Brownian velocity

The original Langevin equation reads

$$m\frac{d\boldsymbol{v}}{dt} = -\zeta\boldsymbol{v} + \boldsymbol{w}. \tag{1}$$

Here, m is the mass of the Brownian particle, and ζ is the friction constant. Also we assume that the system is in equilibrium (including the Brownian particle under study). We may assume

$$\langle \boldsymbol{w}(t)\boldsymbol{w}(s)^T\rangle = 2BI\delta(t-s), \tag{2}$$

where I is the 3×3 unit matrix and B is a positive constant. In th textbook we studies the overdamped case, where a random velocity given by $\boldsymbol{\nu} = \boldsymbol{w}/\zeta$ appears. We have determined ν as

$$\langle \boldsymbol{\nu}(t)\boldsymbol{\nu}(s)^T\rangle = \frac{2k_BT}{\zeta}I\delta(t-s), \tag{3}$$

Therefore, we should have $B = 2k_BT\zeta$. This is also called the fluctuation-dissipation relation. Let us direct obtain this and other relations about the Brownian velocity.

First, let us study the decay rate of the velocity. In 1907 Einstein remarked: for a Brownian particle its average velocity may be obtained from its short-time displacement, but unless extremely short time is used, such average would not be far from the true velocity. Thus 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.

Let us consider the time constant of the velocity decay rate. The ensemble average of the velocity under a given intial condition $\boldsymbol{v}(0)$ obeys

$$m\frac{d}{dt}\langle \boldsymbol{v}(t)\rangle = -\zeta\langle \boldsymbol{v}(t)\rangle, \tag{4}$$

because the system is linear (this agrees with the average of (8) below with a fixed initial condition). Since

$$\langle \boldsymbol{v}(t)\rangle = \boldsymbol{v}(0)e^{-\zeta t/m}, \tag{5}$$

the time constant $\tau = m/\zeta$. If the Brownian particle is of radius 0.1 μm suspended in water at 300 K, then we may use Stokes' law to get

$$\zeta = 6\pi a\eta, \tag{6}$$

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

$$t = \frac{4.2\times 10^{-18}}{6\pi\times 10^{-7}\times 10^{-3}} \simeq 0.22\times 10^{-9}. \tag{7}$$

It is about 0.2 ns. This implies that it takes only $2.3 \times 0.2 \sim 0.5$ ns for the speed to become 1/10 on the average of the initial speed. Therefore, to demonstrate the equipartition law quantitatively, we need at least 1 GHz sampling.

Let us study $\langle \boldsymbol{v}(t)^2 \rangle$, where the average is the ensemble average (we repeat identical experiments). This should not depend on t, because the system is in equilibrium. Solving (4), we get

$$\boldsymbol{v}(t) = e^{-(\zeta/m)t}\boldsymbol{v}(0) + \frac{1}{m}\int_0^t ds\, e^{-(\zeta/m)(t-s)}\boldsymbol{w}(s). \tag{8}$$

This can be obtained by the method of variation of constants: If we ignore the inhomogeneous terms, we get the general solution

$$\boldsymbol{v}(t) = \boldsymbol{C}e^{-(\zeta/m)t}. \tag{9}$$

Now, let us assume that $\boldsymbol{C}$ is time-dependent as $\boldsymbol{C}(t)$ (that is why the method is called 'the method of variation of constants')

$$\frac{d}{dt}\boldsymbol{v}(t) = -\frac{\zeta}{m}\boldsymbol{C}(t)e^{-(\zeta/m)t} + \boldsymbol{C}'(t)e^{-(\zeta/m)t} = -\frac{\zeta}{m}\boldsymbol{C}(t)e^{-(\zeta/m)t} + \frac{1}{m}\boldsymbol{w}(t) \tag{10}$$

Thus, we get the equation for $\boldsymbol{C}(t)$:

$$\frac{d}{dt}\boldsymbol{C}(t) = \frac{1}{m}\boldsymbol{w}(t)e^{(\zeta/m)t}, \tag{11}$$

Using (8), we get

$$\langle \boldsymbol{v}(t)^2 \rangle = e^{-2(\zeta/m)t}\langle \boldsymbol{v}(0)^2 \rangle + \frac{1}{m^2}\int_0^t ds \int_0^t ds'\, e^{-(\zeta/m)(2t-s-s')}\langle \boldsymbol{w}(s)\cdot\boldsymbol{w}(s')\rangle \tag{12}$$

$$= e^{-2(\zeta/m)t}\langle \boldsymbol{v}(0)^2 \rangle + \frac{1}{m^2}\int_0^t ds \int_0^t ds'\, e^{-(\zeta/m)(2t-s-s')} 6B\delta(s-s') \tag{13}$$

$$= e^{-2(\zeta/m)t}\langle \boldsymbol{v}(0)^2 \rangle + \frac{6B}{m^2}\int_0^t ds\, e^{-(2\zeta/m)(t-s)} \tag{14}$$

$$= e^{-2(\zeta/m)t}\langle \boldsymbol{v}(0)^2 \rangle + \frac{3B}{m\zeta}\left(1 - e^{-(2\zeta/m)t}\right) \tag{15}$$

$$= \frac{3B}{m\zeta} + \left(\langle \boldsymbol{v}(0)^2 \rangle - \frac{3B}{m\zeta}\right) e^{-(2\zeta/m)t}. \tag{16}$$

The stationarity implies that the quantity in the parentheses of (16) must be zero:

$$m\langle \boldsymbol{v}(0)^2 \rangle = \frac{3B}{\zeta}. \tag{17}$$

The equipartition of energy implies

$$\frac{3B}{\zeta} = 3k_BT. \tag{18}$$

That is,

$$B = k_B T \zeta \tag{19}$$

as noted above.

Perhaps, we could mimic Langevin to get $\langle \boldsymbol{v}(t)^2 \rangle$. Let us try. Scalar-multiplying $\boldsymbol{v}(t)$ to the equation of motion, we get

$$m\boldsymbol{v}(t) \cdot \frac{d}{dt}\boldsymbol{v}(t) = \frac{1}{2}m\frac{d}{dt}\boldsymbol{v}(t)^2 = -\zeta \boldsymbol{v}(t)^2 + \boldsymbol{v}(t) \cdot \boldsymbol{w}(t). \tag{20}$$

Let us ensemble-average this:

$$\frac{1}{2}m\frac{d}{dt}\langle \boldsymbol{v}(t)^2 \rangle = -\zeta \langle \boldsymbol{v}(t)^2 \rangle + \langle \boldsymbol{v}(t) \cdot \boldsymbol{w}(t) \rangle. \tag{21}$$

Notice that $\langle \boldsymbol{v}(t)^2 \rangle = 3k_B T/m$ due to the equipartition of energy, so the last term cannot be zero. We must require

$$\langle \boldsymbol{v}(t) \cdot \boldsymbol{w}(t) \rangle = 3\zeta k_B T/m. \tag{22}$$

Is this consistent with our explicit solution (8)? According to the result,

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

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

$$\begin{aligned}
\langle \boldsymbol{v}(t) \cdot \boldsymbol{w}(t) \rangle &= \frac{1}{m}\int_0^t ds\, e^{-(\zeta/m)(t-s)} 6k_B T\zeta\delta(t-s) \\
&= \frac{6k_B T\zeta}{m}\int_0^t ds\, \delta(t-s) = \frac{6k_B T\zeta}{m}\int_0^t ds\, \delta(s).
\end{aligned} \tag{23}$$

This should be consistent with the result (22) 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 δ is a zero-variance limit of the Gaussian distribution centered at 0 (see Fig. 6.3).

Next, let us compute the velocity autocorrelation function $\langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(s) \rangle$ $(t \geq s)$. Because of stationarity, this must be identical to $\langle \boldsymbol{v}(t-s) \cdot \boldsymbol{v}(0) \rangle$, which is much easier to compute, but let us first compute $\langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(s) \rangle$. Using (8), we get

$$\langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(s) \rangle = \frac{3k_B T}{m}e^{-(\zeta/m)(t+s)} + \frac{6k_B T}{m^2}\int_0^t ds'\, \Theta(s-s')e^{-(\zeta/m)(t+s-2s')} \tag{24}$$

$$= \frac{3k_B T}{m}e^{-(\zeta/m)(t+s)} + \frac{6k_B T\zeta}{m^2}\int_0^s ds'\, e^{-(\zeta/m)(t+s-2s')} \tag{25}$$

$$= \frac{3k_B T}{m}e^{-(\zeta/m)(t+s)} + \frac{3k_B T}{m}\left(e^{-(\zeta/m)(t-s)} - e^{-(\zeta/m)(t+s)}\right) \tag{26}$$

$$= \frac{3k_B T}{m}e^{-(\zeta/m)(t-s)}. \tag{27}$$

This is indeed identical to $\langle \boldsymbol{v}(t-s)\cdot\boldsymbol{v}(0)\rangle$.

Autocorrelation functions are closely related to the related transport properties (the Green-Kubo relation). We indeed have

$$\frac{1}{3}\int_0^\infty dt\,\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle = \int_0^\infty dt\,\frac{k_BT}{m}e^{-(\zeta/m)t} = \frac{k_BT}{\zeta} = D. \tag{28}$$

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

$$\langle \boldsymbol{r}(t)^2\rangle = 6Dt\,(=2\mathfrak{d}Dt)$$

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

$$\begin{aligned}\langle \boldsymbol{r}(t)^2\rangle &= \left\langle\left(\int_0^t \boldsymbol{v}(s)ds\right)^2\right\rangle = \int_0^t ds\int_0^t ds'\,\langle \boldsymbol{v}(s)\cdot\boldsymbol{v}(s')\rangle \\ &= 2\int_0^t ds\int_0^s ds'\,\langle \boldsymbol{v}(s)\cdot\boldsymbol{v}(s')\rangle = 2\int_0^t ds\int_0^s ds'\,\langle \boldsymbol{v}(s-s')\cdot\boldsymbol{v}(0)\rangle, \end{aligned}\tag{29}$$

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

$$\int_0^t ds\int_0^t ds' = \int_0^t ds\int_0^s ds' + \int_0^t ds\int_s^t ds' = \int_0^t ds\int_0^s ds' + \int_0^t ds'\int_0^s ds.$$

Now,

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

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

$$\langle \boldsymbol{r}(t)^2\rangle = 6Dt = 2t\int_0^\infty ds\,\langle \boldsymbol{v}(s)\cdot\boldsymbol{v}(0)\rangle.$$