Homework 3 Solution

1. In 1907 Einstein remarked: for a Brownian particle its average velocity may be obtained from its short-time displacement, but a very short time average does not make sense (as the average over the true velocity).

It is extremely hard (or almost impossible) to verify the equipartition of energy for a Brownian particle, even though Langevin simply declared the average in (9.4) to be $3k_BT/2$. This was another reason (according to some people) that Brownian motion was not seriously discussed by thermal physicists.

The mean displacement during time $t$ is proportional to $\sqrt{t}$. This implies that the instantaneous velocity must be undefinable; the motion is very erratic. Perrin commented that the Brownian path is nowhere differentiable.

A Brownian particle of radius 0.1 $\mu$m is suspended in water (say, at 300 K). Estimate the time needed for the initial speed to decay to its 1/10. What does this tell you about the observability of the speed of the particle? It is clear that you must have a time resolution at least one order better than this to confirm the equipartition law. [This is a ‘real physics’ question, so you must assume the mass of the Brownian particle you discuss, etc.]

Soln.
The equation of motion for the velocity of a Brownian particle of mass $m$ and radius $a$ reads

$$m \frac{dv}{dt} = -\zeta v + w,$$

where $\zeta = 6\pi \eta a$ with $\eta$ being the shear viscosity of water (we used Stokes’ law), and $w$ the random force due to impingement of water molecules.

We wish to estimate the decay rate of the particle with the initial condition $v(0)$. The ensemble average reads, since the system is linear,

$$m \frac{d}{dt} \langle v(t) \rangle = -\zeta \langle v(0) \rangle,$$

(of course you can honestly solve the equation of motion as required below and then take the ensemble average for a fixed initial velocity.) We can immediately integrate this to get

$$\langle v(t) \rangle = e^{-(6\pi \eta a/m)t} v(0).$$

We wish to estimate $t$ such that $e^{-(6\pi \eta a/m)t} = 0.1$ or

$$t = (m/(6\pi \eta a)) \log 0.1.$$

We must give a reasonable value to $m$ when $a = 10^{-7}$ m. $\eta = 1$ mPa·s may be adopted. Let us assume the particle is made of polystyrene. Its density about 1 g/cm$^3 = 1000$ kg/m$^3$. Therefore, $m = (4\pi/3)(10^{-7})^3 \times 1000 = 4.2 \times 10^{-18}$ kg,

$$t = \frac{4.2 \times 10^{-18} \times 2.3}{6\pi \times 10^{-7} \times 10^{-3}} \approx 0.5 \times 10^{-9}.$$

It is about 5 ns. You need a much higher frequency sampling to demonstrate the equipartition of energy.
2. How long will it take for a complete ribosome to diffuse across a eukaryotic cell or a bacterial cell? Again this is a ‘real science’ question, so you must look for the rough size of the ribosome complex, cell size, etc. (however, let us ignore the so-called macromolecular crowding effect). You must choose reasonable values. In contrast to eukaryotic cells bacterial cells lack molecular transporters such as kinesins. Can you comment on this general observation, referring to your quantitative estimates?

**Soln.**

Remark: since a complete ribosome exists only on mRNA, and when they are not attached, they move as large and small subunits separately, but let us not pay attention to this fact.

For Bacteria: 

\[ a = 1 \times 10^{-8} \text{ m.} \]

If we use the ordinary Stokes' law, then the diffusion constant may be estimated as

\[ D = \frac{k_B T}{6\pi \eta a}. \]

\[ \eta = 9 \times 10^{-4} \text{ Pa-s}, \ T = 300 \text{ K and } k_B = 1.38 \times 10^{-23} \text{ J/K}, \] so

\[ D = \frac{1.38 \times 10^{-23} \times 300}{6\pi \times 9 \times 10^{-4} \times 1 \times 10^{-8}} = 2.44 \times 10^{-11} \text{ m}^2/\text{s}. \]

The cell size of a bacterium is, say, 5 \( \mu \text{m} \) (representative). The mean square displacement in one direction is

\[ \langle x^2 \rangle = 2Dt, \]

so the needed time may be estimated roughly as

\[ t \sim \frac{(5 \times 10^{-6})^2}{(2 \times 2.44 \times 10^{-11})} = 5.4 \times 10^{-1} \text{ s.} \]

For eukaryotes: the ribosome is much larger \( a = 1.5 \times 10^{-8} \text{ m,} \) and the cell size may be 50 \( \mu \text{m}. \) Thus, \( D \simeq 1.5 \times 10^{-9} \text{ m}^2/\text{s}. \) Therefore, the traverse time may be estimated as

\[ t \sim \frac{(5 \times 10^{-5})^2}{(2 \times 1.5 \times 10^{-11})} = 8.3 \times 10 \text{ s.} \]

This is a bit too slow for our daily life. Thus we need transporting molecular machines. However, if there were no bacteria in the world, perhaps we could enjoy slow life. Can some bacteria out-compete other bacteria by inventing or importing (by HGT) molecular motors?

3. Let us assume a free-floating Brownian particle obeys the following Newton’s equation of motion

\[ m \frac{dv}{dt} = -\zeta v + w(t), \] (0.0.1)

where \( w(t) \) is a stationary random force whose time correlation reads

\[ \langle w(t)w^T(s) \rangle = 2\alpha I \delta(t - s). \] (0.0.2)

Here, \( I \) is the 3 \( \times \) 3 unit matrix and \( \alpha \) is a positive constant to be determined.

(1) Assuming the initial velocity to be \( v(0) \), solve the above equation of motion for \( v(t) \) in terms of \( w(s) (s \in [0, t]) \) and \( v(0) \).

(2) Using the result in (1), compute the mean square velocity \( \langle v(t)^2 \rangle \). Throughout 3 the average is an ensemble average over many identical samples.

(3) Assuming that the system is in equilibrium (i.e., we observe the Brownian particle suspended in a fluid in equilibrium at temperature \( T \); you may assume the equipartition of kinetic energy), determine \( \alpha \). Thus, you have fixed the noise amplitude in terms of the friction constant \( \zeta \) and \( T \) (the fluctuation-dissipation relation in this case).

(4) Compute the velocity autocorrelation function \( \langle v(t) \cdot v(s) \rangle \), assuming the system is in equilibrium.
(5) Show the diffusion constant of the Brownian particle reads (the Green-Kubo relation for the diffusion constant)

\[ D = \frac{1}{3} \int_0^\infty \langle v(s) \cdot v(0) \rangle ds. \]  

**Solv.**

Notice that usually the average is an ensemble average as in 4.

(1) We may use the method of variation of constants: If we ignore the inhomogeneous terms, we get the general solution

\[ v(t) = Ce^{-(\zeta/m)t}. \]

Now, let us assume that \( C \) is time-dependent as \( C(t) \) (that is why the method is called ‘the method of variation of constants’)

\[ \frac{d}{dt} v(t) = -\frac{\zeta}{m} C(t)e^{-(\zeta/m)t} + C'(t)e^{-(\zeta/m)t} = -\frac{\zeta}{m} C(t)e^{-(\zeta/m)t} + \frac{1}{m} w(t) \]

Thus, we get the equation for \( C(t) \):

\[ \frac{d}{dt} C(t) = \frac{1}{m} w(t)e^{(\zeta/m)t}, \]

which is easy to solve with the initial condition. Thus, we get

\[ v(t) = e^{-(\zeta/m)t} v(0) + \frac{1}{m} \int_0^t ds e^{-(\zeta/m)(t-s)} w(s). \]

(2) Since \( v(0) \) and \( \omega \) are statistically independent, we have

\[ \langle v(t)^2 \rangle = e^{-2(\zeta/m)t} \langle v(0)^2 \rangle + \frac{1}{m^2} \int_0^t ds \int_0^t ds' e^{-(\zeta/m)(2t-s-s')} \langle w(s) \cdot w(s') \rangle 
\]

\[ = e^{-2(\zeta/m)t} \langle v(0)^2 \rangle + \frac{1}{m^2} \int_0^t ds \int_0^t ds' e^{-(\zeta/m)(2t-s-s')} 6\alpha \delta(s-s') 
\]

\[ = e^{-2(\zeta/m)t} \langle v(0)^2 \rangle + \frac{6\alpha}{m^2} \int_0^t ds e^{-(2\zeta/m)(t-s)} 
\]

\[ = e^{-2(\zeta/m)t} \langle v(0)^2 \rangle + \frac{3\alpha}{m\zeta} \left( 1 - e^{-(2\zeta/m)t} \right) = \frac{3\alpha}{m\zeta} + \left( \langle v(0)^2 \rangle - \frac{3\alpha}{m\zeta} \right) e^{-(2\zeta/m)t}. \]

(3) Since we are in equilibrium, the formula should not depend on time. Therefore,

\[ \frac{3\alpha}{\zeta} = m\langle v(0)^2 \rangle = 3k_B T \text{ equipartition!} \]

That is, we get \( \alpha = k_B T \zeta \) or

\[ \langle w(t)w^T(s) \rangle = 2k_B T \zeta I \delta(t-s). \]
Remark. Notice that this is consistent with the fluctuation-dissipation relation we obtained for the overdamped case, where the random velocity $\nu = w/\zeta$.

Remark. Another interesting comment is about the product $v \cdot w$. As you remember Langevin said $r$ and $w$ are statistically independent, so $\langle r(t) \cdot v(t) \rangle = 0$. However, we cannot conclude a similar conclusion this time. I am afraid we should conclude that Langevin was simply lucky (although luck may be a part of one’s capability). Scalar-multiplying $v(t)$ to the equation of motion, we get

$$mv(t) \cdot \frac{d}{dt} v(t) = \frac{1}{2} m \frac{d}{dt} v(t)^2 = -\zeta v(t)^2 + v(t) \cdot w(t).$$

Let us ensemble-average this:

$$\frac{1}{2} m \frac{d}{dt} \langle v(t)^2 \rangle = -\zeta \langle v(t)^2 \rangle + \langle v(t) \cdot w(t) \rangle.$$

Notice that $\langle v(t)^2 \rangle = 3k_B T/m$ due to the equipartition of energy, so the last term cannot be zero:

$$\langle v(t) \cdot w(t) \rangle = 3 \zeta k_B T/m.$$

Is this consistent with our explicit solution above? According to the result,

$$\langle v(t) \cdot w(t) \rangle = \left\langle \left( e^{-\zeta/m} t v(0) + \frac{1}{m} \int_0^t ds \ e^{-\zeta/m}(t-s) w(s) \right) \cdot w(t) \right\rangle$$

$$= e^{-\zeta/m} t \langle v(0) \cdot w(t) \rangle + \frac{1}{m} \int_0^t ds e^{-\zeta/m}(t-s) \langle w(s) \cdot w(t) \rangle.$$

Here, the velocity at time zero should be statistically independent from the future noise, so the first term vanishes. The second term reads

$$\langle v(t) \cdot w(t) \rangle = \frac{1}{m} \int_0^t ds e^{-\zeta/m}(t-s) 6k_B T \zeta \delta(t - s)$$

$$= \frac{6k_B T \zeta}{m} \int_0^t ds \delta(t - s) = \frac{6k_B T \zeta}{m} \int_0^t ds \delta(s). \quad (0.0.4)$$

This should be consistent with the result above. What must we conclude? The following rule:

$$\int_0^\infty dx \delta(x) = \frac{1}{2}.$$

In theoretical physics we often use this rule. It is reasonable, if we think $\delta$ is a zero-variance limit of the Gaussian distribution centered at 0 (see Fig. 6.3).

(4) The autocorrelation function reads (notice that we may ignore the $v(0)$-$w$ cross terms) [If you are careful, you might worry about subtracting the average from $v(t)$, but it is zero]

$$\langle v(t) \cdot w(s) \rangle = e^{-\zeta/m}(t+s) \langle v(0)^2 \rangle + \frac{1}{m^2} \int_0^t ds^\prime \int_0^s ds^\prime \ e^{-\zeta/m}(t-s^\prime) e^{-\zeta/m}(s-s^\prime) \langle w(s^\prime) \cdot w(s^\prime) \rangle$$

$$= e^{-\zeta/m}(t+s) \frac{3k_B T}{m} \ + \frac{1}{m^2} \int_0^t ds^\prime \int_0^s ds^\prime \ e^{-\zeta/m}(t-s^\prime) e^{-\zeta/m}(s-s^\prime) 6k_B T \zeta \delta(s^\prime - s^\prime).$$
The inside integral (wrt $s''$) is zero if $s' > s$, so

\[
\langle \mathbf{v}(t) \cdot \mathbf{v}(s) \rangle = \frac{3k_B T}{m} e^{-(\zeta/m)(t+s)} + \frac{6k_B T}{m^2} \int_0^t ds' \Theta(s-s') e^{-(\zeta/m)(t+s-2s')}
\]

\[
= \frac{3k_B T}{m} e^{-(\zeta/m)(t+s)} + \frac{6k_B T\zeta}{m^2} \int_0^s ds' e^{-(\zeta/m)(t+s-2s')}
\]

\[
= \frac{3k_B T}{m} e^{-(\zeta/m)(t+s)} + \frac{3k_B T}{m} \left( e^{-(\zeta/m)(t-s)} - e^{-(\zeta/m)(t+s)} \right)
\]

\[
= \frac{3k_B T}{m} e^{-(\zeta/m)(t-s)}.
\]

Of course, since you are wise, you should have realized that the stationarity implies that

\[
\langle \mathbf{v}(t) \cdot \mathbf{v}(s) \rangle = \langle \mathbf{v}(t-s) \cdot \mathbf{v}(0) \rangle.
\]

The above result is immediate from this. However, at least once in your life you should explicitly check the stationarity.

(5) Since we have computed the autocorrelation function, we integrate it to get (3 in 1/3 is actually 3)

\[
\frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = \int_0^\infty dt \frac{k_B T}{m} e^{-(\zeta/m)t} = \frac{k_B T}{\zeta}.
\]

This is $D$, thanks to Einstein’s relation.

If you wish to demonstrate this without the use of Einstein’s relation, but from the definition of the diffusion constant, we use

\[
\langle r(t)^2 \rangle = 6Dt (= 2Ddt)
\]

that is an outcome of the diffusion equation as Einstein used. Using the stationarity and the fact that decay time is much shorter than $t$, we can approximate

\[
\langle r(t)^2 \rangle = \left\langle \left( \int_0^t \mathbf{v}(s) ds \right)^2 \right\rangle = \int_0^t ds \int_0^t ds' \langle \mathbf{v}(s) \cdot \mathbf{v}(s') \rangle
\]

\[
= 2 \int_0^t ds \int_0^s ds' \langle \mathbf{v}(s) \cdot \mathbf{v}(s') \rangle = 2 \int_0^t ds \int_0^s ds' \langle \mathbf{v}(s-s') \cdot \mathbf{v}(0) \rangle,
\]

where we have used (if you have some difficulty, draw a figure of the integration domain $[0, t] \times [0, t]$)

\[
\int_0^t ds \int_0^t ds' = \int_0^t ds \int_0^s ds' + \int_0^t ds \int_s^t ds' = \int_0^t ds \int_0^s ds' + \int_0^s ds' \int_0^t ds.
\]

Now,

\[
2 \int_0^t ds \int_0^s ds' \langle \mathbf{v}(s') \cdot \mathbf{v}(0) \rangle = 2t \int_0^s ds' \langle \mathbf{v}(s') \cdot \mathbf{v}(0) \rangle = 2t \int_0^\infty ds \langle \mathbf{v}(s) \cdot \mathbf{v}(0) \rangle,
\]

because the integral over $s'$ does not depend on $s$, if $s$ is large (which is allowed if $t$ is large). That is

\[
\langle r(t)^2 \rangle = 6Dt = 2t \int_0^\infty ds \langle \mathbf{v}(s) \cdot \mathbf{v}(0) \rangle.
\]
Using particles of radius $a = 0.550 \, \mu m$ suspended in water at $T = 23.6^\circ C$ (shear viscosity $\eta = 0.919 \, mPa-s$), the mean square displacements were measured. The results on a 2D observation table are summarized in the following figure.\footnote{taken from Marco A. Catipovic, Paul M. Tyler, Josef G. Trapani, and Ashley R. Carter, Improving the quantification of Brownian motion, Am. J. Phys. 81 435 (2013).} The black line indicates the average behavior.

Assuming that we know $R = 8.31 \, J/mol-K$, estimate Avogadro’s constant $N_A$.

**Soln.**

This is 2D, so

$$\text{MSD} = 4Dt$$

The slope is about $9/5 \, \mu m^2/s$, so $D = 9/20 \times 10^{-12} = 0.45 \times 10^{-12} \, m^2/2$. Stokes’ law tells us

$$\zeta = 6\pi \times 0.55 \times 10^{-6} \times 0.919 \times 10^{-3} = 9.52 \times 10^{-9}.$$ 

$$k_B = D\zeta/T = 0.45 \times 10^{-12} \times 9.52 \times 10^{-9} / 296.6 = 1.44 \times 10^{-23}$$

in the SI unit system. $N_A = 5.75 \times 10^{23}$.

**Remark.** (stimulated by Elle Shaw’s question) The stage fluid thickness is usually thicker than 0.1 mm ($\gg$ the Brownian particle size). Therefore, the fluid is a 3D fluid, not a 2D thin layer. Brownian particles execute 3D random motion, but we observe, in this problem, its 2D projection onto the stage. Since every coordinate direction is statistically independent, the projection is just a 2D random-walk-like motion. Incidentally, remember that 2D ‘macro’ fluid dynamics is not well defined (when 2D turbulence is discussed the basic hydrodynamics is still 3D but its thickness is much smaller than the turbulence vortex sizes).