5.3.5 Einstein's relation

Let us focus on the center of mass degree of freedom for bodies immersed in a fluid bath. For each body we can observe the steady state velocity v_i under the action of a strong force F_i, and hence calculate a mobility factor $\mu_i = v_i/F_i$. In the absence of any external potential the body will diffuse in the fluid, and by observing its mean-squared displacements after a long time t, we can obtain a diffusion constant D_i. If the particle is now trapped in a potential $V_i(x_i)$, after a sufficiently long time its probability distribution must satisfy $p^*(x_i) \propto \exp\left(-\frac{\mu_i V_i(x_i)}{D_i}\right)$ according to Eq. (5.3.11). However, following Eq. (5.3.20), the maximum likelihood distribution is $p \propto \exp\left(-\beta V_i(x_i)\right)$ irrespective of the characteristics of the object. Both distributions have exponential forms, and coincide if

$$\beta = \frac{\mu_i}{D_i}\,, \quad \Longrightarrow \quad D_i = \mu_i k_B T\,. \tag{5.3.21}$$

The above, *Einstein relation* quantifying the relations between fluctuations and dissipation, relating the diffusion coefficient (a manifestation of fluctuations in force) to the mobility (characterizing the dissipative force through $F_i = (1/\mu_i)v_i$.

While we focused on the potential energy of the center of mass, according to the *Boltzmann probability*, all additive components of the energy must be exponentially distributed. For example, let us consider the kinetic energy of the center of mass $K(v) = mv^2/2$. In the absence of a trapping potential, we can rewrite Eq. (5.3.1) as

$$m\,\dot{v} = -\frac{v}{\mu} + f_{\text{random}}(t)\,, \quad \Rightarrow \quad \dot{v} + \frac{v}{m\mu} = \eta(t)\,, \tag{5.3.22}$$

where $\eta(t) = f_{\text{random}}(t)/\mu$ as before, and for simplicity we consider motion in only one direction. This linear ODE can be solved for arbitrary forcing function $\eta(t)$, since it is equivalent to

$$\frac{d}{dt}\left[e^{\frac{t}{m\mu}}v(t)\right] = e^{\frac{t}{m\mu}}\eta(t)\,, \tag{5.3.23}$$

which integrates to

$$e^{\frac{t}{m\mu}}v(t) - v(0) = \int_0^t dt' e^{\frac{t'}{m\mu}}\eta(t')\,. \tag{5.3.24}$$

Thus, starting from $v(t=0) = v(0)$, we obtain

$$v(t) = v(0)e^{\frac{-t}{m\mu}} + \int_0^t dt' e^{\frac{t'-t}{m\mu}}\eta(t')\,. \tag{5.3.25}$$

Since $\langle \eta(t) \rangle = 0$, averaging the above equation yields

$$\langle v(t) \rangle = v(0)e^{\frac{-t}{m\mu}} \to 0 \quad \text{for} \quad t \gg m\mu\,. \tag{5.3.26}$$

The initial velocity thus makes a transient contribution that decays over a characteristic time $\tau = m\mu$. In ignoring the inertial term in Eq. (5.3.2), we implicitly looked at longer time scales than τ. The variance of the velocity is then given by

$$\langle v(t)^2 \rangle_c = \int_0^t dt_1 dt_2 \exp\left(\frac{t_1 + t_2 - 2t}{m\mu}\right) \langle \tilde{\eta}(t_1)\tilde{\eta}(t_2) \rangle . \tag{5.3.27}$$

Using the co-variance of noise from Eq. (5.3.5) leads to

$$\langle v(t)^2 \rangle_c = 2D \int_0^t dt' e^{-2(t-t')/(m\mu)} . \tag{5.3.28}$$

At long times $t \to \infty$ the integral over time equals $(2\mu m)^{-1}$, leading to the simple result

$$\langle v(t)^2 \rangle_c = \frac{D}{m\mu} = \frac{k_B T}{m} . \tag{5.3.29}$$

As a sum over many Gaussian random variables, the velocity $v(t)$ at long times is itself Gaussian distributed. From the computed mean and variance, we can then construct its PDF as

$$p(v) = \exp\left(-\frac{mv^2}{2k_B T}\right) \sqrt{\frac{m}{2\pi k_B T}} , \tag{5.3.30}$$

confirming the exponential distribution of the kinetic energy component of the total energy.