

LANGEVIN THEORY OF BROWNIAN MOTION

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1 Langevin theory

Einstein (as well as Smoluchowski) was well aware that the theory of Brownian motion was valid for experimental observations that occur at time intervals spaced by an amount larger than the characteristic time scale τ_B for the loss of the speed gained in a single collision. For shorter time intervals, the motion of the Brownian particle cannot be described as a diffusive process, which is a valid approximation only for times larger than τ_B .

When the motion is observed on times larger than τ_B is erratic and

irregular as a sample path of the Wiener process (see picture above), so that if one tries to measure the velocity

$$\frac{\Delta X}{\Delta t} \sim \frac{1}{\sqrt{\Delta t}}$$

one finds a result depending on the time interval size Δt that becomes larger and larger the more the time interval is reduced. This is just a manifestation of the basic scaling law of the Wiener process. But this approximation is not valid for times shorter than τ_B . Thus the divergence of the velocity is just an artifact of the approximation.

One wishes to go beyond the approximation and describe the motion at small times intervals. This is what Langevin (1908) did. He imagined that successive collisions with fluid molecules had an effect on the variations of each velocity component that could be described in terms of a random impulsive force $F(t)$. and, hence, the equation of motion of a coordinate of a Brownian particle of mass M would be:

$$M\dot{V} = -\gamma V + F(t). \quad (1)$$

The principal assumptions concerning this fluctuating force $F(t)$ are the following:

- (i) $F(t)$ is statistically independent of $V(t)$,
- (ii) the variations of $F(t)$ are much more frequent than the variations in $V(t)$, and
- (iii) the average of $F(t)$ is zero.

The **Langevin equation** (1) can be formally solved as it were an ordinary differential equation:

$$V_t = V_0 e^{-\alpha t} + \frac{1}{M} \int_0^t e^{-\alpha(t-s)} F(s) ds, \quad \alpha = \frac{\gamma}{M}. \quad (2)$$

Note that $1/\alpha = \tau_B$, the characteristic time of Brownian motion.

Statistical analysis Now let us be careful with the statistical analysis of the solution. We assume that the initial velocity $V_0 = v_0$ be given. So $f(v, t)$, the probability distribution of V_t has the property that

$$f(v, t) \rightarrow \delta(v - v_0) \quad \text{as} \quad t \rightarrow 0$$

Further, we know from statistical physics that the density $f(v, t)$ must approach the Maxwellian density for the temperature T of the surrounding medium, independently of v_0 as $t \rightarrow \infty$. Hence

$$f(v, t) \rightarrow \sqrt{\frac{M}{2\pi k_B T}} e^{-\frac{Mv^2}{2k_B T}} \quad \text{as } t \rightarrow \infty$$

(recall that we are focussing just on one coordinate of the velocity). This demand on $f(v, t)$, in turn, requires $F(t)$ to have certain statistical properties: From eq. (2) we have

$$V_t - V_0 e^{-\alpha t} = \frac{1}{M} \int_0^t e^{-\alpha(t-s)} F(s) ds$$

Consequently, the statistical properties of the integral must be the same as those of the difference $V_t - V_0 e^{-\alpha t}$. Since

$$V_t - V_0 e^{-\alpha t} \sim V(t) \quad \text{for large } t,$$

the integral must have in the limit a Gaussian distribution. We write the integral as a finite Riemann sum

$$\begin{aligned} \int_0^t e^{-\alpha(t-s)} F(s) ds &\approx e^{-\alpha t} \sum_k e^{\alpha k \Delta t} F(k \Delta t) \Delta t \\ &= e^{-\alpha t} \sum_k e^{\alpha k \Delta t} \Delta J_k \end{aligned}$$

where

$$\Delta J_k = F(k \Delta t) \Delta t$$

are the impulses suffered by the particle in the time intervals $(k \Delta t, (k + 1) \Delta t)$. Thus for large t we obtain

$$V_t \approx \frac{1}{M} \sum_k e^{\alpha(k \Delta t - t)} \Delta J_k = \sum_k e^{\alpha(k \Delta t - t)} \Delta A_k, \quad (3)$$

The random variables $\Delta A_k = \Delta J_k / M$ are the random accelerations suffered by the Brownian particle in the time interval $(k \Delta t, (k + 1) \Delta t)$. Thus we may assume that the variables ΔA_k are statistically **independent** of

each other, since the successive collisions are (almost) **uncorrelated**. We shall assume that the time intervals Δt are large compared to the average period of a single fluctuation of $F(t)$. The period of fluctuation of $F(t)$ is of the order of the time τ_s between successive collisions between the Brownian particle and the molecules of the surrounding fluid; in a liquid, this is generally of the order of 10^{-20} sec. Accordingly, each acceleration ΔA_k is the result of many collisions, so that we may assume that all ΔA_k have the same statistical properties, that is that they are **i.i.d. random variables**. Therefore, if we choose ΔA_k to be zero mean Gaussian variables, then V_t will be Gaussian, as required. To compute the variance of ΔA_k , we set

$$\text{Var}(\Delta A_k) = 2q\Delta t$$

and using eq. (3), we obtain

$$\begin{aligned} \langle V_t^2 \rangle &= \sum_k 2q\Delta t e^{2\alpha(k\Delta t - t)} \quad \rightarrow \quad \frac{2q}{M^2} \int_0^t e^{2\alpha(s-t)} \\ &= \frac{q}{\alpha} (1 - e^{-\alpha(t+s)}) \quad \text{as } \Delta t \rightarrow 0 \end{aligned}$$

On the other hand we have

$$\langle V_t^2 \rangle \rightarrow \frac{k_B T}{M}$$

Thus

$$q = \frac{\alpha k_B T}{M} = \frac{2\gamma k_B T}{M^2}$$

whence the variance of the impulses:

$$\text{Var}(\Delta J_k) = 2\gamma k_B T \Delta t \quad (4)$$

From this, Langevin was able to show that

$$X_t = X_0 + \int_0^t V_t dt, \quad (5)$$

while differentiable on a short time scale, it behaves diffusively on a long time scale with probability distribution for large times given approximately by

$$p(x, t) \approx \frac{1}{(4\pi Dt)^{1/2}} e^{-\frac{x^2}{4Dt}} \quad (6)$$

with D the diffusion constant found by Einstein.

2 The Ornstein-Uhlenbeck process

In 1930, Uhlenbeck and Ornstein reformulated the theory of Langevin in the modern language of stochastic processes. According to their reformulation, the motion of a Brownian particle is given by the following process:

$$\begin{cases} \dot{X} &= V \\ M\dot{V} &= -\gamma V + \sigma\dot{W}, \end{cases} \quad (7)$$

where $\dot{W}(t)$ is **white noise** and γ and σ satisfy the following relation

$$\sigma^2 = 2\gamma k_B T. \quad (8)$$

The solution of eq. (7) is just that found by Langevin translated in the language of stochastic processes:

$$\begin{cases} X_t &= X_0 + \int_0^t V_s ds \\ V_t &= V_0 e^{-\alpha t} + \frac{\sigma}{M} \int_0^t e^{-\alpha(t-u)} \dot{W} du, \quad \alpha = \frac{\gamma}{M} \end{cases} \quad (9)$$

Thus V is a gaussian process with mean

$$\langle V_t \rangle = \langle V_0 \rangle e^{-\alpha t}. \quad (10)$$

Recalling the basic property of white noise,

$$\langle \dot{W}(t)\dot{W}(s) \rangle = \delta(t - s),$$

and noting that V_0 and \dot{W} are independent, we can compute the correla-

tion function of the velocity process. For $s < t$, we have

$$\begin{aligned}
\langle \mathbf{V}_t \mathbf{V}_s \rangle &= \langle \mathbf{V}_0^2 \rangle e^{-\alpha(t+s)} + \frac{\sigma^2}{M^2} \int_0^t du e^{-\alpha(t-u)} \int_0^s e^{-\alpha(s-v)} \langle \dot{\mathbf{W}}_u \dot{\mathbf{W}}_v \rangle \\
&= \langle \mathbf{V}_0^2 \rangle e^{-\alpha(t+s)} + \frac{\sigma^2}{M^2} \int_0^t du e^{-\alpha(t-u)} \int_0^s e^{-\alpha(s-v)} \delta(u-v) dv \\
&= \langle \mathbf{V}_0^2 \rangle e^{-\alpha(t+s)} + \frac{\sigma^2}{M^2} \int_0^t du e^{-\alpha(t-u)} e^{-\alpha(s-u)} \\
&= \langle \mathbf{V}_0^2 \rangle e^{-\alpha(t+s)} + \frac{\sigma^2}{M^2} \int_0^t du e^{-\alpha(t+s-2u)} \\
&= \langle \mathbf{V}_0^2 \rangle e^{-\alpha(t+s)} + \frac{\sigma^2}{2\alpha M^2} [e^{-\alpha(t-s)} - e^{-\alpha(t+s)}] \\
&= \left[\langle \mathbf{V}_0^2 \rangle - \frac{\sigma^2}{2\alpha M^2} \right] e^{-\alpha(t+s)} + \frac{\sigma^2}{2\alpha M^2} e^{-\alpha(t-s)},
\end{aligned}$$

whence, recalling eq. (8),

$$\langle \mathbf{V}_t \mathbf{V}_s \rangle = \left[\langle \mathbf{V}_0^2 \rangle - \frac{k_B T}{M} \right] e^{-\alpha(t+s)} + \frac{k_B T}{M} e^{-\alpha(t-s)}.$$

If $s > t$ the result will be the same but with t and s exchange. Thus,

$$\langle \mathbf{V}_t \mathbf{V}_s \rangle = \left[\langle \mathbf{V}_0^2 \rangle - \frac{k_B T}{M} \right] e^{-\alpha(t+s)} + \frac{k_B T}{M} e^{-\alpha|t-s|}. \quad (11)$$

So we see that at equilibrium, when, by equipartition,

$$\langle \mathbf{V}_0 \rangle = 0, \quad \langle \mathbf{V}_0^2 \rangle = \frac{k_B T}{M}, \quad (12)$$

the Uhlenbeck and Ornstein process is a mean zero stationary gaussian process with correlation function

$$\langle \mathbf{V}_t \mathbf{V}_s \rangle = \frac{k_B T}{M} e^{-\alpha|t-s|} \quad (13)$$

For an initial non equilibrium velocity, the variance $C_V(t)$ of the velocity process is obtained from eq. (10) and eq. (11) for $t = s$:

$$C_V(t) = \langle (\mathbf{V}_t - \langle \mathbf{V}_t \rangle)^2 \rangle = \langle \mathbf{V}_t^2 \rangle - \langle \mathbf{V}_t \rangle^2 = \frac{k_B T}{M} (1 - e^{-2\alpha t}) \quad (14)$$

Exercise Let

$$C_X(t) = \langle (X_t - \langle X_t \rangle)^2 \rangle$$

be the covariance of the position process. Show that

$$C_X(t) = \begin{cases} \frac{k_B T}{M} t^2 & \text{as } t \rightarrow 0 \\ \frac{2k_B T}{\gamma} t & \text{as } t \rightarrow \infty \end{cases} \quad (15)$$

The result for short times is the free particle term, $X_t - X_0 = v_0 t$. The result for long times can be compared with the diffusion result

$$\langle (X_t - \langle X_t \rangle)^2 \rangle = 2Dt$$

which gives the Einstein result

$$D = \frac{k_B T}{\gamma} = \frac{k_B T}{6\pi\eta a}. \quad (16)$$