TD 9: Langevin Equation - Solutions

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Consider the Langevin equation

$$\frac{d\mathbf{v}}{dt} = -\gamma \mathbf{v} + \frac{\mathbf{F}(t)}{m}, \tag{1}$$

where $\mathbf{v} = \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t}$ is the velocity of a particle of mass m, γ is the linear (Stokes) drag coefficient and $\mathbf{F}(t)$ a random force experienced by the particle. We assume that the random force is 0 on average $\overline{\mathbf{F}} = 0$, uncorrelated in time $\overline{\mathbf{F}(t_1) \cdot \mathbf{F}(t_2)} = 6Dm^2\delta(t_2 - t_1)$ and that $\overline{\mathbf{x}(t) \cdot \mathbf{F}(t)} = 0$, where the bar represents the ensemble average.

How to calculate the Avogadro number?

1. At thermal equilibrium, what is the average $\overline{\mathbf{v}^2}$?
2. Deduce that velocity and acceleration are not correlated in equilibrium, *i.e.* $\overline{\mathbf{v} \cdot \mathbf{a}} = 0$.
3. Show that at late times a particle in thermal equilibrium obeys

$$\overline{\mathbf{x}^2} = \frac{6k_B T}{m\gamma} t, \tag{2}$$

   where k_B is the Boltzmann constant and T the temperature.
4. How can you deduce experimentally the Avogadro number?

Analytic study of the Langevin equation. In this part, we solve explicitly the equation.

5. Prove that the explicit solution of Langevin equation for initial conditions $\mathbf{x}(t=0) = 0$ and $\mathbf{v}(t=0) = \mathbf{v}_0$ is

$$\mathbf{x}(t) = \frac{\mathbf{v}_0}{\gamma}\left(1 - e^{-\gamma t}\right) + \int_0^t dt' \int_0^{t'} dt'' \frac{\mathbf{F}(t'')}{m} e^{-\gamma(t'-t'')}. \tag{3}$$

6. Why is it reasonable to assume $\overline{\mathbf{x}(t) \cdot \mathbf{F}(t)} = 0$? Derive $\overline{\mathbf{x}(t_1) \cdot \mathbf{F}(t_2)}$ from the solution $\mathbf{x}(t)$ calculated in the previous question. When is $\overline{\mathbf{x}(t) \cdot \mathbf{F}(t)} = 0$ violated?
7. Compute $\sigma_x^2 = \overline{(\mathbf{x} - \overline{\mathbf{x}})^2}$ directly from the solution $\mathbf{x}(t)$ of the Langevin equation. What conclusion can we deduce.

Einstein relation. We link the diffusivity with the mobility and the drag.

8. The mobility μ is defined by $\overline{\mathbf{v}}_\infty = \mu \mathbf{F}_{ext}$, where $\mathbf{F}_{ext}$ is an applied external force and $\overline{\mathbf{v}}_\infty$ is the average velocity of the particle of mass m in the long-time limit. If we have a density ρ of molecules, what is the induced flux $\mathbf{j}_\mu$?
9. Additionally, when ρ is non-uniform there is a diffusive flux $\mathbf{j}_\rho = -D_x \nabla \rho$. Show that for a classical particle in a heat path at thermal equilibrium we get

$$D_x = \mu k_B T. \tag{4}$$

   This result is known as Einstein relation and is a special case of the more general fluctuation-dissipation theorem. It relates the diffusion constant to measurable observables of the system.
10. Explicit the links between γ and μ and between D and D_x. Deduce the the diffusivity for a particle in the context of a Stokes force.

Correction

1. The equipartition of energy states that $\frac{1}{2}m\overline{\mathbf{v}^2} = \frac{3}{2}k_B T$ *i.e.* $\overline{v^2} = 3\frac{k_B T}{m}$.

2. A simple way to show this is to argue that, in equilibrium, the non-connected instantaneous autocorrelation function of the velocity is given by, $\overline{\mathbf{v}^2} = k_B T/m$ and so,

$$\frac{d}{dt}\overline{\mathbf{v}^2} = 0 \Longrightarrow 2\overline{\mathbf{v}\cdot\frac{d\mathbf{v}}{dt}} = 0 \Longrightarrow \overline{\mathbf{v}\cdot\mathbf{a}} = 0, \quad (5)$$

and so the velocity and acceleration are not correlated in equilibrium.

3. Multiplying by $\mathbf{x}$ we get,

$$\mathbf{x}\cdot\frac{d^2\mathbf{x}}{dt^2} = -\gamma\mathbf{x}\cdot\frac{d\mathbf{x}}{dt} + \frac{\mathbf{x}\cdot\mathbf{F}(t)}{m}. \quad (6)$$

Taking the ensemble average, and assuming $\overline{\mathbf{x}(t)\cdot\mathbf{F}(t)} = 0$,

$$\overline{\mathbf{x}\cdot\frac{d^2\mathbf{x}}{dt^2}} = -\gamma\overline{\mathbf{x}\cdot\frac{d\mathbf{x}}{dt}} = -\frac{1}{2}\gamma\frac{d\overline{\mathbf{x}^2}}{dt}, \quad (7)$$

where we have taken $\overline{\mathbf{x}\cdot\frac{d\mathbf{x}}{dt}} = \frac{1}{2}\frac{d\overline{\mathbf{x}^2}}{dt}$, since the ensemble average is time independent. To arrive at the required solution, we can average the fact that at thermal equilibrium the equipartition theorem dictates that $\overline{\mathbf{v}^2} = 3\frac{k_B T}{m}$, so we should rewrite $\overline{\mathbf{x}\cdot\frac{d^2\mathbf{x}}{dt^2}}$ in terms of $\overline{\left(\frac{d\mathbf{x}}{dt}\right)^2}$. This can be done by taking

$$\frac{d}{dt}\left(\mathbf{x}\cdot\frac{d\mathbf{x}}{dt}\right) = \left(\frac{d\mathbf{x}}{dt}\right)^2 + \mathbf{x}\cdot\frac{d^2\mathbf{x}}{dt^2} \Longrightarrow \frac{1}{2}\frac{d^2\mathbf{x}^2}{dt^2} = \mathbf{x}\cdot\frac{d^2\mathbf{x}}{dt^2} + \mathbf{v}^2. \quad (8)$$

Using $\overline{\mathbf{x}\cdot\frac{d^2\mathbf{x}}{dt^2}} = -\frac{1}{2}\gamma\frac{d\overline{\mathbf{x}^2}}{dt}$ and the equipartition theorem we get,

$$\frac{d^2}{dt^2}\overline{\mathbf{x}^2} + \gamma\frac{d}{dt}\overline{\mathbf{x}^2} = \frac{6k_B T}{m}. \quad (9)$$

We can now solve for $\overline{\mathbf{x}^2}$ as a function of time. Using an integrating factor $e^{\gamma t}$ and writing $y = \overline{\mathbf{x}^2}$,

$$\frac{d}{dt}\left(e^{\gamma t}\frac{dy}{dt}\right) = e^{\gamma t}\frac{6k_B T}{m} \Longrightarrow e^{\gamma t}\frac{dy}{dt} = \frac{e^{\gamma t}}{\gamma}\frac{6k_B T}{m} + C \Longrightarrow y(t) = \frac{6k_B T}{\gamma m}t + Ce^{-\gamma t} + D. \quad (10)$$

Taking the limit of $t \to \infty$, we get the expected behaviour,

$$\overline{\mathbf{x}^2}(t) = \frac{6k_B T}{\gamma m}t. \quad (11)$$

The linear growth of $\overline{\mathbf{x}^2}$ with time is characteristic of brownian diffusion. Other classes of random processes result in different $\overline{\mathbf{x}^2}(t) \propto t^\alpha$, with the exponents α characterising the diffusive behaviour.

4. Using the Stokes drag, $\gamma m = 6\pi\eta r$ with r the radius of the considered particle and η the dynamic viscosity, and writing the Boltzmann constant in terms of the ideal gas constant R, $k_B = R/\mathcal{N}_a$, we can measure $\frac{\overline{\mathbf{x}^2}}{t} = \frac{6k_B T}{m\gamma} = \frac{RT}{\mathcal{N}_A}\frac{1}{\pi\eta r}$. The formula was derived by Einstein in 1905 and used by Perrin in 1909 to deduce experimentally the constant.

5. Multiplying equation 1 by an integrating factor $e^{\gamma t}$ and integrating both sides, we find,

$$\frac{d}{dt}\left(e^{\gamma t}\mathbf{v}\right) = e^{\gamma t}\frac{\mathbf{F}(t)}{m} \Longrightarrow \mathbf{v}(t) = e^{-\gamma t}\mathbf{v}_0 + \int_0^t \frac{\mathbf{F}(t')}{m}e^{-\gamma(t-t')}dt' \quad (12)$$

where we used the fact that $\mathbf{v}(t=0) = \mathbf{v}_0$. Using the initial condition for the position $\mathbf{x}(t=0) = 0$, we get

$$\mathbf{x}(t) = \int_0^t \mathbf{v}(t)dt = \frac{\mathbf{v}_0}{\gamma}\left(1 - e^{-\gamma t}\right) + \int_0^t dt' \int_0^{t'} dt'' \frac{\mathbf{F}(t'')}{m}e^{-\gamma(t'-t'')}. \quad (13)$$

6. Regarding the assumption of $\overline{\mathbf{x}(t)\cdot\mathbf{F}(t)} = 0$, this was indeed the assumption of Langevin, who argued that the effects of the random noise cannot act instantaneously. We can show that this is true by computing $\overline{\mathbf{x}(t)\cdot\mathbf{F}(t)}$ using the solution of the Langevin equation for $\mathbf{x}(t)$. Multiplying by $F(t^*)$ and taking the ensemble average we find,

$$\overline{\mathbf{x}(t)\cdot\mathbf{F}(t^*)} = \frac{1}{m}\int_0^t dt' \int_0^{t'} dt'' \overline{\mathbf{F}(t'')\cdot\mathbf{F}(t^*)}e^{-\gamma(t'-t'')}, \quad (14)$$

where the first term vanishes because $\overline{\mathbf{F}} = 0$. Using the given two point correlation for the random force we obtain,

$$\begin{aligned}
\overline{\mathbf{x}(t) \cdot \mathbf{F}(t^*)} &= 6Dm \int_0^t dt' \int_0^{t'} dt'' \delta(t'' - t^*) e^{-\gamma(t'-t'')} && (15) \\
&= 6Dm \int_0^t dt' e^{-\gamma(t'-t^*)} \theta(t' - t^*) && (16) \\
&= 6Dm \int_{t^*}^t dt' e^{-\gamma(t'-t^*)} && (17) \\
&= \frac{6Dm}{\gamma} \left(1 - e^{-\gamma(t-t^*)}\right). && (18)
\end{aligned}$$

Where $\theta(\cdot)$ is the Heaviside step function, which results from integrating the delta function in $t'' \in [0, t']$; the integration is only non-zero if $t' > t^*$, thus the subsequent change in the limits of integration. Indeed, for $t = t^*$, $\overline{\mathbf{x}(t) \cdot \mathbf{F}(t)} = 0$. It seems intuitive that there should not be a correlation between force position and particle at the same time. However, the assumption $\overline{\mathbf{x}(t) \cdot \mathbf{F}(t)} = 0$ is violated whenever the force has a non-zero auto-correlation time (the collision time scale), in this case the sharp cut-off at $\tau = 0$ is smoothed out over an interval $\tau \in [-\tau_c, \tau_c]$. In this sense, approximating the collisions with the heat bath through uncorrelated white noise is a time scale separation between the time scale of random fluctuations and the macroscopic time scales of the system.

7. From the solution of $\mathbf{x}(t)$ and using the fact that $\overline{\mathbf{F}(t)} = 0$, the ensemble average of the position is given by,

$$\overline{\mathbf{x}} = \frac{\mathbf{v}_0}{\gamma} \left(1 - e^{-\gamma t}\right), \quad (19)$$

and thus

$$\mathbf{x} - \overline{\mathbf{x}} = \int_0^t dt' \int_0^{t'} dt'' \frac{\mathbf{F}(t'')}{m} e^{-\gamma(t'-t'')}, \quad (20)$$

so the variance is given by,

$$\begin{aligned}
\sigma_x^2 &= \frac{1}{m^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^t dt_3 \int_0^{t_3} dt_4 \mathbf{F}(t_2) \cdot \mathbf{F}(t_4) e^{-\gamma(t_1 - t_2 + t_3 - t_4)} && (21) \\
&= 6D \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^t dt_3 \int_0^{t_3} dt_4 \delta(t_2 - t_4) e^{-\gamma(t_1 - t_2 + t_3 - t_4)} && (22) \\
&= 6D \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^t dt_3 \theta(t_3 - t_2) e^{-\gamma(t_1 + t_3 - 2t_2)} && (23) \\
&= -\frac{6D}{\gamma} \int_0^t dt_1 \int_0^{t_1} dt_2 \, e^{-\gamma(t_1 + t_3 - 2t_2)} \Big|_{t_2}^{t} && (24) \\
&= \frac{6D}{\gamma} \int_0^t dt_1 \int_0^{t_1} dt_2 e^{-\gamma(t_1 - t_2)} - \frac{2D}{\gamma} \int_0^t dt_1 \int_0^{t_1} dt_2 e^{-\gamma(t_1 + t - 2t_2)} && (25) \\
&= \frac{6D}{\gamma^2} \int_0^t dt_1 \, e^{-\gamma(t_1 - t_2)} \Big|_0^{t_1} - \frac{D}{\gamma^2} \int_0^t dt_1 \, e^{-\gamma(t_1 + t - 2t_2)} \Big|_0^{t_1} && (26) \\
&= \frac{6D}{\gamma^2} t + \frac{2D}{\gamma^3} \, e^{-\gamma t_1} \Big|_0^t - \frac{D}{\gamma^3} \, e^{-\gamma(t - t_1)} \Big|_0^t - \frac{D}{\gamma^3} \left(e^{-2\gamma t} - e^{-\gamma t}\right) && (27) \\
&= \frac{6D}{\gamma^2} \left[t + \frac{2}{\gamma} \left(e^{-\gamma t} - 1\right) - \frac{1}{2\gamma} \left(e^{-2\gamma t} - 1\right) \right]. && (28)
\end{aligned}$$

Interestingly, for large times $t \to \infty$,

$$\sigma_x^2 \sim \frac{6D}{\gamma^2} t, \quad (29)$$

which comparing with the result of question 2 allows us to identify the diffusion constant as

$$D = \frac{\gamma k_B T}{m} \Longrightarrow \frac{Dm}{\gamma} = k_B T. \quad (30)$$

The fact that the system is in equilibrium and thus obeys the equipartition-theorem, yields in a thermal noise magnitude that precisely balances the dissipation to keep the system in equilibrium. This is called the fluctuation-dissipation theorem.

8. We simply have $\mathbf{j}_\mu = \rho \mu \mathbf{F}_{ext}$.

9. At equilibrium we know that there is no net flux, meaning that $\mathbf{j}_\rho + \mathbf{j}_\mu = 0$. Additionally, the particles will be distributed according to the canonical ensemble (Boltzmann distribution). Denoting $\mathbf{F}_{ext} = -\nabla V$, we have

$$\rho(\mathbf{x}) = \frac{e^{-\beta V(\mathbf{x})}}{Z} \Longrightarrow \nabla \rho = -\beta \rho \nabla V = \beta \rho \mathbf{F}_{ext}. \quad (31)$$

Combining these we get,

$$\rho \mu \mathbf{F}_{ext} - D_x \beta \rho \mathbf{F}_{ext} = 0 \Longrightarrow D_x = \mu k_B T \quad (32)$$

10. Taking Langevin equation and choosing $\overline{\mathbf{F}} = \mathbf{F}_{ext}$ gives, when averaging, $\mathbf{v}_\infty = \frac{\mathbf{F}_{ext}}{\gamma m}$ *i.e.* $\mu = \frac{1}{\gamma m}$. Comparing the previous results we deduce $D = \gamma^2 D_x$. We assume $\gamma m = 6\pi \eta r$. Thus, $D_x = \frac{k_B T}{\gamma m} = \frac{k_B T}{6\pi \eta r}$.