VIII. Dissipative Dynamics

VIII.A Brownian Motion of a Particle

Observations under a microscope indicate that a dust particle in a liquid drop undergoes a random jittery motion. This is because of the random impacts of the much smaller fluid particles. The theory of such (*Brownian*) motion was developed by Einstein in 1905 and starts with the equation of motion for the particle. The displacement $\vec{x}(t)$, of a particle of mass m is governed by,

$$m\,\ddot{\vec{x}} = -\frac{\dot{\vec{x}}}{\mu} - \frac{\partial \mathcal{V}}{\partial \vec{x}} + \vec{f}_{\text{random}}(t). \qquad \text{(VIII.1)}$$

The three forces acting on the particle are:

(i) A friction force due to the viscosity of the fluid. For a spherical particle of radius R, the mobility in the low Reynolds number limit is given by $\mu = (6\pi\bar{\eta}R)^{-1}$, where $\bar{\eta}$ is the specific viscosity.

(ii) The force due to the external potential $\mathcal{V}(\vec{x})$, e.g. gravity.

(iii) A random force of zero mean due to the impacts of fluid particles.

The viscous term usually dominates the inertial one (i.e. the motion is overdamped), and we shall henceforth ignore the acceleration term. Eq.(VIII.1) now reduces to a *Langevin equation*,

$$\dot{\vec{x}} = \vec{v}(\vec{x}) + \vec{\eta}(t), \qquad \text{(VIII.2)}$$

where $\vec{v}(\vec{x}) = -\mu\partial\mathcal{V}/\partial\vec{x}$ is the *deterministic* velocity. The *stochastic* velocity, $\vec{\eta}(t) = \mu\vec{f}_{\text{random}}(t)$, has zero mean,

$$\langle \vec{\eta}(t) \rangle = 0. \qquad \text{(VIII.3)}$$

It is usually assumed that the probability distribution for the noise in velocity is Gaussian, i.e.

$$\mathcal{P}\left[\vec{\eta}(t)\right] \propto \exp\left[-\int d\tau\, \frac{\eta(\tau)^2}{4D}\right]. \qquad \text{(VIII.4)}$$

Note that different components of the noise, and at different times, are independent, and the covariance is

$$\langle \eta_\alpha(t)\eta_\beta(t')\rangle = 2D\delta_{\alpha,\beta}\delta(t-t'). \qquad \text{(VIII.5)}$$

The parameter D is related to *diffusion* of particles in the fluid. In the absence of any potential, $\mathcal{V}(\vec{x}) = 0$, the position of a particle at time t is given by

$$\vec{x}(t) = \vec{x}(0) + \int_0^t d\tau \vec{\eta}(\tau).$$

Clearly the separation $\vec{x}(t) - \vec{x}(0)$ which is the sum of random Gaussian variables is itself Gaussian distributed with mean zero, and a varaince

$$\left\langle (\vec{x}(t) - \vec{x}(0))^2 \right\rangle = \int_0^t d\tau_1 d\tau_2 \left\langle \vec{\eta}(\tau_1) \cdot \vec{\eta}(\tau_2) \right\rangle = 3 \times 2Dt.$$

For an ensemble of particles released at $\vec{x}(t) = 0$, i.e. with $\mathcal{P}(\vec{x}, t=0) = \delta^3(\vec{x})$, the particles at time t are distributed according to

$$\mathcal{P}(\vec{x}, t) = \left(\frac{1}{\sqrt{4\pi Dt}} \right)^{3/2} \exp\left[-\frac{x^2}{4Dt} \right],$$

which is the solution to the diffusion equation

$$\frac{\partial \mathcal{P}}{\partial t} = D \nabla^2 \mathcal{P}.$$

A simple example is provided by a particle connected to a Hookian spring, with $\mathcal{V}(\vec{x}) = Kx^2/2$. The deterministic velocity is now $\vec{v}(\vec{x}) = -\mu K \vec{x}$, and the Langevin equation, $\dot{\vec{x}} = -\mu K \vec{x} + \vec{\eta}(t)$, can be rearranged as

$$\frac{d}{dt}\left[e^{\mu K t} \vec{x}(t) \right] = e^{\mu K t} \vec{\eta}(t). \tag{VIII.6}$$

Integrating the equation from 0 to t yields

$$e^{\mu K t} \vec{x}(t) - \vec{x}(0) = \int_0^t d\tau e^{\mu K \tau} \vec{\eta}(\tau), \tag{VIII.7}$$

and

$$\vec{x}(t) = \vec{x}(0) e^{-\mu K t} + \int_0^t d\tau e^{-\mu K (t-\tau)} \vec{\eta}(\tau). \tag{VIII.8}$$

Averaging over the noise indicates that the mean position,

$$\langle \vec{x}(t) \rangle = \vec{x}(0) e^{-\mu K t}, \tag{VIII.9}$$

decays with a characteristic *relaxation time*, $\tau = 1/(\mu K)$. Fluctuations around the mean behave as

$$
\begin{aligned}
\left\langle \left(\vec{x}(t) - \langle \vec{x}(t)\rangle\right)^2 \right\rangle = & \int_0^t d\tau_1 d\tau_2 e^{-\mu K(2t-\tau_1-\tau_2)} \overbrace{\langle \vec{\eta}(\tau_1)\cdot\vec{\eta}(\tau_2)\rangle}^{2D\delta(\tau_1-\tau_2)\times 3} \\
= & 6D\int_0^t d\tau e^{-2\mu K(t-\tau)} \\
= & \frac{3D}{\mu K}\left[1-e^{-2\mu K t}\right] \quad \stackrel{t\to\infty}{\longrightarrow} \quad \frac{3D}{\mu K}.
\end{aligned}
\qquad \text{(VIII.10)}
$$

However, once the dust particle reaches equilibrium with the fluid at a temperature T, its probability distribution must satisfy the normalized Boltzmann weight

$$
\mathcal{P}_{\text{eq.}}(\vec{x}) = \left(\frac{K}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{Kx^2}{2k_BT}\right], \qquad \text{(VIII.11)}
$$

yielding $\langle x^2\rangle = 3k_BT/K$. Since the dynamics is expected to bring the particle to equilibrium with the fluid at temperature T, eq.(VIII.10) implies the condition

$$
D = k_B T \mu\,. \qquad \text{(VIII.12)}
$$

This is the Einstein relation connecting the *fluctuations* of noise to the *dissipation* in the medium.

Clearly the Langevin equation at long times reproduces the correct mean and variance for a particle in equilibrium at a temperature T in the potential $\mathcal{V}(\vec{x}) = Kx^2/2$, provided that eq.(VIII.12) is satisfied. Can we show that the whole probability distribution evolves to the Boltzmann weight for any potential? Let $\mathcal{P}(\vec{x},t) \equiv \langle \vec{x}|\mathcal{P}(t)|0\rangle$ denote the probability density of finding the particle at $\vec{x}$ at time t, given that it was at 0 at $t=0$. This probability can be constructed recursively by noting that a particle found at $\vec{x}$ at time $t+\epsilon$ must have arrived from some other point $\vec{x}\,'$ at t. Adding up all such probabilities yields

$$
\mathcal{P}(\vec{x}, t+\epsilon) = \int d^3\vec{x}\,'\,\mathcal{P}(\vec{x}\,',t)\,\langle \vec{x}|T_\epsilon|\vec{x}\,'\rangle, \qquad \text{(VIII.13)}
$$

where $\langle \vec{x}|T_\epsilon|\vec{x}\,'\rangle \equiv \langle \vec{x}|\mathcal{P}(\epsilon)|\vec{x}\,'\rangle$ is the transition probability. For $\epsilon \ll 1$,

$$
\vec{x} = \vec{x}\,' + \vec{v}\,(\vec{x}\,')\epsilon + \vec{\eta}_\epsilon \quad , \qquad \text{(VIII.14)}
$$

where $\vec{\eta}_\epsilon = \int_t^{t+\epsilon} d\tau \vec{\eta}(\tau)$. Clearly, $\langle \vec{\eta}_\epsilon \rangle = 0$, and $\left\langle \eta_\epsilon^2 \right\rangle = 2D\epsilon \times 3$, and following eq.(VIII.4),

$$p(\vec{\eta}_\epsilon) = \left(\frac{1}{4\pi D\epsilon}\right)^{3/2} \exp\left[-\frac{\eta_\epsilon^2}{4D\epsilon}\right]. \tag{VIII.15}$$

The transition rate is simply the probability of finding a noise of the right magnitude according to eq.(VIII.14), and

$$\begin{aligned} \langle \vec{x}\,|T(\epsilon)|\vec{x}\,'\rangle = p(\eta_\epsilon) &= \left(\frac{1}{4\pi D\epsilon}\right)^{3/2} \exp\left[-\frac{\left(\vec{x} - \vec{x}\,' - \epsilon\vec{v}(\vec{x}\,')\right)^2}{4D\epsilon}\right] \\ &= \left(\frac{1}{4\pi D\epsilon}\right)^{3/2} \exp\left[-\epsilon\,\frac{\left(\dot{\vec{x}} - \vec{v}(\vec{x})\right)^2}{4D}\right]. \end{aligned} \tag{VIII.16}$$

By subdividing the time interval t, into infinitesimal segments of size ϵ, repeated application of the above evolution operator yields

$$\begin{aligned} \mathcal{P}(\vec{x}, t) &= \left\langle \vec{x}\,\left|T(\epsilon)^{t/\epsilon}\right|0\right\rangle \\ &= \int_{(0,0)}^{(\vec{x},t)} \frac{\mathcal{D}\vec{x}(\tau)}{\mathcal{N}} \exp\left[-\int_0^t d\tau \frac{\left(\dot{\vec{x}} - \vec{v}(\vec{x})\right)^2}{4D}\right]. \end{aligned} \tag{VIII.17}$$

The integral is over all paths connecting the initial and final points; each path's weight is related to its deviation from the classical trajectory, $\dot{\vec{x}} = \vec{v}(\vec{x})$. The recursion relation (eq.(VIII.13)),

$$\mathcal{P}(\vec{x}, t) = \int d^3\vec{x}\,' \left(\frac{1}{4\pi D\epsilon}\right)^{3/2} \exp\left[-\frac{\left(\vec{x} - \vec{x}\,' - \epsilon\vec{v}(\vec{x}\,')\right)^2}{4D\epsilon}\right] \mathcal{P}(\vec{x}\,', t-\epsilon), \tag{VIII.18}$$

can be simplified by the change of variables,

$$\begin{aligned} \vec{y} &= \vec{x}\,' + \epsilon\vec{v}(\vec{x}\,') - \vec{x} \quad \Longrightarrow \\ d^3\vec{y} &= d^3\vec{x}\,'\left(1 + \epsilon\nabla\cdot\vec{v}(\vec{x}')\right) = d^3\vec{x}\,'\left(1 + \epsilon\nabla\cdot\vec{v}(\vec{x}) + \mathcal{O}(\epsilon^2)\right). \end{aligned} \tag{VIII.19}$$

Keeping only terms at order of ϵ, we obtain

$$\begin{aligned} \mathcal{P}(\vec{x}, t) = &[1 - \epsilon\nabla\cdot\vec{v}(\vec{x})] \int d^3\vec{y} \left(\frac{1}{4\pi D\epsilon}\right)^{3/2} e^{-\frac{y^2}{4D\epsilon}}\, \mathcal{P}(\vec{x} + \vec{y} - \epsilon\vec{v}(\vec{x}), t-\epsilon) \\ = &[1 - \epsilon\nabla\cdot\vec{v}(\vec{x})] \int d^3\vec{y} \left(\frac{1}{4\pi D\epsilon}\right)^{3/2} e^{-\frac{y^2}{4D\epsilon}} \times \\ &\left[\mathcal{P}(\vec{x}, t) + (\vec{y} - \epsilon\vec{v}(\vec{x}))\cdot\nabla\mathcal{P} + \frac{y_iy_j - 2\epsilon y_iv_j + \epsilon^2 v_iv_j}{2}\nabla_i\nabla_j\mathcal{P} - \epsilon\frac{\partial\mathcal{P}}{\partial t} + \mathcal{O}(\epsilon^2)\right] \\ = &[1 - \epsilon\nabla\cdot\vec{v}(\vec{x})]\left[\mathcal{P} - \epsilon\vec{v}\cdot\nabla + \epsilon D\nabla^2\mathcal{P} - \epsilon\frac{\partial\mathcal{P}}{\partial t} + \mathcal{O}(\epsilon^2)\right]. \end{aligned} \tag{VIII.20}$$

Equating terms at order of ϵ leads to the *Fokker-Planck equation*,

$$\frac{\partial \mathcal{P}}{\partial t} + \nabla \cdot \vec{J} = 0, \qquad \text{with} \qquad \vec{J} = \vec{v}\,\mathcal{P} - D\nabla\mathcal{P} \quad . \tag{VIII.21}$$

The Fokker-Planck equation is simply the statement of conservation of probability. The probability current has a deterministic component $\vec{v}\,\mathcal{P}$, and a stochastic part $-D\nabla\mathcal{P}$. A *stationary distribution*, $\partial\mathcal{P}/\partial t = 0$, is obtained if the net current vanishes. It is now easy to check that the Boltzmann weight, $\mathcal{P}_{\text{eq.}}(\vec{x}) \propto \exp[-\mathcal{V}(\vec{x})/k_B T]$, with $\nabla\mathcal{P}_{\text{eq.}} = \vec{v}\,\mathcal{P}_{\text{eq.}}/(\mu k_B T)$, leads to a stationary state as long as the fluctuation–dissipation condition in eq.(VIII.12) is satisfied.