1 - t_2|}}_{=2\int_0^t dt_1 \int_0^{t_1} dt_2 e^{-\gamma(t_1 - t_2)}} - \left(\int_0^t dt_1 e^{-\gamma t_1} \right)^2 \right] + v_0^2 \left(\int_0^t dt_1 e^{-\gamma t_1} \right)^2 \\
&= \frac{\sigma^2}{2m^2\gamma} \left[2 \left(\frac{t}{\gamma} + \frac{e^{-\gamma t} - 1}{\gamma^2} \right) - \left(\frac{1}{\gamma} \left(e^{-\gamma t} - 1 \right) \right)^2 \right] + v_0^2 \left(\frac{1}{\gamma} \left(e^{-\gamma t} - 1 \right) \right)^2,
\end{aligned} \tag{78}$$

Giving,

$$\boxed{\langle s^2(t) \rangle_{v_0} = \frac{\sigma^2}{m^2\gamma^2} t + \frac{\sigma^2}{2m^2\gamma^3} \left(4e^{-\gamma t} - e^{-2\gamma t} - 3 \right) + v_0^2 \left(\frac{1}{\gamma} \left(e^{-\gamma t} - 1 \right) \right)^2} \tag{79}$$

Now let us look at two extreme cases:

Ballistic (early times) regime For very small time scales $t \simeq 0$ and by developing the terms $e^{-\gamma t}$ and $e^{-2\gamma t}$ of Eq. (79) in power of t one can see that, in order to have a non zero contribution, the terms up t^3 must be taken into account. Indeed

$$\begin{aligned}
\langle s^2(t) \rangle_{v_0} &\simeq \frac{\sigma^2}{m^2\gamma^2} t \\
&+ \frac{\sigma^2}{2m^2\gamma^3} \left(4 \left(1 - \gamma t + \frac{\gamma^2 t^2}{2} - \frac{\gamma^3 t^3}{6} \right) - \left(1 - 2\gamma t + \frac{4\gamma^2 t^2}{2} - \frac{8\gamma^3 t^3}{6} \right) - 3 \right) \\
&+ \frac{v_0^2}{\gamma^2} (-\gamma t)^2 \\
&= (v_0 t)^2 + \frac{\sigma^2}{3m^2} t^3 + \text{other terms in } t^3.
\end{aligned} \tag{80}$$

Finally

$$\boxed{\langle s^2(t)\rangle_{v_0} \simeq (v_0 t)^2.} \tag{81}$$

Hence, for small t one finds the law of ballistic motion $\sqrt{\langle s^2\rangle_{v_0}} \simeq v_0 t$. This is reasonable since, in the early time regime ($t \simeq \tau_c$) the collisions with the fluid molecules have not been sufficiently effective.

Diffusive (large times) regime For large times scales, i.e. for $\gamma t >> 1$ one has:

$$\begin{aligned} \langle s^2(t)\rangle_{v_0} &\simeq \frac{\sigma^2}{m^2\gamma^2}t + \frac{v_0^2}{\gamma^2} - \frac{3\sigma^2}{2m^2\gamma^3} \\ &\simeq \frac{\sigma^2}{m^2\gamma^2}t. \end{aligned} \tag{82}$$

On the other hand $\sigma^2 = 2\gamma\kappa_B T m = 2Dm^2\gamma^2$ giving at late times:

$$\boxed{\langle s^2\rangle_{v_0} \equiv \langle (x(t)-x_0)^2\rangle_{v_0} \simeq \frac{2\kappa_B T}{\gamma m}t = 2Dt.} \tag{83}$$

This regime, where $\sqrt{\langle (x(t)-x_0)^2\rangle_{v_0}} \propto \sqrt{t}$ is called *Diffusive regime.*

Note. In d dimensions, since $\langle s^2\rangle = \langle \sum_{i=1}^d x_i^2\rangle$ we have

$$\langle s^2\rangle_{v_0} = 2dDt \tag{84}$$

that in three dimensions becomes

$$\langle s^2\rangle_{v_0} = 6Dt, \qquad d = 3 \tag{85}$$

In figure 4 the time dependence of the averaged squared position is plotted for two different values of γ. One can indeed notice the two time scale regimes. In summary we can say that the Langevin theory interpolates quite well between the ballistic and the diffusive regime.

Note. Up to now we have supposed that the particle has a well defined initial value of the velocity v_0. If this is not the case one can assume, for example, that the particle, before being inserted in the heat bath with temperature T was is in solution with a fluid at equilibrium at different temperature T_1. It is then natural to replace v_0^2 with its thermal average $\kappa_B T_1/m$. The previous relations (19) and (79) then become (dropping now the subscript v_0):

$$\boxed{\langle v(t_1)v(t_2)\rangle = \frac{k_B T_1}{m}e^{-\gamma(t_1+t_2)} + \frac{\sigma^2}{2m^2\gamma}\left(e^{-\gamma|t_1-t_2|} - e^{-\gamma(t_1+t_2)}\right).} \tag{86}$$

and

$$\boxed{\langle s^2(t)\rangle = \frac{\sigma^2}{m^2\gamma^2}t + \frac{\sigma^2}{2m^2\gamma^3}\left(4e^{-\gamma t} - e^{-2\gamma t} - 3\right) + \frac{k_B T_1}{m}\left(\frac{1}{\gamma}\left(e^{-\gamma t}-1\right)\right)^2} \tag{87}$$

Note that in order to obtain eqs. (86) and (87) one is implicitly assuming that $\langle v_0\rangle_{T_1} = \langle x_0\rangle_{T_1} = 0$ and that x_0 and v_0 are statistically independent so that $\langle x_0 v_0\rangle_{T_1} = 0$.

0.3.7 Positions distribution function

As in the case of the velocities it is possible to show that the random variable

$$\boxed{S(t) \equiv s(t) - \frac{v_0}{\gamma}(1-e^{-\gamma t}) = x(t) - x_0 - \frac{v_0}{\gamma}(1-e^{-\gamma t})} \tag{88}$$

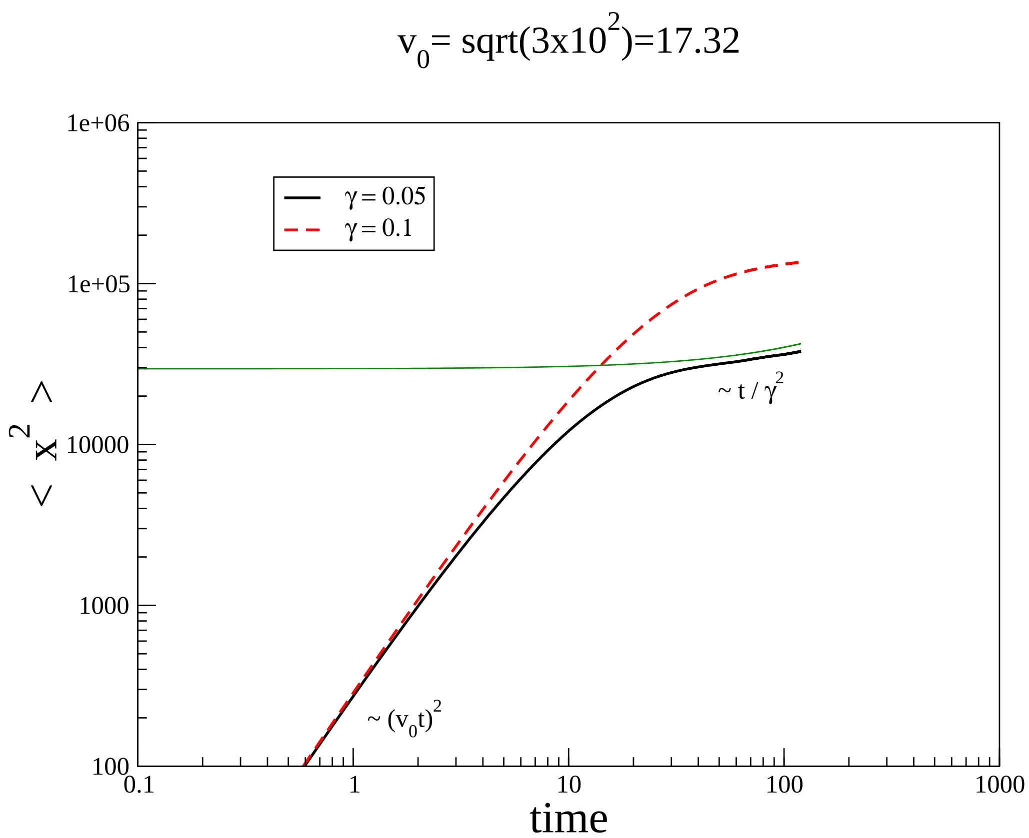

Figure 4: Log-Log plots of the time dependence of the averaged squared distance for a d=3 Brownian motion. The curves are obtained by averaging over 1000 independent configurations. The two curves correspond to two different values the γ.

follows a Normal distribution, i.e., $S(t) \in \mathbb{N}(0, \mathrm{var})$, with

$$\mathrm{var} = \langle S^2(t)\rangle = \langle s^2(t)\rangle - 2\langle s(t)\rangle \frac{v_0}{\gamma}(1-e^{-\gamma t}) + \frac{v_0^2}{\gamma^2}(1-e^{-\gamma t})^2. \quad (89)$$

As for the velocity case one has to show that

$$\begin{aligned} \langle S^{2m+1}\rangle &= 0 \\ \langle S^{2m}\rangle = (2m-1)!\langle S^2\rangle. \end{aligned} \quad (90)$$

The proof is similar to the case of the velocity and relies on the assumption that the statistics of the random force is the one of the white noise with Gaussian statistics. One then obtains for the one-point distribution function

$$p(x,t)_{x_0} = \left[\frac{m\gamma^2}{2\pi\kappa_B T(2\gamma t - 3 + 4e^{-\gamma t} - e^{-2\gamma t})}\right]^{1/2} \exp\left[\frac{m\gamma^2}{2\kappa_B T}\frac{\left(x - x_0 - \frac{v_0}{\gamma}(1-e^{-\gamma t})\right)^2}{2\gamma t - 3 + 4e^{-\gamma t} - e^{-2\gamma t}}\right], \quad (91)$$

and for large time scales one gets

$$\boxed{p(x,t)_{x_0} \simeq \left(\frac{1}{4\pi Dt}\right)^{1/2} e^{\frac{1}{4\pi Dt}(x-x_0-v_0/\gamma)^2}.} \quad (92)$$

0.4 Remarks on the Langevin approach

There are some remarks on the meaning of the random force that are worth to be mentioned:

1. The statistical properties of the random force considered in the Langevin approach are the ones of a *delta-correlated noise*, i.e.

$$\langle F(t)\rangle = 0 \quad (93)$$

$$\langle F(t_1)F(t_2)\rangle = \sigma^2\delta(t_1 - t_2) \quad (94)$$

   It is also known as *withe noise* since the power spectrum of $F(t)$, namely the Fourier transform of its autocorrelation function (the $F(t)$ is a stationary process) is given by

$$S(\omega) = \int_{\mathbb{R}} e^{i\omega\tau}\langle F(0)^* F(\tau)\rangle d\tau = \int_{\mathbb{R}} e^{i\omega\tau}\sigma^2\delta(\tau)d\tau = \sigma^2. \quad (95)$$

   In other words *the power spectrum does not depend on the frequency* (it does not depend on the colour i.e. is white).

2. We have seen that, by integrating the equation of motion, starting from a white noise force we get a new random variable $v(t)$ with the following statistical properties

$$\langle v(t)\rangle = v_0 e^{-\gamma t} \quad (96)$$

$$\langle v(t_1)v(t_2)\rangle = v_0^2 e^{-\gamma(t_1+t_2)} + \frac{\sigma^2}{2m^2\gamma}\left(e^{-\gamma|t_1-t_2|} - e^{-\gamma(t_1+t_2)}\right) \quad (97)$$

   that in the large time scale limit become

$$\langle v(t)\rangle \simeq 0 \quad (98)$$

$$\langle v(t_1)v(t_2)\rangle \simeq \frac{\sigma^2}{2m^2\gamma}e^{-\gamma|t_1-t_2|}. \quad (99)$$

In this limit the $v(t)$ is a stationary stochastic process but *it is not delta-correlated.* The process exhibits instead a correlation function that decays exponentially with $\tau = t_1 - t_2$ as

$$\langle v(t_1)v(t_2)\rangle \simeq \frac{D}{\tau_v} e^{-\tau/\tau_v} \tag{100}$$

where $\tau_v = 1/\gamma$ and $D = \frac{\sigma^2}{2m^2\gamma^2}$. This statistics is typical of a *coloured noise* since its power spectrum is given by

$$\begin{aligned} S(\omega) &= \int_{\mathbb{R}} e^{i\omega\tau} C_v(\tau)\rangle d\tau \qquad (101) \\ &\simeq \frac{D}{\tau_v} \int_{\mathbb{R}} e^{i\omega\tau} e^{-\tau/\tau_v} d\tau \\ &= \frac{D}{\tau_v} \frac{1/\tau_v}{\omega^2 + 1/\tau_v^2} \\ &= \frac{D}{\tau_v^2\omega^2 + 1}. \qquad (102) \end{aligned}$$

This spectrum show a Lorentzian behaviour that depends on the frequency ω.

3. When we have made the hypothesis

$$\langle A(t)A(t+s)\rangle = \frac{\sigma^2}{m^2}\delta(s) \tag{103}$$

we have implicitly introduced a pathological term in the mathematical description of the Brownian motion and some caution must be taken into account. Indeed $\delta(s)$ is not a function and this is reflected somehow from the fact that is not possible to draw $A(t)$ as so it is dv/dt. The fact that dv/dt is not a function implies that $v(t)$ is nowhere differentiable. On the other hand if one looks at the motion of the particle on time intervals that are smaller than the average time between two consecutive collisions one would see a free motion. The limit $s \to 0$ really means that very small time, but not infinitesimal, are considered. The key point (already mentioned before) is that the time evolution of $v(t)$ is much slower then the one of the fluctuating force. To see that let us integrate the Langevin equation (14) between t and $t + \Delta t$. By assuming that in the time interval Δt many collisions occur but the variable $v(t)$ does not vary significantly one gets

$$\Delta v \equiv v(t+\Delta t) - v(t) = -\gamma v(t)\Delta t + \int_t^{t+\Delta t} A(s)ds. \tag{104}$$

The term

$$\int_t^{t+\Delta t} A(s)ds \equiv \Delta W(\Delta t) \tag{105}$$

represents the net acceleration experienced by the Brownian particle in a time interval Δt due to collisions. Clearly

$$\Delta W \equiv W(t+\Delta t) - W(t) \tag{106}$$

where

$$\boxed{W(t) = \int_0^t A(s)ds.} \tag{107}$$

Let us now deduce the statistical properties of $W(t)$ knowing the ones of $A(t)$. Clearly, from $\langle A(t)\rangle = 0$ one gets

$$\langle W(t)\rangle = \int_0^t \langle A(s)\rangle ds = 0 \tag{108}$$

whereas from the property $\langle A(s_1)A(s_2)\rangle = \frac{\sigma^2}{m^2}\delta(s_1 - s_2)$ one obtains

$$\begin{aligned}
\langle W(t_1)W(t_2)\rangle &= \int_0^{t_1} ds_1 \int_0^{t_2} ds_2 \langle A(s_1)A(s_2)\rangle \\
&= \frac{\sigma^2}{m^2}\int_0^{t_1} ds_1 \int_0^{t_2} ds_2 \delta(s_1 - s_2) \\
&= \frac{\sigma^2}{m^2}\int_0^{\infty} ds_1 \int_0^{\infty} ds_2 \delta(s_1 - s_2)\theta(s_1 - t_1)\theta(s_2 - t_2) \\
&= \sigma^2 \int_0^{\infty} ds_1 \theta(s_1 - t_1)\theta(s_1 - t_2) \\
&= \frac{\sigma^2}{m^2}\int_0^{\infty} ds_1 \theta\left(\min(t_1, t_2) - s_1\right) \\
&= \frac{\sigma^2}{m^2}\int_0^{\min(t_1,t_2)} ds_1 = \frac{\sigma^2}{m^2}\min(t_1, t_2). \qquad (109)
\end{aligned}$$

Moreover, if we assume $A(t)$ to be Gaussian also $W(t)$ will be Gaussian since the two processes are related through a linear transformation (the integral) (see Lemma **??**). Summarizing we have for $W(t)$ the following properties

- $W(t)$ is a Gaussian process. Hence is completely determined by the properties
- $\langle W(t)\rangle = 0$,
- $\langle W(t_1)W(t_2)\rangle = \frac{\sigma^2}{m^2}\min(t_1, t_2)$.

It is then clear that the integral of the white noise $A(t)$ is a Wiener-Levy process.

Remark. Despite $A(t)$ is a stationary process, $W(t)$ is not stationary since $\langle W(t_1)W(t_2)\rangle = \frac{\sigma^2}{m^2}\min(t_1, t_2)$ is not a function of the difference $t_1 - t_2$.

Given that $W(t)$ is a Wiener process we have (see eq. (**??**) in chapter on stochastic processes)

$$\left\langle (W(t + \Delta t) - W(t))^2 \right\rangle = \frac{\sigma^2}{m^2}\Delta t. \qquad (110)$$

Hence from eqs. (**??**) and (105) one obtains the Langevin equation in differential form:

$$\begin{aligned}
\Delta v(t) &= -\gamma v(t)\Delta t + \frac{\sigma}{m}\Delta t^{1/2}\Delta\hat{W}(t) \qquad (111) \\
v(0) &= v_0
\end{aligned}$$

where $\Delta\hat{W}(t)$ is an uncorrelated stationary Gaussian process with variance 1 and average 0 (i.e. $\Delta\hat{W}(t) \in \mathbb{N}(0, 1)$. Since $\sigma^2 = 2\gamma m k_B T$ eq. (112) can be more written more explicitely ad

$$\Delta v(t) = -\gamma v(t)\Delta t + \sqrt{\frac{2\gamma k_B T \Delta t}{m}}\Delta\hat{W}(t) \qquad (112)$$

Eq. (112) is the usual starting equation for a numerical simulation of a Brownian motion.

Remark. There are different classes of white noise that are defined in terms of the derivative

$$A(t) = \frac{dz(t)}{dt} \qquad (113)$$

where $z(t)$ is a stochastic process with independent and stationary increments. We will see later that the derivative of the Wiener process defines the *Gaussian white noise*. The derivative of a Poisson process defines instead the so called *white shot noise*.

0.5 Brownian motion as Markov process

The next question that arises naturally is the following:
Is the Brownian motion a Markov process ?
First it is important to notice that for Brownian motion one could mean the stochastic processes $x(t)$, $v(t)$ or the bi-dimensional process $[x(t), v(t)]$. Let us consider first the processes $v(t)$.

Ornstein-Uhlenbeck process $v(t)$ We have seen that this process is the solution of the stochastic equation (112) where $d\hat{W}(t)$ is a temporally uncorrelated normal random variable. From eq. (112) one can immediately says that

- The process $v(t)$ is *continuous*, because eq. (112) implies that $v(t + dt) \to v(t)$ as $dt \to 0$.
- The process $v(t)$ is *memoryless* or *Markovian*, because, following (112), the computation of $v(t + dt)$ starting from $v(t)$ requires no knowledge of any values of $v(t')$ for $t' < t$. Another important property of eq. (112) is its so called *unique self-consistency* [7]. This goes as follows: if we split the time evolution from $v(t)$ to $v(t + dt)$ into the two steps $t \to t + dt/2$ and $t + dt/2 \to t + dt$, the corresponding two iterations of eq. (112) will give the same result (statistically and to lowest order in dt) as the single application $t \to t + dt$. Note that for $\sigma^2 = 0$ eq. (112) defines the evolution of a *deterministic* process $v(t)$ that not only is *continuous* but also *differentiable.* If on the other hand $\sigma^2 > 0$ the last term of the equation is ill behaved in the limit $dt \to 0$ and the process $v(t)$ is *not* differentiable.

Process $x(t)$ Since this process is the *integral* of the continuous Markov process $v(t)$ it is perfectly defined and it evolution equation would be given by

$$x(t + dt) = x(t) + v(t)dt. \tag{114}$$

On the other hand this equation does not have the form of eq. (112) since its right-hand side involves a process other than $x(t)$. For this reason $x(t)$, i.e. the integral of the Markov process $v(t)$, is *not* itself a Markov process. (However we will see later that the overall process $\{x(t), v(t)\}$ constitute a *bivariate* Markov process.

Wiener process $W(t)$ It is interesting to notice that within the stochastic differential approach the Wiener process can be defined as the solution of the Langevin equation obtained by putting $\gamma = 0$ in eq. (112) i.e. a Brownian motion with no damping term:

$$\Delta v(t) = \frac{\sigma}{m}\Delta\hat{W}(t). \tag{115}$$

Clearly in this case the particle wouldn't reach any stationary state and the connection between σ^2 and γ is lost. It is then apparent that the Wiener process is a *continuous Markov* process.

0.6 Hydrodynamic effects on Brownian motion

In the classical Langevin's theory presented above when have seen that the friction force is *istantaneously* linear with the particle's velocity, i.e. $F_v \sim -\alpha v$. However, when the particle receives momentum, it displaces the fluid molecules in its immediate vicinity and beacuse of a *non-negligible fluid inertia* the sorrounding flow field is altered and acts back on the particle motion. In particular the time development of the vorticity field that forms around the particle is not taken into account properly by the classical Langevin theory. The friction force then must included some terms that depends on the past motion of the particle. These *long-memory* (*hydrodynamic*) effects give rise to the following new effects in the Brownian motion.

- The motion of the Brownian particle persists in a given direction until the fluid momentum (or vorticity) generated by the particle itself diffuses away. If a is the radius of the particle and η and ρ_{fl} are respectively the viscosity and the density of the fluid, this occurs in a time scale $\tau_{fl} = \rho a^2/\eta$ which corresponds to the time it takes the vorticity to diffuse a particle radius away.

- Because of the ffect just described the transition from the ballistic to the diffusive regime occurs at later times than the ones predicted by the simple Langevin theory. One can say roughly that a purely diffusion regime sets in on time scales of the order of $10^3\tau_{fl}$. More precisely, it turns out that the classical Langevin prediction

$$\frac{\langle s^2 \rangle}{2Dt} \sim 1 + \frac{C\tau_v}{t}(e^{-t/\tau_v} - 1) \tag{116}$$

where $\tau_v = 1/\gamma = m/\alpha = \frac{4a^3\rho_p\pi/4}{6\pi a\eta} = \frac{2}{9}a^2\rho_p/\eta$, must be replaced by

$$\frac{\langle s^2 \rangle}{2Dt} \sim 1 - 2\sqrt{\frac{\tau_{fl}}{\pi t}} + B\frac{\tau_{fl}}{t} - \frac{\tau_v}{t} + \text{corr. terms.} \tag{117}$$

- The exponential decay of the velocity autocorrelation function

$$C_v(\tau) \sim \exp -(t\gamma) \tag{118}$$

must be replaced by an algebraic decay, the so-called *long-time tail* behaviour

$$C_v(\tau) \equiv \langle v(t)v(0) \rangle \sim D\sqrt{\tau_{fl}/4\pi}t^{-3/2}, \tag{119}$$

at times $t \geq \tau_{fl}$. This long-tail behaviour was first observed by Adler and Wainwright [13] in a simulation of the motion of a tagged particle in a hard-sphere fluid. In general they obtained a long-time-tail behaviour $t^{-d/2}$ where d is the dimensionality of the system. This algebraic long-time tail gives a crucial contribution to the diffusion coefficient in $d = 3$. In $d = 1$ and $d = 2$ this contribution is more dramatic since the integral

$$D = \int_{\mathbb{R}} C_v(\tau)d\tau \tag{120}$$

diverges and the diffusion law is not obeyed any more.

A simple,qualitatively, explanation of the velocity correlation function slow decay referes back to the picture of the Brownian molecules moving inside the fluid. In fact a moving particle compresses the liquid in front of it and rarefies the liquid behind it. This causes the formation of a vortex flow that circulate around the particle. The vortex creates a long-time push from behind. The vortex field occupies a volume of the fluid whose typical dimension grows diffusively i.e. as $t^{1/2}$. Hence its volume increases with time as $t^{d/2}$. Momentum coservation in this region leads to the strength of the push felt by the Brownian particle decreasing as $t^{-d/2}$.

A way to take into account the conservation of momentum of the fluid in Brownian motion is by using a *modified Langevin equation* (known also as *Stokes-Boussinesq equation*) of the following kind

$$m\frac{dv}{dt} = -\xi(\rho(a))v - \frac{2\pi}{3}\rho_p a^3\frac{dv}{dt} - 6a^2(\pi\rho_p\eta)^{1/2}\int_{-\infty}^{t}\frac{dv}{dt'}(t-t')^{-1/2}dt' + F(t) \tag{121}$$

where the Stokes-Cunningham coefficient $\xi(a)$ becomes $6\pi\eta q$ and $4\pi\eta a$ respectively for *stick* and *slip* boundary conditions. The first rerm in the right hand side of the equation is the usual friction coefficient, the second is connected with the virtual mass of sphere in an uncompressible fluid, and th ethird is a memory term associated with the hydrodynamic retardation effects and related to the penetration depth of viscous unsteady flow around a sphere. A way to solve the above equation is by Laplace transform (see Clercx and Schram PRA , **46**, 1942 (1992)).

Typical lenghts involved in experiments on Brownian motion

If one considers a, say, silica sphere of $2.25\mu m$ ($\rho_p = 1.96 g/cm^3$) immersed in water ($\rho_{fl} = 1g/cm^3, \eta = 10^{-3} Pa \cdot s$) we have $\tau_v = 2.2\mu s$ and $\tau_{fl} = 5.1\mu s$.

0.7 Testing the Langevin theory of Brownian Motion

0.7.1 Direct observation of nondiffusive motion for a Brownian Particle

Main reference: [12]
The thermal fluctuations of the position of a single micron-sized sphere (polysterene: radius= $a = 0.265, 0.5, 1.205, 1.25\mu m$ or silica ($a = 1.2\mu m$) suspended in water were recorded by optical trapping interferometry with nanometer spatial and microsecond temporal resolution. More precisely the particle was confined inside a weak and harmonic optical trapping potential which adds a force term $F_{ext} = -kx$ to the Langevin equation.

The authors in [12] found that, in accord with the theory of Brownian motion including hydrodynamic memory effects (see section above), the transition from ballistic to diffusive motion is delayed to significantly longer times than predicted by the standard Langevin equation. This delay is a consequence of the inertia of the fluid. On the shortest time scales investigated, the spheres inertia has a small, but measurable, effect.

0.7.2 A direct measure of instant velocity in rarified gases

Main reference: [10]
They report on the Brownian motion of a single, micrometer-sized of glass held in air by a dual-beam optical tweezer, over a wide range of pressures, and they measured the instantaneous velocity of a Brownian particle. The velocity data were used to verify the Maxwell-Boltzmann velocity distribution and the equipartition theorem for a Brownian particle. For short times, the ballistic regime of Brownian motion was observed, in contrast to the usual diffusive regime.

For a $1\mu m$-diameter silica (SiO_2) sphere in water, τ_v is about $0.1\mu s$ and the root mean square (rms) velocity is about mm/s in one dimension. Hence, in order to measure the instantaneous velocity with 10% of uncertainty, one would require $2-pm$ spatial resolution in $10ns$, far beyond what is experimentally achievable today. On the other hand, because of the lower viscosity of gases, compared to liquids, the $\tau_v = m/\alpha$ of a particle for example in air is much larger. This lowers the technical demand for both temporal and spatial resolution. The main difficulty of performing high-precision measurements of a Brownian particle in air, however, is that the particle will fall under the influence of gravity. The authors overcome this problem by using optical tweezers to simultaneously trap and monitor a silica bead in air and vacuum, allowing long-duration, ultrahigh-resolution measurements of its motion.

With these measures the authors have been able to have a direct verification of the Maxwell-Boltzmann distribution of velocities and the equipartition theorem of energy for Brownian motion:

$$\lim_{t\to\infty} \sqrt{\langle v^2(t)\rangle} = \sqrt{k_B T/m}. \tag{122}$$

0.8 The Johnson (thermal) noise and the Nyquist theory.

One might naively believe that if all sources of electrical power are removed from a circuit than there will be no voltage across any of the components, a resistor for example. On average this is correct but a closer look at the rms voltage would reveal the presence of a "noise" voltage at equilibrium. This intrinsic noise was first discovered by Johnson in 1928 [5] when he shows that its nature is purely a thermal one. This effect was then explained thermodynamically by Nyquist [6] who gave for the averaged squared noise voltage (in a given band of frequency Δf) the following expression

$$\boxed{\langle \Delta V(t)^2 \rangle = 4\kappa_B R T \Delta f,} \tag{123}$$

where κ_B is the Boltzmann constant and T , R are respectively the temperature and the resistance of the circuit.

0.8.1 Microscopic derivation of the Nyquist formula

By using the Langevin approach it is possible to deduce the Nyquist formula for the Johson starting from the microscopic system. Let us suppose that the motion of the electrons in a circuit of resistance R and at equilibrium with temperature T can be described by the following Langevin equation (we still consider a 1D system for semplicity) :

$$m\frac{du}{dt} = -\frac{m}{t_c}u + F(t) \tag{124}$$

where $u(t)$ is the velocity of the electrons and t_c is the collision time i.e. the time after which the collisions between the electron and the atoms of the crystal destroys completely the memory of the previous dynamical state of the electron itself. As for the Brownian motion $F(t)$ is a Gaussian white noise.

Note. In the classical Brownian motion the mass of the Brownian particle is usually much bigger than the one of the molecules of the fluid. Here this is not true since the electrons have mass much smaller than the ones of the atoms of the conductor. On the other hand the Langevin picture is still valid since at each interaction the average energy transferred from the medium to the electrons is much smaller of their average kinetic energy. That's was also true for the Brownian particle because of its big mass (compared to the mass of the fluid molecules).

By calling $\gamma = 1/t_c$ we then have the usual Langevin equation:

$$\frac{du}{dt} = -\gamma u + \frac{1}{m}F(t). \tag{125}$$

This equation has been already integrated before and in particular it gives for the velocity correlation function the expression (see Eq. (19)):

$$\begin{aligned}\langle u(t)u(t+\tau)\rangle_{u_0} &= u_0^2 e^{-\gamma(2t+\tau)} + \frac{\sigma^2}{2m^2\gamma}\left(e^{-\gamma|\tau|} - e^{-\gamma(2t+\tau)}\right) \\ &= \left(u_0^2 - \frac{\sigma^2}{2m^2\gamma}\right)e^{-\gamma(2t+\tau)} + \frac{\sigma^2}{2m^2\gamma}e^{-\gamma|\tau|}.\end{aligned} \tag{126}$$

Since in a metal at room temperature t_c is of order $10^{-13}s$ the first term of Eq. (126) can be neglected being t/t_c very big. This is the usual approximation for large time scale and gives

$$C_u(\tau) = \bar{u}^2 e^{-\gamma\tau}, \qquad \text{where} \quad \bar{u}^2 = \frac{\sigma^2}{2m^2\gamma} = \frac{\sigma^2 t_c}{2m^2}. \tag{127}$$

If we now consider a conductor of resistance R with a charge carrier density n, and unitary cross-sectional area and length, the voltage V across the conductor is

$$V = IR = Rj = Rne\bar{u} \tag{128}$$

where I is the current, j the current density, e the electron charge, and $\bar{u}$ is the average speed along the conductor. Since n is the total number of electrons in the conductor,

$$\sum_i u_i(t) = n\bar{u} \tag{129}$$

Solving for $\bar{u}$ in eq. (129) and substituting into eq. (128) gives,

$$V = \sum_i V_i = eR\sum_i u_i \tag{130}$$

where $u_i(t)$ and $V_i(t)$ are stochastic processes. The correlation function of the velocity can then be converted to the correlation function of the potential in the following way:

$$C_{V_i}(\tau) = \langle V_i(t)V_i(t+\tau)\rangle = (eR)^2\bar{u}^2 e^{-\tau/t_c} \tag{131}$$

In the stationary state the W-K theorem applies and we get the spectral density of V^2 as

$$\begin{aligned} G(f) &= 4\int_0^\infty C_{V_i}(\tau)\cos(2\pi f\tau)d\tau \\ &= 4(eR)^2\bar{u}^2\int_0^\infty e^{-\tau/t_c}\cos(2\pi f\tau)d\tau \\ &= 4(eR)^2\bar{u}^2\frac{t_c}{1+(2\pi f t_c)^2}. \end{aligned} \tag{132}$$

Since $t_c \simeq 10^{-13}s$ and unless one considers signals with very high frequencies one can assume $2\pi f t_c << 1$ giving

$$G(f) \simeq 4(eR)^2\bar{u}^2 t_c. \tag{133}$$

Now let us suppose that at equilibrium the statistics of the electrons is the Boltzmann's one. From the equipartition theorem we know that $\sigma^2 = 2\gamma m\kappa_B T$ and since $\bar{u}^2 = \frac{\sigma^2}{2m^2\gamma}$ we get $\bar{u}^2 = \frac{\kappa_B T}{m}$. Hence

$$G(f) = 4(eR)^2\frac{\kappa_B T}{m}t_c. \tag{134}$$

Hence the mean-square voltage in the frequency range Δf becomes:

$$\begin{aligned} \langle\Delta V^2\rangle &= n\langle\Delta V_i^2\rangle \\ &= nG(f)\Delta f \\ &= n4(eR)^2\left(\frac{\kappa_B T}{m}\right)t_c\Delta f \\ &= 4\left(\frac{ne^2 t_c}{m}\right)R^2\kappa_B T\Delta f. \end{aligned} \tag{135}$$

We now note that, from the classical (microscopic) theory of the electronic conduction (Drude model), the electrical conductivity σ_c is given by

$$\sigma_c = \frac{ne^2 t_c}{m}. \tag{136}$$

On the other hand, if one considers a resistor of unitary dimension (unit section area and unit length) $R = 1/\sigma_c$ and by putting all together we finally get the result, i.e

$$\langle\Delta V^2\rangle = 4\underbrace{\sigma_c}_{1/R}R^2\kappa_B T\Delta f, \tag{137}$$

and the Nyquist theorem

$$\boxed{\langle\Delta V^2\rangle = 4\kappa_B TR\Delta f} \tag{138}$$

is recovered.

Note. It is possible to show that the Nyquist formula holds also in the case in which we use the Fermi-Dirac statistics for the electrons at equilibrium.

0.8.2 Experimental estimate of the Boltzmann constant κ_B

In the previous sub-section we have just shown that in an interval of frequencies Δf the average squared potential difference at the ends of a resistor R for an open circuit at temperature T is given by

$$\langle \Delta V^2(t) \rangle = 4R\kappa_B T \Delta f. \tag{139}$$

In generale this potential difference is too small to be measured without amplifying the signal. If, on the other hand, the resistance R is connected to one end with an amplifier having an high gain $Ga(f)$ and a very small noise, at the exit of the amplifier there will be the following signal

$$\langle \Delta V^2(t) \rangle = 4\kappa_B TR \int_0^\infty [Ga(f)]^2 \, df + \langle V(t)^2_N \rangle, \tag{140}$$

where $\langle V(t)^2_N \rangle$ is the output noise generated by the amplifier itself. By measuring and plotting $\langle V(t)^2 \rangle$ as a function of R one then obtains the quantity

$$4\kappa_B T \int_0^\infty [Ga(f)]^2 \, df \tag{141}$$

from the slope, while the intercept will give an estimate of $\langle V(t)^2_N \rangle$. On the other hand, the gain $Ga(f)$ of the amplifier can be measured through an independent measure and, consequently, an estimate of the integral $\int_0^\infty [Ga(f)]^2 \, df$ can be obtained. Hence the slope will give (since the temperature T can be estimated by different means) an estimate of κ_B ($\sim 1.38 \times 10^{-23} J/K$).

0.8.3 Shot noise

While the thermal noise is due to the thermal motion of the charged particles , the shot noise represents the fluctuations of the current around its average value that are due of the finite value (quantum) of the charge carried by the particles. The name shot noise was given by Schotty in 1919 that compared this phenomenon to the noise that make the bullets when they hit a target. It turned out that one of the simplest and efficient method to detect this noise consists in using a circuit in which the current is generated by a photo-diod. The first theory that explained this phenomenon was formulated by Goldman in 1948. The main point is actually to show that the number of electrons emitted in a time interval τ follows the Poisson statistics. This can be achieved for example by looking at the statistics of electrons being emitted by a hot metal. Such emission are generally observed to occur according to the following rule:

$$\alpha dt \;=\; \text{the probability that an electron will be emitted from the metal in the time interval } dt \tag{142}$$

The simplest theory for the thermoionic emission of electrons from metals is the (free electron approximation) gives the Richardson-Dushman theory in which the electrons inside the metal are treated as an ideal gas and emission occurs whenever an electron strikes the boundary of the metal with enough energy to escape. This gives rise to the formula

$$\alpha = CT^\phi \exp(-\Phi/\kappa_B T) \tag{143}$$

where Φ is the work function and ϕ is iether 2 or 1/2 depending on whether one assumes the electron gas obeys Maxwell-Boltzmann statistics or Fermi-Dirac statistics. Since the electron charge is quantized the electric current is spikey. Moreover the current is stochastic since the randomness implicit in the emission law (142) means that one cannot predict when a given bit of charge will pass.

0.9 Stochastic forcing in the dynamics of geophysics fluids.

Several geophysics systems interacting between each others and having different dynamical times scales can be described through the theory of stochastic processes. One example is the system *Ocean-Atmosphere*. This system includes different time scales depending on the process considered. For example the phenomenon of the glaciation has time scales of the order of $t_c \sim 10^5 years$ while the atmospheric phenomena occur at most in periods of $t_c \sim 10^{-2} years$. If one is interested to the time evolution of the "climatic" averages of some observables, it convenient to distinguish between variables that

- vary (in an appreciate way) over long time scale
- vary over short time scales. These ones can then be seen as "stochastic force" in the equation of motion for the "slow" variables.

As in the case of the motion of electrons inside a conductor the "mesoscopic object" (i.e. the Brownian particle) is not, in particular, characterized by a much bigger size with respect to the molecules of the thermal bath but it has in general a much bigger inertia with respect to the dynamical variations of some physical quantities that determine its dynamics.

0.9.1 Study of the temperature variations in a given region of the oceanic surface

In this problem the "fast" part of the system is given by the atmosphere above the surface ocean whose dynamics varies over time scales of the order of days. The effects of these variations will be described as a noise term over the "slow" part of the system i.e. the ocean characterized by a much bigger thermal inertia.

Let T be the average temperature in a given point of the ocean surface. As a first approximation the ocean can be sketched as a uniform layer of width h (average deep). Let H the total heat flux that hit the unit area of surface ocean considered. The variation of the heat in the layer by unit time is then given by

$$\frac{dQ}{dt} = H \tag{144}$$

where we have neglected reflection phenomena. On the other hand the ocean will release, in a time interval, $t_{ocean} = 1/\gamma$, a given quantity of heat Q and the full equation will be of the form

$$\frac{dQ}{dt} = -\gamma Q + H \tag{145}$$

If ρ and c_p are respectively the density and the specific heat (at constant pressure) of the ocean, since $Q = c_p \rho V \Delta T$, eq. (145) can be written in terms of the temperature field as

$$\frac{dT}{dt} = -\gamma T + g \tag{146}$$

where

$$\frac{H}{\rho c_p h} = g. \tag{147}$$

Note. The term g can be considered as a fluctuating force and if we limit ourselves to the study of the climatic variations within an interval t such that

$$t_{atm} << t << t_{ocean} \tag{148}$$

the noise can be considered a delta-correlated stationary and Gaussian process (i.e. white noise)

$$\langle g(t)g(t')\rangle = 2D\delta(t - t') \tag{149}$$

By looking at the solution of the Langevin equation for the Brownian motion we have that the average of the square of the temperature behaves as (m=1)

$$\langle T(t)^2 \rangle = T_0^2 e^{-2\gamma t} + \frac{D}{\gamma}\left(1 - e^{-2\gamma t}\right) \tag{150}$$

The power spectrum of the variance is then given by

$$\begin{aligned} T(f) &= \int_{\mathbb{R}} \langle T(t)^2 \rangle e^{i2\pi f t} dt \\ &= (T_0^2 - D/\gamma) \int_{\mathbb{R}} e^{-2\gamma t} e^{i2\pi f t} \\ &+ \int_{\mathbb{R}} \frac{D}{\gamma} e^{i2\pi f t} dt. \end{aligned} \tag{151}$$

Hence

$$\boxed{T(f) = (T_0^2 - D/\gamma)\sqrt{2/\pi}\frac{2\gamma}{4\pi^2 f^2 + 4\gamma} + \frac{2\pi D}{\gamma}\delta(2\pi f).} \tag{152}$$

Since the above argument is meaningful in intervals t such that $t_{atmo} << t << t_{ocean}$, the spectrum $T(f)$ must be limited to frequencies f such that

$$f_{ocean} << f << f_{atmo}. \tag{153}$$

In this case the term $\delta(f)$ can be neglected (since it is different from zero for $f = 0$) obtaining

$$T(f) = (T_0^2 - D/\gamma)\sqrt{2/\pi}\frac{2\gamma}{4\pi^2 f^2 + 4\gamma}. \tag{154}$$

The diffusion coefficient can be expressed in term of h since $D \sim 1/h^2$ and we get

$$T(f) = \frac{A}{h^2(\pi^2 f^2 + \gamma)}. \tag{155}$$

If one considers the h and γ as fitting parameters (h is of the order of tens of meters and γ of the order of $monts^{-1}$) the equation above turns out to be indeed a good fitting formula for the experimental data that concern the oceanic temperatures.

Problems

1. Consider a 1D Brownian particle of mass m which is attached to a harmonic spring with elastic constant k. The Langevin equations are

$$\frac{dv}{dt} = -\gamma v(t) - \omega_0^2 x(t) + A(t) \qquad \text{and} \frac{dx}{dt} = v(t) \tag{156}$$

where $\omega_0 = \sqrt{k/m}$. Let x_0 and v_0 be the initial position and velocity of the Brownian particle and assume it is initially in equilibrium at temperature T with the surrounding fluid. Then, by the equipartition theorem, the average kinetic energy is $\frac{1}{2}m\langle v_0^2\rangle_T = \frac{1}{2}k_B T$ and the average vibrational energy $\frac{1}{2}\omega_0^2\langle x_0^2\rangle_T = \frac{1}{2}k_B T$. One also assumes that x_0 and v_0 are statistically independent so that $\langle x_0 v_0\rangle_T = 0$.

(A) Show that a condition for the process to be stationary is that the noise strength is $\sigma^2 = 4\gamma k_B T$.

(B) Compute the velocity correlation function $\langle\langle v(t_1)v(t_2)\rangle_{x_0,v_0}\rangle_T$

2. A Brownian particle of mass m is attached to a harmonic spring with force constant k and is driven by an external force $F(t)$. The particle is constrained to move in 1D. The Langevin equation is

$$m\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + m\omega_0^2 x(t) = A(t) + F(t) \tag{157}$$

where $\omega_0^2 = (k/m)$ and $A(t)$ is the white noise.

(A) Compute the two-point correlation function $\langle x(t+\tau)x(t)\rangle$ in the stationary regime.

(B) Clearly $x(t)$ is not a Markov process. However the two-dimensional process $[x(t), v(t)]$ is Markov with evolution equation

$$\frac{dv}{dt} = -\gamma v(t) - \omega_0^2 x(t) + A(t) \qquad \text{and} \frac{dx}{dt} = v(t). \tag{158}$$

Compute in this case the correlation matrix

$$\langle\left(\begin{array}{cc} \langle x(t)x(t+\tau)\rangle & \langle x(t)v(t+\tau)\rangle \\ \langle v(t)v(t+\tau)\rangle & \langle v(t)v(t+\tau)\rangle \end{array} \right)\rangle \tag{159}$$

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