

Physical Interpretation of Solution of Langevin Equation

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11:33 AM

Homework 1 solutions to be posted tonight.

Let's concentrate on the correlation function of the velocity after we wait a long time so that the system has settled down into thermal equilibrium and forgotten the initial conditions.

$$\lim_{t \rightarrow \infty} \text{Cov}(\vec{V}(t), \vec{V}(t+\tau)) = \frac{k_B T}{m} \mathbf{1} e^{-\frac{\gamma}{m} \tau} \equiv C^{VV}(\tau)$$

We see two combinations of physical constants that govern the behavior of the velocity of a Brownian particle in thermal equilibrium.

The root-mean-square velocity along any direction is:

$$V_{rms} = \sqrt{\langle (V_j(t))^2 \rangle} = \sqrt{C_{jj}^{VV}(0) + \langle V_j(t) \rangle^2}$$

(in thermal equilibrium)

$$= \sqrt{\frac{k_B T}{m}} \quad \left(\sqrt{\langle |\vec{V}(t)|^2 \rangle} = \sqrt{\langle \sum_{j=1}^3 V_j(t)^2 \rangle} = \sqrt{\frac{3 k_B T}{m}} \right)$$

$$k_B = 1.38 \times 10^{-16} \text{ g cm}^2 / \text{s}^2 \text{ K}$$

$$T \approx 300 \text{ K}$$

$$m \approx \frac{4}{3} \pi \rho a^3 \quad (\text{sphere of radius } a \text{ mass density } \rho)$$

$$\rho \approx 1 \text{ g/cm}^3$$

$$m \approx 4 \text{ g} \left(\frac{a}{\text{cm}} \right)^3$$

$$V_{rms} \approx \sqrt{\frac{4 \times 10^{-14} \text{ g cm}^2 / \text{s}^2}{4 \text{ g} \left(\frac{a}{\text{cm}} \right)^3}} = \sqrt{\frac{10^{-14} \text{ cm}^2 / \text{s}^2}{(a/\text{cm})^3}}$$

Colloid, suspension $\sim a \approx 10^{-4} \text{ cm}$

$$V_{rms} \approx 10^{-1} \text{ cm/s}$$

Small molecules $a \approx 10^{-7} \text{ cm}$

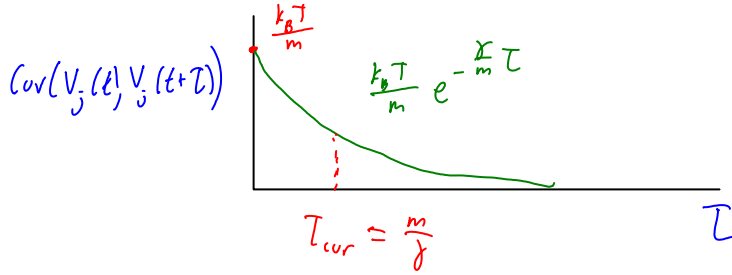
$$V_{rms} \approx 3 \times 10^3 \text{ cm/s}$$

The other key quantity describing the dynamics of the velocity is the time scale on which the velocity of the particle is forgotten

$$T = \frac{m}{\gamma}$$

τ_{cor} δ

This is the time scale over which correlations (as measured by the correlation function) of the velocity persists.

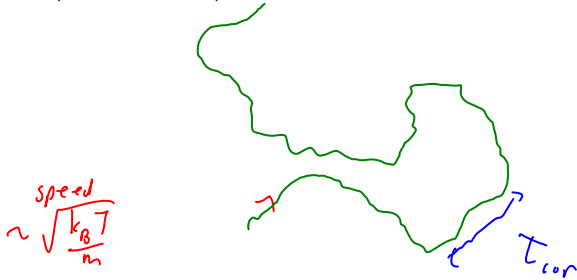


More general formula for correlation time:

$$\tau_{cor} = \frac{\int_0^{\infty} Cov(V_j(t), V_j(t+\tau)) d\tau}{Var(V_j(t))}$$

$\approx Cov(V_j(0), V_j(0))$

Dynamically this indicates that the particle motion looks as follows:



$\gamma = 6\pi \rho_{env} r a$ for rigid sphere in low Reynolds fluid

$\rho_{env} \sim 1 \frac{g}{cm^3}$ in liquids (smaller in gas)

$r = 0.01 \frac{cm^2}{s}$ for water at room temp
kinematic viscosity

$\gamma \approx 20 \times 0.01 \frac{g}{s} \left(\frac{a}{cm}\right) = 0.2 \left(\frac{a}{cm}\right) \frac{g}{s}$

$\tau_{cor} \approx \frac{4 \left(\frac{a}{cm}\right)^3 g}{0.2 \left(\frac{a}{cm}\right) \frac{g}{s}} = 20 \left(\frac{a}{cm}\right)^2 s$

For colloid $a \sim 10^{-4} cm$

$$\tau_{cur} \sim 2 \times 10^{-7} \text{ s}$$

For small molecule $a \sim 10^{-7} \text{ cm}$

$$\tau_{cur} \sim 2 \times 10^{-13} \text{ s}$$

So now we turn to the behavior of the position of the particle.

$$d\vec{X} = \vec{v} dt$$

$$\vec{X}(t) = \int_0^t \vec{v}(s) ds + \vec{X}(0)$$

↑
sub in

$$= \int_0^t \left(\vec{v}(0) e^{-\frac{\gamma}{m}s} + \frac{\sqrt{g}}{m} \int_0^s e^{-\frac{\gamma}{m}(s-s')} d\vec{W}(s') \right) ds$$

$$\vec{X}(t) = \frac{m}{\gamma} \vec{v}(0) (1 - e^{-\frac{\gamma}{m}t}) + \frac{\sqrt{g}}{m} \int_0^t ds \int_0^s d\vec{W}(s') e^{-\frac{\gamma}{m}(s-s')} + \vec{X}(0)$$

By inspecting this formula, we see that if the initial values of the position and velocity are deterministic or jointly Gaussian distributed, then the position of the particle at a later time is just sums and integrals of Gaussian random variables with deterministic weights, so the result is again that the position obeys Gaussian statistics. $X(t)$ is a Gaussian random function. Therefore it can be completely described by its mean and covariance function. Doing direct averaging on this formula will work using the basic stochastic calculus rules but very tedious.

A less painful to proceed is to keep the observation from this formula that $X(t)$ is a Gaussian random function, but compute its mean and covariance using the previously computed results for the mean and covariance of the velocity $v(t)$.

$$\vec{X}(t) = \int_0^t \vec{v}(s) ds + \vec{X}(0)$$

Just directly average this expression rather than substituting in the exact formula for the velocity

$$\begin{aligned} \langle \vec{X}(t) \rangle &= \left\langle \int_0^t \vec{v}(s) ds \right\rangle + \langle \vec{X}(0) \rangle \\ &= \int_0^t \langle \vec{v}(s) \rangle ds + \langle \vec{X}(0) \rangle \\ &= \int_0^t \langle \vec{v}(s) \rangle ds = \int_0^t \langle \vec{v}(s) \rangle ds \end{aligned}$$

because averages of sums are sums of averages, and integrals \approx Riemann sums

Now substitute the expression for the mean velocity

$$= \int_0^t \langle \vec{v}(s) \rangle e^{-\frac{\gamma}{m}s} ds + \langle \vec{x}(0) \rangle$$

$$\langle \vec{x}(t) \rangle = \underbrace{\frac{1}{\gamma} \langle \vec{v}(0) \rangle}_{\text{bounded}} (1 - e^{-\frac{\gamma}{m}t}) + \langle \vec{x}(0) \rangle$$

We can similarly compute the covariance of the position at different times as follows:

$$\text{Cov}(\vec{x}(t), \vec{x}(s)) = \langle \vec{x}(t) \otimes \vec{x}(s) \rangle - \langle \vec{x}(t) \rangle \otimes \langle \vec{x}(s) \rangle$$

$$\langle \vec{x}(t) \otimes \vec{x}(s) \rangle = \langle (A + B) \otimes (C + D) \rangle$$

$$= \langle A \otimes C \rangle + \langle A \otimes D \rangle + \langle B \otimes C \rangle + \langle B \otimes D \rangle$$

$$\text{using } \vec{x}(t) = \int_0^t \underbrace{\vec{v}(t')}_{A} dt' + \underbrace{\vec{x}(0)}_B$$

$$\vec{x}(s) = \int_0^s \underbrace{\vec{v}(s')}_{C} ds' + \underbrace{\vec{x}(0)}_D$$

$$\langle \vec{x}(t) \otimes \vec{x}(s) \rangle = \langle \int_0^t \vec{v}(t') dt' \otimes \int_0^s \vec{v}(s') ds' \rangle$$

$$+ \langle \int_0^t \vec{v}(t') dt' \otimes \vec{x}(0) \rangle$$

$$+ \langle \vec{x}(0) \otimes \int_0^s \vec{v}(s') ds' \rangle$$

$$+ \langle \vec{x}(0) \otimes \vec{x}(0) \rangle$$

$$= \int_0^t dt' \int_0^s ds' \langle \vec{v}(t') \otimes \vec{v}(s') \rangle$$

$$+ \int_0^t \langle \vec{v}(t') \otimes \vec{x}(0) \rangle dt'$$

$$+ \int_0^s \langle \vec{x}(0) \otimes \vec{v}(s') \rangle ds'$$

$$+ \langle \vec{x}(0) \otimes \vec{x}(0) \rangle$$

from initial conditions

Need to work out:

$$\begin{aligned}
 \langle \vec{V}(t') \otimes \vec{X}(t) \rangle &= \langle \vec{V}(t) e^{-\frac{\gamma}{m} t'} + \int_0^{t'} e^{-\frac{\gamma}{m}(t-t'')} d\vec{W}(t'') \rangle \otimes \vec{X}(t) \\
 &= \langle \vec{V}(t) \otimes \vec{X}(t) \rangle e^{-\frac{\gamma}{m} t'} \\
 &\quad + \int_0^{t'} e^{-\frac{\gamma}{m}(t-t'')} \langle d\vec{W}(t'') \otimes \vec{X}(t) \rangle
 \end{aligned}$$

\uparrow
 only involves information about noise at time ≤ 0 .

$$\langle \vec{V}(t') \otimes \vec{X}(t) \rangle = \langle \vec{V}(t) \otimes \vec{X}(t) \rangle e^{-\frac{\gamma}{m} t'}$$

Similarly

$$\langle \vec{X}(t) \otimes \vec{V}(s') \rangle = \langle \vec{X}(t) \otimes \vec{V}(t) \rangle e^{-\frac{\gamma}{m} s'}$$

So this shows that the covariance of the position of the Brownian particle at two different times t and s can be computed through integrating some exponentials a few times -- details are just calculus exercise. Such detailed results can be seen for example in Chandrasekhar's article (to be posted in optional reading).

For our purposes, let's focus just on the central question of what is the covariance of the position of the particle at one time t and we'll just look at the behavior at long time, which is usually of fundamental interest. First we observe that only the first term in the above expansion will grow with time; the other terms are bounded (as is either clear from being constant or being an integral of a decaying exponential). Just look at first term:

$$\begin{aligned}
 \text{Cov}(\vec{X}(t), \vec{X}(t)) &= \int_0^t \int_0^t dt' ds' \left(\text{Cov}(\vec{V}(t'), \vec{V}(t')) e^{-\frac{\gamma}{m}(t'+s')} \right. \\
 &\quad \left. + \frac{g}{2m\gamma} \left(e^{-\frac{\gamma}{m}(t'-s')} - e^{-\frac{\gamma}{m}(t+s')} \right) \right)
 \end{aligned}$$

also integrate to bounded expression

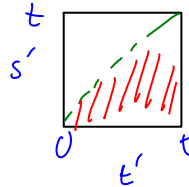
$$+ O(1)$$

$$= \frac{g}{2m\gamma} \int_0^t \int_0^t dt' ds' e^{-\frac{\gamma}{m}|t'-s'|} + O(1)$$

\uparrow bounded in time

$$= \frac{g}{2m\gamma} \int_0^t \left(2 \int_0^{t'} e^{-\frac{\gamma}{m}(t'-s')} ds' \right) dt'$$

$s' < t'$ contribution
 $s' > t'$ contribution is omitted but is the same so



Change

$$\begin{aligned}
 u &= t' - s' \\
 t' &= t'
 \end{aligned}$$

$$\text{Cov}(\vec{V}(t), \vec{V}(t)) = \frac{g}{2m\gamma} \int_0^t dt + O(1)$$

$$\text{Cov}(\vec{X}(t), \vec{X}(t)) = \frac{g}{\gamma} \propto t + o(1)$$

$$g = 2\gamma k_B T$$

$$\text{Cov}(\vec{X}(t), \vec{X}(t)) = \frac{2k_B T}{\gamma} \propto \textcircled{t} + o(1)$$