IV.1.5 Harmonic analysis

In the regime in which the Brownian particle is in equilibrium with the fluid, the velocity $v(t)$ becomes a stationary stochastic process, as is the fluctuating force $F_{\rm L}(t)$ itself. One can thus apply to them the concepts introduced in Appendix C.3, and in particular introduce their Fourier transforms[(62)]

$$\tilde{F}_{\rm L}(\omega) \equiv \int F_{\rm L}(t)\, {\rm e}^{{\rm i}\omega t}\, {\rm d}t, \qquad \tilde{v}(\omega) \equiv \int v(t)\, {\rm e}^{{\rm i}\omega t}\, {\rm d}t. \tag{IV.29}$$

In Fourier space, the Langevin equation (IV.1) leads to the relation

$$\tilde{v}(\omega) = \frac{1}{M}\frac{1}{\gamma - {\rm i}\omega}\, \tilde{F}_{\rm L}(\omega). \tag{IV.30}$$

One also introduces the respective *spectral densities* of the stochastic processes[(62)]

$$S_F(\omega) \equiv \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}}\left\langle \big|\tilde{F}_{\rm L}(\omega)\big|^2 \right\rangle, \qquad S_v(\omega) \equiv \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}}\left\langle \big|\tilde{v}(\omega)\big|^2 \right\rangle. \tag{IV.31}$$

For these spectral densities, Eq. (IV.30) yields at once the relation

$$S_v(\omega) = \frac{1}{M^2}\frac{1}{\gamma^2+\omega^2}\, S_F(\omega). \tag{IV.32}$$

The spectral density of the velocity if thus simply related to that of the force, for which we shall consider two possibilities.

IV.1.5 a White noise

A first possible ansatz for $S_F(\omega)$, compatible with the assumptions in §IV.1.1 b, is that of a frequency-independent spectral density, i.e. of *white noise*

$$S_F(\omega) = S_F. \tag{IV.33a}$$

According to the Wiener–Khinchin theorem (C.46), the autocorrelation function of the fluctuating force is then the Fourier transform of a constant, i.e. a Dirac distribution

$$\big\langle F_{\rm L}(t) F_{\rm L}(t+\tau)\big\rangle = \int S_F\, {\rm e}^{-{\rm i}\omega\tau}\, \frac{{\rm d}\omega}{2\pi} = S_F\, \delta(\tau). \tag{IV.33b}$$

This thus constitutes the case in which Eq. (IV.3d) holds, with $S_F = 2D_v M^2$.

With this simple form for $S_F(\omega)$, the spectral density (IV.32) of the velocity is given by the Lorentzian distribution

$$S_v(\omega) = \frac{2D_v}{\gamma^2+\omega^2},$$

(62) Remember that, formally, one defines the transforms considering first the restrictions of the processes to a finite-size time interval of width $\mathcal{T}$, and at the end of calculations one takes the large-$\mathcal{T}$ limit. Here we drop the subscript $\mathcal{T}$ designating these restrictions to simplify the notations.

which after an inverse Fourier transformation yields for the autocorrelation function

$$\langle v(t)v(t+\tau)\rangle = \frac{D_v}{\gamma}\,\mathrm{e}^{-\gamma|\tau|}, \tag{IV.34}$$

in agreement with what was already found in Eq. (IV.27).

IV.1.5 b Colored noise

While a frequency-independent white noise spectrum of Langevin-force fluctuations amounts to a vanishingly small autocorrelation time τ_c, a very wide—but not everywhere constant—spectrum corresponds to a finite τ_c. One then talks of *colored noise*.

Assume for instance that the density spectrum of the fluctuating force is given by a Lorentzian distribution centered on $\omega = 0$, with a large typical width ω_c, where the precise meaning of "large" will be specified later:

$$S_F(\omega) = S_F\,\frac{\omega_c^2}{\omega_c^2+\omega^2}. \tag{IV.35a}$$

Since $S_F(\omega\!=\!0)$ equals the integral of the autocorrelation function $\kappa(\tau)$, condition (IV.3c) leads to the identity $S_F = 2D_vM^2$. With the Wiener–Khinchin theorem (C.46) and relation (IV.32), this corresponds to an autocorrelation function of the fluctuating force given by

$$\langle F_{\rm L}(t)F_{\rm L}(t+\tau)\rangle = \int 2D_vM^2\,\frac{\omega_c^2}{\omega_c^2+\omega^2}\,\mathrm{e}^{-\mathrm{i}\omega\tau}\,\frac{\mathrm{d}\omega}{2\pi} = D_vM^2\omega_c\,\mathrm{e}^{-\omega_c|\tau|}, \tag{IV.35b}$$

i.e. the autocorrelation time of the Langevin force is $\tau_c = \omega_c^{-1}$.

Using Eq. (IV.32), the spectral density of the velocity is

$$S_v(\omega) = 2D_v\omega_c^2\frac{1}{\gamma^2+\omega^2}\frac{1}{\omega_c^2+\omega^2} = \frac{2D_v\omega_c^2}{\omega_c^2-\gamma^2}\left(\frac{1}{\gamma^2+\omega^2}-\frac{1}{\omega_c^2+\omega^2}\right).$$

The autocorrelation function of the velocity then reads

$$\langle v(t)v(t+\tau)\rangle = \frac{D_v}{\gamma}\frac{\omega_c^2}{\omega_c^2-\gamma^2}\left(\mathrm{e}^{-\gamma|\tau|}-\frac{\gamma}{\omega_c}\mathrm{e}^{-\omega_c|\tau|}\right). \tag{IV.36}$$

At small $|\tau| \ll \omega_c^{-1} \ll \gamma^{-1}$, this becomes

$$\langle v(t)v(t+\tau)\rangle \sim \frac{D_v}{\omega_c+\gamma}\left(\frac{\omega_c}{\gamma}-\frac{\gamma\omega_c}{2}\,\tau^2\right),$$

i.e. it departs quadratically from its value at $\tau = 0$. In particular, the singularity of the derivative at $\tau = 0$ which appears when τ_c is neglected [cf. Eq. (IV.34)] has been smoothed out.

Remark: The autocorrelation function (IV.36) actually involves two time scales, namely $\tau_c = \omega_c^{-1}$ and $\tau_r = \gamma^{-1}$. The Langevin model only makes sense if $\tau_c \ll \tau_r$, i.e. $\gamma \ll \omega_c$, in which case the second term in the brackets in the autocorrelation function is negligible, and the only remaining time scale for the fluctuations of velocity is τ_r. Velocity if thus a "slow" stochastic variable, compared to the more quickly evolving Langevin force. Physically, many collisions with lighter particles are necessary to change the velocity of the Brownian particle.

IV.1.6 Response to an external force

Let us eventually assume momentarily that the Brownian particle is submitted to an additional external force $F_{\rm ext.}(t)$, independent of its position and velocity. The equation of motion describing the Brownian particle dynamics then becomes

$$M\frac{\mathrm{d}v(t)}{\mathrm{d}t} = -M\gamma v(t) + F_{\rm L}(t) + F_{\rm ext.}(t). \tag{IV.37}$$

Averaging over many realizations, one obtains

$$M\frac{\mathrm{d}\langle v(t)\rangle}{\mathrm{d}t} = -M\gamma\langle v(t)\rangle + F_{\mathrm{ext.}}(t), \tag{IV.38}$$

where we have used property (IV.3a) of the Langevin noise. This is now a linear ordinary differential equation, which is most easily solved by introducing the Fourier transforms

$$\langle\tilde{v}(\omega)\rangle \equiv \int \langle v(t)\rangle\, \mathrm{e}^{\mathrm{i}\omega t}\, \mathrm{d}t, \qquad \tilde{F}_{\mathrm{ext.}}(\omega) \equiv \int F_{\mathrm{ext.}}(t)\, \mathrm{e}^{\mathrm{i}\omega t}\, \mathrm{d}t.$$

In Fourier space, Eq. (IV.38) becomes $-\mathrm{i}\omega M\langle\tilde{v}(\omega)\rangle = -M\gamma\langle\tilde{v}(\omega)\rangle + \tilde{F}_{\mathrm{ext.}}(\omega)$, i.e.

$$\langle\tilde{v}(\omega)\rangle = Y(\omega)\,\tilde{F}_{\mathrm{ext.}}(\omega), \tag{IV.39a}$$

with

$$Y(\omega) \equiv \frac{1}{M}\frac{1}{\gamma - \mathrm{i}\omega} \tag{IV.39b}$$

the (complex) *admittance* of the Langevin model. That is, the (sample) average velocity of the Brownian particle responds *linearly* to the external force.

In the Hamilton function describing the Brownian particle, the external force $F_{\mathrm{ext.}}$ couples to the position x. Thus, the admittance (IV.39b) represents, in the language used in Chapter III, the generalized susceptibility $\tilde{\chi}_{vx}$ that characterizes the linear response of the velocity to a perturbation of the position. Accordingly, Eq. (IV.40) below is nothing but relation (III.65) with $K_{v\dot{x}} = K_{vv}$, in the classical case.

Consider now the autocorrelation function at equilibrium (IV.27). Setting $t' = 0$ and assuming that the environment is at thermodynamic equilibrium with temperature T, in which case relation (IV.12) holds, one finds

$$\big\langle v(t)v(0)\big\rangle = \frac{k_BT}{M}\,\mathrm{e}^{-\gamma|t|}.$$

The Fourier–Laplace transform of this autocorrelation function reads

$$\int_0^\infty \langle v(t)v(0)\rangle\, \mathrm{e}^{\mathrm{i}\omega t}\, \mathrm{d}t = \frac{k_BT}{M}\frac{1}{\gamma - \mathrm{i}\omega},$$

that is, given expression (IV.39b) of the admittance

$$\boxed{Y(\omega) = \frac{1}{k_BT}\int_0^\infty \big\langle v(t)v(0)\big\rangle\, \mathrm{e}^{\mathrm{i}\omega t}\, \mathrm{d}t.} \tag{IV.40}$$

This result relating the admittance to the autocorrelation function is again a form of the fluctuation–dissipation theorem.

If the Brownian particle carries an electric charge q, then one may consider an electrostatic force $F_{\mathrm{ext.}}(t) = q\mathscr{E}(t)$ as external force. Inserting this form in Eq. (IV.38), one sees that the average velocity of the Brownian particle in the stationary regime is $\langle v\rangle = q\mathscr{E}/M\gamma$. Defining the electrical mobility as $\mu_{\mathrm{el.}} \equiv \langle v\rangle/\mathscr{E}$, one finds

$$\mu_{\mathrm{el.}} = \frac{q}{M\gamma} = q\,Y(\omega\!=\!0),$$

where the stationary regime obviously corresponds to the vanishing-frequency limit.