

## Chapter 2

# Dynamics of Open Classical Systems

### 2.1 Introduction

Traditionally, in classical mechanics conservative forces derivable from interaction potentials—and therefore dependent on particle positions—have received much more attention than dissipative or damping ones. The latter have been postulated to follow a power law of the velocity, to be dependent on accelerations or even to be nonlocal in space and time. However, the corresponding nonconservative systems, i.e., systems that lose energy as motion takes place, are ubiquitous in Nature. Therefore, despite of dealing with them is not exempt from difficulties, they are becoming more and more attractive from a theoretical viewpoint in recent years. Nowadays classical dissipation constitutes a very active field of research. For example, in a relatively recent monograph, Razavy [1] surveys the very extensive literature on the subject, paying special attention to the quantization of simple, solvable classical systems.

Open classical systems are usually defined as those where the system of interest is surrounded by an *environment*. When the environment is constituted by many degrees of freedom, characterized by a certain temperature (a measure of its internal energy), it is called a *bath* (*heat bath*) or *reservoir*. In this sense, open systems can also be defined as systems exchanging or *dissipating* energy with another one. The dissipative forces leading to such energy transfers can be derived from a conservative many-body problem. In this case, the full conservative system is typically split up into two interacting parts or subsystems: the subsystem of interest or dissipating system and the heat bath. Because the bath is usually an extended system with many degrees of freedom, according to its definition, energy will not flow equally in both directions. Eventually the system relaxes, losing its energy as time goes on. Hence, dissipation is seen as an *irreversible process*. This fact is in apparent contradiction with the time-symmetry exhibited by the equations of motion of classical mechanics. To understand it, one has to consider that the concept of *irreversibility* is related to the so-called *Poincaré recurrence time*, which is extremely large for an extended system and, therefore, any process will appear to be irreversible. Of course, relaxation processes may also display recurrences if energy flows in both directions, which

usually happens when the environment has a few degrees of freedom. If bath noise or fluctuations influence importantly the dynamics of the dissipative system, then stochasticity will play a fundamental role. In this Chapter, only white noise will be considered, for which the noise autocorrelation function is governed by a Dirac  $\delta$ -function. This is also called a *Markovian regimen*. Detailed discussions of the action of colored noise on dynamical systems can be found in [2], for example.

In this context, space–time correlation functions (as defined in Sect. 1.4.2) play a fundamental role since they are measurable quantities. These functions provide a rather complete information about the decay of spontaneous thermal fluctuations through thermodynamic averages of the product of two dynamical variables. Different theoretical approaches have been developed for their calculation at finite wavenumbers and frequencies. These approaches range from continuum description (very low wavenumbers and frequencies) in terms of hydrodynamic equations to molecular dynamics simulations; in between, molecular hydrodynamic descriptions are usually preferred. Irreversible time-dependent nonequilibrium properties are very often analyzed within the so-called *linear response theory*, where systems are supposed to be close to equilibrium. The cornerstone of this theory is the *fluctuation–dissipation theorem* [3] and one of its important consequences: Onsager’s regression hypothesis. As has already been mentioned in Chap. 1, this hypothesis states that the relaxation of macroscopic nonequilibrium perturbations is also governed by the regression law of spontaneous microscopic fluctuations in systems at equilibrium. A direct evaluation of such correlation functions is a very difficult task when dealing with many-body system. Thus, the most general formalism starts with the Liouville equation for a dynamical variable—in general, depending on all the system coordinates and momenta. Then, by means of the projection-operator technique, one reaches a generalized Langevin equation for such a dynamical variable. This equation is given in terms of a random force and its autocorrelation or *memory function* (sometimes it is also called delayed function). A similar equation can also be obtained for its normalized space–time autocorrelation function without the random force term, known as the *equation of the memory function*. Modelling memory functions is a very standard procedure to obtain correlation functions. Nonetheless, there are other alternative, well-known approaches to calculate correlation functions, such as the kinetic theory based on the linearization of the Boltzmann equation (in phase space), the so-called mode-coupling theory, or the short-time (sum rules) and long-time behavior (transport coefficients). A detailed presentation and discussion of these interesting and important topics, which can be found in the more specialized literature [4–6], are out of the scope of this monograph.

In dissipative dynamics, there are several oscillator models considered paradigmatic, which can describe phenomenologically many elementary classical and quantum processes. This is the case, for example, of the damped and driven harmonic oscillator, typically considered in applications involving linear damping. This oscillator obeys a differential equation of motion in configuration space given by

$$\ddot{q} + \gamma \dot{q} + \omega_0^2 q = F(t), \quad (2.1)$$

where  $\omega_0$  is the natural or harmonic frequency of the oscillator,  $\gamma$  is the friction parameter and  $F(t)$  is the force acting on it. Analogously, there is the so-called parametric driven harmonic oscillator, which arises originally from the study of electric circuits. This oscillator is described by the differential equation

$$\ddot{q} + \gamma(t)\dot{q} + \omega_0^2(t)q = 0, \quad (2.2)$$

where  $\gamma$  and  $\omega_0$  depend only on time and not on the state of the oscillator. In general, the dependence on time is assumed to be periodic with the same period. Moreover, an extra driving force,  $F(t)$ , can also be added. By assuming Ohmic damping, or constant friction, and substituting the position  $q$  by  $qe^{-\gamma t/2}$  into (2.2), the damping can be formally removed. This yields the equation of motion of an undamped oscillator evolving under the action of a modified potential,

$$\ddot{q} + \left[ \omega_0^2(t) - \gamma^2/4 \right] q = 0. \quad (2.3)$$

For periodic forces or functions, Floquet's theorem can be applied to this second-order differential equation to find the corresponding periodic solutions (for certain cases, some of them become unstable). Mathieu's oscillator is a special case of this oscillator, where  $\omega_0^2(t) = \omega_0^2 + \epsilon \cos(\Omega t)$ . This oscillator has been used to interpret several experiments. For example, parametric resonances take place when the external excitation frequency of a given parameter is equal to twice the oscillator natural frequency.

Among the different nonlinear differential equations describing the motion of a classical system, the so-called van der Pol and Duffing equations play a special role. The van der Pol equation is a second order differential equation original from self-sustained electric circuits that displays nonlinear damping. In one-dimension, its general form reads as

$$\ddot{y} + \gamma(y^2 - \alpha)\dot{y} + y = F(t), \quad (2.4)$$

with  $\gamma$  and  $\alpha$  real. In a similar vein, the Duffing equation describes the damping motion of an oscillator subject to the influence of a nonharmonic force (Hooke's law is not obeyed). This equation, given by

$$\ddot{y} + \gamma\dot{y} + \alpha y + \beta y^3 = A \cos(\omega t + \phi), \quad (2.5)$$

with  $\gamma$ ,  $\alpha$ , and  $\beta$  real, leads to chaotic dynamics. These important topics, nonlinear damping [1] or chaotic dissipative motion [7] are also out of the scope of this monograph.

The literature about the four oscillator models mentioned above and their applications is very extensive. The reader interested in a more detailed analysis is addressed to any standard textbook dealing with linear and nonlinear dynamical systems. This Chapter focuses on a general and simple introduction to dissipative and stochastic dynamics in classical mechanics, with the purpose of supplying the means for a better understanding of the dynamics of open quantum systems later on in [Chap. 5](#).

## 2.2 Dissipative Dynamics

Forces are usually assumed as conservative and derivable from interaction potentials. As it was shown in [Chap. 1](#), the canonical formulations of classical mechanics for conservative systems are essentially the Lagrangian, Hamiltonian and Hamilton–Jacobi formulations. These formalisms have been developed and extended to find quantum analogues of conservative systems. However, for nonconservative systems this extension is much more troublesome. One of the most important issues in analytical dynamics is the so-called *inverse problem*, i.e., the problem of determining the Lagrangian and Hamiltonian functions from the equations of motion (see [Sect. 1.2.1](#)). This problem has been widely studied due to the non-uniqueness implicit in those formulations. The conditions for the existence of a Lagrangian function are called the *Helmholtz conditions*, which provide a way to construct Lagrangians. However, not all of them are acceptable because of the violation of some physical requirement. Moreover, when the number of degrees of freedom is equal or greater than two, not always a Lagrangian can be found for a given classical system. The connection between invariance or symmetry properties and conserved quantities is given by *Nöther’s theorem* [8]. This theorem allows to determine constants of motion, if they exist, from the equations of motion in those cases where the problem cannot be formulated in terms of the variational principle. This issue becomes critical when dealing with dissipation, for dissipative systems cannot always be described by means of a Lagrangian or a Hamiltonian. Hence finding an appropriate quantum description for these systems is not exempt from difficulties and controversy.

Even when not all forces acting on a system can be derived from a potential function, the Lagrange equations (1.3) can still be written [8] as

$$\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = Q_i, \quad i = 1, 2, \dots, N, \quad (2.6)$$

where the Lagrangian  $L$  contains the potential of the conservative forces and  $Q_i$  represents the remaining forces. The simplest way to include dissipation within the Lagrangian formulation is by adding the so-called *dissipation function* to the Lagrange equations,

$$Q_i = -\frac{\partial \mathcal{F}}{\partial \dot{q}_i}. \quad (2.7)$$

This idea, due to Rayleigh, is based on considering that the gradient of  $Q_i$  with respect to the velocity just gives the dissipative force. In order to include nonlinear damping forces, this Rayleigh function has been generalized by Lur’e [1]. Dissipative dynamics can be considered by following different routes, which will be briefly analyzed below.

### 2.2.1 Effective Hamiltonians. The Caldirola–Kanai Model

One of the simpler ways to incorporate environment effects is by considering time-dependent Lagrangian and/or Hamiltonian functions, thus avoiding to deal explicitly with the environment degrees of freedom. This approach allows to preserve the canonical formalism, which can be a good starting point to find out the quantum analogue of the corresponding dissipative dynamics.

The paradigm of the dissipative dynamics is the damped harmonic oscillator model, where the damping force is linear with the velocity. In a one-dimensional configuration space, its equation of motion is (for  $m = 1$ )

$$\ddot{q} + \gamma \dot{q} + \omega_0^2 q = 0, \quad (2.8)$$

where  $\gamma$  is the damping constant or friction. Physically, this equation describes a classical dissipative system losing energy at a constant rate  $\gamma$  as time increases. The Hamiltonian model associated with this simple system is the so-called *Caldirola–Kanai (CK) Hamiltonian* [1, 9, 10],

$$H_{\text{CK}} = \frac{p^2}{2m} e^{-\gamma t} + V(q) e^{\gamma t}, \quad (2.9)$$

which was initially considered for a particle with time-dependent mass. In this Hamiltonian,

$$V(q) = \frac{1}{2} m \omega_0^2 q^2 \quad (2.10)$$

is the potential for a harmonic oscillator with frequency  $\omega_0$  and mass  $m$ . As shown below, this Hamiltonian has also been considered extensively for damping motion. The corresponding Lagrangian is

$$L_{\text{CK}} = \left( \frac{1}{2} m \dot{q}^2 - \frac{1}{2} m \omega_0^2 q^2 \right) e^{\gamma t}. \quad (2.11)$$

As mentioned above, different Hamiltonians and Lagrangians from those given respectively by (2.9) and (2.11) may also lead to the same equation of motion (2.8) in configuration space. Actually, the correct equation of motion in phase space cannot be obtained from the CK Hamiltonian.

From (2.9), the associated CK Hamilton–Jacobi equation now reads as

$$\frac{\partial S}{\partial t} + \frac{1}{2m} \left( \frac{\partial S}{\partial q} \right)^2 e^{-\gamma t} + \frac{1}{2} m \omega_0^2 q^2 e^{\gamma t} = 0. \quad (2.12)$$

Following the usual procedure of separation of variables (see Sect. 1.2.2),  $S$  can be expressed as

$$S(q; t) = \mathcal{W}(q) - \alpha t. \quad (2.13)$$

After some algebraic manipulations, one obtains the solution of (2.8),

$$q(t) = \sqrt{\frac{2\alpha}{m\omega^2}} e^{-\gamma t/2} \sin[\omega(t + \beta)], \quad (2.14)$$

where  $\beta = \partial S / \partial \alpha$  and the oscillation frequency is

$$\omega = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}. \quad (2.15)$$

In the case of a charged particle moving in an external electromagnetic field and subject to a conservative force, the Lorentz force can be added to the equation of motion. Alternatively, using the principle of minimal coupling [1], the canonical momentum can be replaced by a momentum involving the vector potential—adding to the corresponding Hamiltonian a term with the scalar potential. For conservative systems, since  $H$  represents the total energy of the particle both formulations lead to the same result. However, for dissipative systems, such as the problem of radiation damping, the minimum coupling scenario does not apply, for it does not lead to the correct equation of motion. On the other hand, the classical equation of motion for a harmonically bound electron coupled to an electromagnetic field gives rise to the classical theory of line widths. As mentioned above, other very well-known models can also be found in the literature, such as the driven damped oscillator, Raleigh's oscillator or the variable mass oscillator.

The previous examples are all formulated in real space. However, the discussion can be extended to a complex coordinate formulation. In this sense, the so-called Dekker Hamiltonian [11] plays a special role. From the damped harmonic oscillator, complex coordinates are introduced according to the change of variable

$$\xi = \frac{1}{\sqrt{\omega}} \left[ p + \left( \frac{\gamma}{2} - i\omega \right) q \right]. \quad (2.16)$$

Then, given the Lagrangian

$$L = \frac{i}{2} [\xi^* \dot{\xi} - \xi \dot{\xi}^*] - \left( \omega - \frac{i\gamma}{2} \right) \xi^* \xi, \quad (2.17)$$

the complex Hamiltonian that arises from it reads as

$$H = - \left( i\omega + \frac{\gamma}{2} \right) \pi \xi, \quad (2.18)$$

where  $\pi = \partial L / \partial \dot{\xi}$ . In terms of the physical (real-valued) variables, this Hamiltonian can also be expressed as

$$H = \frac{1}{2}p^2 + \frac{\gamma}{2}(pq + qp) + \frac{1}{2}\left(\omega^2 + \frac{\gamma^2}{4}\right)q^2 - i\frac{\gamma}{2}. \quad (2.19)$$

### 2.2.2 Lagrangians for Dissipative Systems and Diffusion Equations

An alternative way to tackle the problem of the Lagrangian formulation for dissipative systems is as follows. Consider the equation of motion (2.8) for the damped harmonic oscillator. As mentioned above, in principle this equation cannot be derived from any Lagrangian, since there is no stationary solution. In order to find out a suitable Lagrangian, one can assume that the energy lost by the system goes into another system, namely a *mirror-image system*, which absorbs it [12]. That is, if the energy of the oscillator described by (2.8) is lost at a rate  $\gamma$ , it will be gained at the same rate (with negative friction,  $-\gamma$ ) by the mirror-image system, here denoted by  $\bar{q}$ . This implies a zero total energy balance and, more importantly, that stationary (extremal) solutions for the larger system can be found. Thus, consider the Lagrangian describing these coupled systems is

$$L = m\dot{q}\dot{\bar{q}} - \frac{1}{2}m\gamma(\bar{q}\dot{q} - \dot{\bar{q}}q) - m\omega_0^2 q\bar{q}, \quad (2.20)$$

where  $m$  is the system mass. Applying variations [13] with respect to  $\bar{q}$  and  $q$ , one obtains (2.8) as well as its homologous for  $\bar{q}$ ,

$$\ddot{\bar{q}} - \gamma\dot{\bar{q}} + \omega_0^2\bar{q} = 0. \quad (2.21)$$

By further proceeding, it is possible to extract the Hamiltonian equations of motion. Thus, applying the expression corresponding to the calculation of generalized momenta from Lagrangian mechanics (see Chap. 1),

$$p = \frac{\partial L}{\partial \dot{q}} = m\dot{\bar{q}} - \frac{1}{2}m\gamma\bar{q} = me^{-\gamma t/2} \frac{d}{dt} \left( e^{-\gamma t/2} \bar{q} \right), \quad (2.22a)$$

$$\bar{p} = \frac{\partial L}{\partial \dot{\bar{q}}} = m\dot{q} - \frac{1}{2}m\gamma q = me^{-\gamma t/2} \frac{d}{dt} \left( e^{-\gamma t/2} q \right). \quad (2.22b)$$

Taking into account the functional form displayed by the last equalities in each equation, a new set of generalized coordinates and momenta can be defined,

$$Q \equiv e^{-\gamma t/2} q, \quad P \equiv e^{-\gamma t/2} p, \quad \bar{Q} \equiv e^{-\gamma t/2} \bar{q}, \quad \bar{P} \equiv e^{-\gamma t/2} \bar{p}, \quad (2.23)$$

such that (2.22) become

$$P = m\dot{Q}, \quad \bar{P} = m\dot{\bar{Q}}. \quad (2.24)$$

These relations somehow show the energetic balance in the full system described by the Lagrangian (2.20), where the energy loss due to dissipation in the system of interest is balanced with an energy increase, at the same rate, in its image. The associated Hamiltonian is then given by

$$H = p\dot{q} + \bar{p}\dot{\bar{q}} - L = \frac{p\bar{p}}{m} + \frac{1}{2}\gamma(\bar{q}\bar{p} - qp) + m\omega^2 q\bar{q}, \quad (2.25)$$

where  $\omega$  is given by (2.15). With this change of variables, the Hamiltonian equations of motion now read as

$$\dot{q} = \frac{\bar{p}}{m} - \frac{1}{2}\gamma q, \quad (2.26a)$$

$$\dot{\bar{p}} = -m\omega^2 q - \frac{1}{2}\gamma\bar{p}, \quad (2.26b)$$

$$\dot{\bar{q}} = \frac{p}{m} + \frac{1}{2}\gamma\bar{q}, \quad (2.26c)$$

$$\dot{p} = -m\omega^2\bar{q} + \frac{1}{2}\gamma p. \quad (2.26d)$$

In these equations, the intertwining between coordinates is very apparent—in the pairs  $(q, \bar{p})$  and  $(\bar{q}, p)$ . This intertwining eventually leads to the system energy dissipation and its absorption by the image system. This can also be noticed from the eigenvalues of the matrix associated with the system of equations (2.26), when the latter is expressed in symplectic notation. These eigenvalues are  $\lambda_{\pm}^{\pm} = -\gamma/2 \pm \omega$  and  $\lambda_{\pm}^{\mp} = \gamma/2 \pm \omega$ , where  $\lambda_{\pm}^{\pm}$  describes the system damping and  $\lambda_{\pm}^{\mp}$  the image-system energy absorption (at the same rate that the system losses it).

The mirror–image method thus allows to apply the variational techniques to dissipative problems, since a Lagrangian density can be defined for them. In other words, whenever one deals with dissipative problems with a gradual energy loss at a constant rate and there is no knowledge on the bath dynamics (neither it is necessary), this technique can be used to derive the corresponding equations of motion. This is the case, for example, of the *heat equation*, which describes the time-evolution of temperature (heat distribution) in a certain space region. In this case, one can construct a Lagrangian density for this *diffusion equation* [12], which reads as

$$\mathcal{L} = -\frac{1}{2} \left( \bar{\psi} \frac{\partial \psi}{\partial t} - \psi \frac{\partial \bar{\psi}}{\partial t} \right) - D \nabla \psi \cdot \nabla \bar{\psi}, \quad (2.27)$$

where  $\psi$  represents the density of the diffusing heat ( $\bar{\psi}$  represents the mirror–image of  $\psi$ ) and  $D$  is the so-called *diffusion constant* or *diffusion coefficient*. Proceeding as before, one finds the Euler–Lagrange equations



$$D\nabla^2\psi = \frac{\partial\psi}{\partial t}, \quad (2.28a)$$

$$D\nabla^2\bar{\psi} = -\frac{\partial\bar{\psi}}{\partial t}, \quad (2.28b)$$

where (2.28a) is the heat equation and (2.28b) is an equation describing the absorption of the heat flux leaving the system. Equation (2.28a) can also be regarded as the diffusion equation with constant  $D$  for a swarm of identical, noninteracting particles. In this case,  $\psi \equiv P$  is the probability density function describing the position of one of such particles, which move pursuing random trajectories. This type of motion is called *Brownian motion*. If all particles start at  $t_0 = 0$  and  $\mathbf{r}_0 = \mathbf{0}$  (with  $q \equiv \mathbf{r} = (x, y, z)$ ), the subsequent time-evolution of the ensemble will be described (see Sect. 2.3.2) by

$$P(\mathbf{r}, t) = \left(\frac{1}{4\pi Dt}\right)^{3/2} e^{-\mathbf{r}^2/4Dt}. \quad (2.29)$$

### 2.2.3 The Many-Body Problem

Dissipative forces can also be derivable from conservative many-body problems. In general, any system of  $N$  interacting particles can be split up into two interacting parts or subsystems,  $S_1$  and  $S_2$ . This splitting is introduced on purpose to analyze the time-evolution of one of these subsystems, say  $S_1$ , while the other one ( $S_2$ , in this case) is regarded to play the role of an environment. If both subsystems have a few degrees of freedom, the energy exchange goes in both directions, from  $S_1$  to  $S_2$  and vice versa, as seen in Sect. 1.5.1. However, if one of them has a very large number of degrees of freedom, say  $S_2$ , and its dynamics becomes rather complex, the energy will only flow in one direction, from  $S_1$  to  $S_2$ . The dynamics of  $S_1$  then becomes dissipative, and the corresponding force is determined by the nature of the coupling with the extended system  $S_2$ . For example, well-known models exhibiting this type of dynamics are [1]:

- The Schrödinger chain, formed by an infinite number of mass points coupled by elastic springs. Here the decay law of any of its constituents is non-exponential.
- The Rubin model, where a massive particle is coupled to a semi-infinite chain of oscillators.
- The dynamics of a nonuniform chain (different masses and elastic spring couplings), where the decay law for a given particle is exponential.

A special case arises when a collection of harmonic oscillators is analyzed, all of them linearly coupled to a given system, e.g., a particle or a harmonic oscillator. For example, the van Kampen model describes an electron harmonically coupled to an electromagnetic field expressed in terms of confined waves in a large but finite sphere. Another example is Sollfrey's model, which describes an oscillator coupled

to a string of finite or infinite length. Among these models, the most celebrated one is the Ullersma Hamiltonian model [14–17],

$$H = \frac{p^2}{2M} + V(q) + \sum_{i=1}^N \left( \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 q_i^2 + \kappa_i q_i q \right), \quad (2.30)$$

where  $\kappa_i$  stands for the system-environment coupling coefficients. Usually, it is assumed that the masses of all oscillators are equal. At  $t = 0$ , all of them are at rest at their equilibrium positions. The formal solution for each  $q_i$  is

$$q_i(t) = -\frac{\kappa_i}{\omega_i} \int_0^t \sin[\omega_i(t-t')] q(t') dt', \quad (2.31)$$

while the equation of motion for  $q$  reads as

$$\ddot{q} + \frac{\partial V}{\partial q} + \int_0^t K(t-t') q(t') dt' = 0. \quad (2.32)$$

In the latter equation, the kernel  $K(t-t')$  has the general form

$$K(t-t') = \sum_{i=1}^N \frac{\kappa_i^2}{\omega_i} \sin[\omega_i(t-t')], \quad (2.33)$$

although other different forms can also be envisaged, for example,  $K(t-t') = 2\gamma\delta(t-t')$ , which is widely used. Thus, by extending to infinity the upper limit of the integral in (2.32) and assuming that  $V(q)$  is harmonic, this equation reduces to the damped harmonic oscillator equation of motion (2.8). In this particular case, the Hamiltonian (2.30) becomes a quadratic function of the coordinates and momenta. As is well known, this type of Hamiltonian can be diagonalized exactly by means of a canonical transformation. The resulting Hamiltonian is also harmonic and consists of  $N + 1$  independent oscillators with renormalized frequencies or normal mode frequencies [1].

Another interesting case arises when  $V(q)$  describes a potential barrier, so that only tunneling allows a particle to pass through. In classical mechanics the momentum becomes imaginary and therefore an imaginary time formulation for the particle motion can be used. The corresponding Lagrangian (Euclidean Lagrangian) is expressed as

$$L = \frac{\dot{q}^2}{2} + V(q) + \sum_{j=1}^N \left( \frac{\dot{q}_j^2}{2} + \frac{1}{2} \omega_j^2 q_j^2 + \kappa_j q_j q \right), \quad (2.34)$$

where the time derivatives are taken with respect to the imaginary time  $\tau = it$  (*Wick rotation*). Now, the classical dynamics occurs in the inverted potential, with the equation of motion for  $q$  being

$$\ddot{q} - \frac{\partial V}{\partial q} + \int_{-\infty}^{+\infty} K(\tau - \tau') q(\tau') d\tau' = 0, \quad (2.35)$$

where the explicit form of the kernel is

$$K(\tau - \tau') = - \sum_{j=1}^N \frac{\kappa_j^2}{2\omega_j} e^{-\omega_j |\tau - \tau'|}. \quad (2.36)$$

## 2.3 Stochastic Dynamics

As mentioned at the beginning of [Sect. 1.3](#), when dealing with many-body systems described by Hamiltonian functions like (1.38), dynamics may exhibit stochastic features. This is a “coarse-grained” effect arising when one only focuses on the dynamics of the system of interest, neglecting details about the environment dynamics. At present there are high performance numerical techniques (e.g., the so-called *Molecular Dynamics* methods [18]), which carry out sophisticated simulations of many degree-of-freedom classical systems. Relatively large sets of Hamiltonian or Newtonian coupled differential equations can be solved provided there is a complete information of the initial conditions for all the degrees of freedom involved. To some extent, these simulations mimic the own experiment (of course, at the level of accuracy of the model employed). Indeed, in those cases where no experiment is available, they play the role of an experiment itself. This is a very important advantage, although there are also some disadvantages. For example, among the main disadvantages, one finds that in these approaches some physical insight is unavoidably lost, for statistical methods have to be eventually considered in order to understand the underlying physics—the study of isolated trajectories in systems described by a large number of degrees of freedom is useless. This flaw can be surmounted through the use of some theoretical model devised within the framework of the theory of open classical systems. From this viewpoint,  $N$ -body problems can be replaced by simpler single-body ones, where an effective (phenomenological) interaction between the system of interest and the environment is assumed. In general, the effective interaction is introduced by means of a noise or fluctuating force coming from the bath and whose intensity is accounted for by a friction coefficient, and typically linear with temperature. The case where the friction coefficient is constant in space and time, as in (2.8), is called *Ohmic friction*. The drastic reduction of dimensionality of the original problem arising when stochastic models are assumed is very advantageous computationally, since the specific dynamics of the environment—with dimensions typically much larger than those associated with the subsystem of interest—is neglected. Furthermore, more importantly, this allows us to apply analytical statistical treatments to study the subsystem of interest, so that its dissipation mechanisms can be better characterized and understood.

The stochastization or randomization of a general physical process thus consists of carrying out a sort of coarse-graining in space and time [3]. The degree of “crudeness”

required by a stochastization is directly related to the level of accuracy required by the spatial and temporal measurements of dynamical variables. A stochastic physical process is called *Markovian* if its time evolution is determined by the present and not its past (see Appendix B), losing very quickly any memory of its past. As a consequence, Markovian laws of motion are first-order differential equations with respect to time. Delayed effects and nonlocal properties are therefore not taken into account. The paradigm of stochastic processes is the Brownian motion, i.e., the seemingly random movement of particles suspended in a fluid, but also, in a more modern conception, the mathematical model used to describe similar random motions in other systems [19–21]. The random-walk problem is often considered as a model for such a motion. Brownian motion is not only Markovian, but also Gaussian, since the central limit theorem applies for sufficiently long times, at least longer than the system correlation time, so that the system has lost memory of its initial conditions. If the number of particles is not too large and the particularities of the interactions among them can be ignored, Brownian particles are governed by the standard diffusion equation. The mean time between collisions of Brownian particles and their surrounding is of the same order of magnitude or even slightly shorter than the average period of the environment fluctuating force.

There are mainly three ways to introduce stochasticity. First, phenomenologically, describing Brownian-like motions by means of the standard Langevin equation, where the system-environment interaction is governed by two parameters: temperature and friction [6, 22]. Second, starting from the Liouville equation, which is satisfied by any dynamical variable. Within this approach, Fokker–Planck-type equations can be easily reached. Actually, projection-operator techniques are very often used to obtain a generalized Langevin equation [4], where its kernel or memory function also fulfills a given integro-differential equation written in terms of its corresponding time-correlation function [5]. And third, as shown in Sect. 1.2.2, following the Ullersma model [14–17] or the so-called Caldeira–Leggett Hamiltonian model [23], the equations of motion can be expressed in terms of a generalized Langevin equation whenever the oscillators are not assumed to be at rest at  $t_0 = 0$ . The trajectories issued from solving such equations are called (classical) stochastic trajectories. Notice that this stochasticity is due to an external noise source, quite different from the inherent or intrinsic stochasticity related to chaotic dynamics (see Sect. 1.3).

A central issue which is not going to be treated here is the role played by external noise in nonequilibrium phase transitions, also called *noise-induced transitions* [24].

### 2.3.1 Brownian Motion and the Langevin Equation

Stochastic dynamics deals with random or stochastic variables and stochastic processes (see Appendix B), Brownian motion being a paradigm of this type of dynamics. This singular motion was formerly described by Ingen-Housz [25] in 1785 as an irregular motion of coal dust on a surface of alcohol—similar conclusions were drawn by Bywater [26] in 1819—and later on by Brown [27, 28] in 1827 when studying pollen particles suspended on water. Some of the mathematics behind the

Brownian motion are already incipient in Thiele's works on the least-square method in the 1880s [29]. However, it was not until 1880 when the first stochastic model to describe the stock option market as a Brownian motion was proposed by Bachelier [30]. Then, shortly after, independent physical solutions to the problem of Brownian motion were given by Einstein [31, 32], in 1905, and Smoluchowski [33], in 1906, who used this type of motion as an indirect proof of the existence of atoms and molecules. According to Einstein, the MSD of a Brownian particle is proportional to the first power of time—a result reminiscent of the random-walk problem—, this being the main feature defining Brownian motion.

For simplicity, a one-dimensional description of Brownian motion is going to be considered, since the essential physics is well contained in this simple case. This motion, for example, takes place when a particle is adsorbed on a flat surface. Due to the fact the particle–surface interaction is zero, no direction is privileged. Furthermore, this dynamics will be the starting point to discuss simple physical processes in terms of quantum stochastic trajectories in Volume 2. The equation of motion describing a Brownian particle of mass  $m$  embedded in a fluid, proposed by Langevin [34] in 1908, is given by

$$m\dot{v} = -m\gamma v + mR_G(t), \quad (2.37)$$

or, in the form of a stochastic differential equation, as

$$mdv = -m\gamma v dt + mdW(t), \quad (2.38)$$

where  $dW(t) = R_G(t)dt$  is a *Wiener process* [35, 36] (see Appendix B). The right-hand side of this equation can be split up into two contributions:

1. A deterministic part, characterized by the friction force  $-m\gamma v$ , with  $\gamma$  being the friction coefficient depending on the fluid viscosity.
2. A random part, governed by the random force  $mR_G(t)$  or *Gaussian white noise*.

Since the random force is described by a Wiener process, it satisfies the two conditions of a typical *Gaussian white noise*:

1. The stochastic process  $R_G(t)$  is Gaussian with zero mean, i.e.,

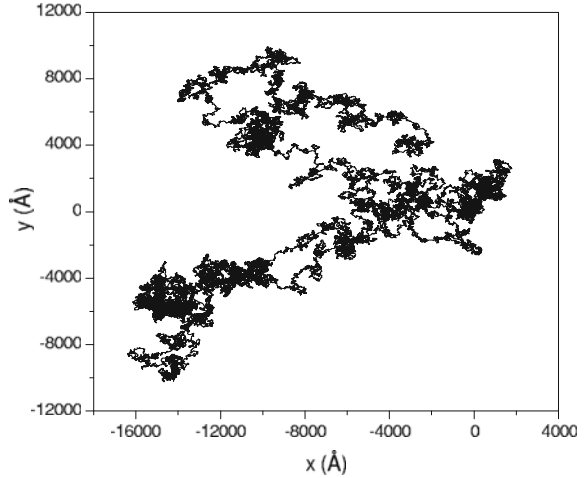
$$\langle R_G(t) \rangle = 0.$$

2. The force–force time-correlation function is infinitely short, i.e.,

$$m^2 \langle R_G(0)R_G(\tau) \rangle = A\delta(\tau),$$

with  $A$  being a constant giving the strength of the coupling between particle and environment and determined by the energy equipartition theorem.

**Fig. 2.1** As an example of Brownian motion driven by a Gaussian white noise, as in Fig. 1.2, the classical stochastic trajectory pursued by a Na atom is also displayed here at  $T = 300$  K, though on a flat surface ( $V = 0$ ). The friction constant is  $\gamma = 0.5 \text{ ps}^{-1}$  and the evolution is up to  $t = 20,000 \text{ ps}$



The validity of this model relies on the fact that the Brownian particle is much heavier than the environmental ones. This implies that the kicks received by the particle, although relatively weak, they are very effective when considered in a very large number—the central limit theorem holds and, therefore, the noise becomes Gaussian. Actually, these kicks can be seen as coming from thermal fluctuations of the surroundings. Remember that the detailed time-evolution of the environment degrees of freedom is not taken into account because their correlations decay faster than those of the particle (Markovian approximation), as expressed by the property 2. Thus, they are accounted for by assuming the presence of fluctuations that perturb the free evolution of the particle. In Fig. 2.1 one classical stochastic trajectory driven by a Gaussian white noise is plotted, which simulates a realization of a two-dimensional Brownian motion. In order to obtain information about the diffusion process, a swarm of these trajectories (i.e., a sampling over many Brownian realizations) should be considered.

The relationship between the friction in the Langevin equation and the fluctuations of the random force is given by the *fluctuation–dissipation theorem* [3], which reads as

$$\gamma(\omega) = \frac{m}{2k_B T} \int_{-\infty}^{\infty} \langle \delta R_G(0) \delta R_G(\tau) \rangle e^{-i\omega\tau} d\tau, \quad (2.39)$$

where

$$\delta R_G(t) \equiv R_G(t) - \langle R_G(t) \rangle \quad (2.40)$$

is the fluctuation due to the random noise function  $R_G(t)$  and  $k_B$  is the Boltzmann constant. Whenever properties 1 and 2 for a Gaussian white noise apply, the friction coefficient becomes independent of the frequency

$$\gamma(\omega) = \frac{A}{2mk_B T}, \quad (2.41)$$

with  $T$  being the heat bath temperature. Thus, the frequency spectrum of the friction force is flat or *white*, in the sense that all frequencies contribute equally to it, in analogy to white light, i.e.,

$$\gamma(\omega) \equiv \gamma. \quad (2.42)$$

The strength of the coupling between the Brownian particle and the environment will be

$$A = 2m\gamma k_B T, \quad (2.43)$$

and the Gaussian white noise correlation function

$$\mathcal{G}_G(\tau) \equiv \langle \delta R_G(0) \delta R_G(\tau) \rangle = \frac{2\gamma k_B T}{m} \delta(\tau). \quad (2.44)$$

Physically, this dynamics implies that, at thermal equilibrium, the equipartition theorem holds.

In general, there exists an interaction between the particle and the surface (for example, if the surface is corrugated). Thus, (2.37) can be rewritten as

$$\ddot{q}(t) = -\gamma \dot{q}(t') dt' + F(q(t)) + \delta R_G(t), \quad (2.45)$$

where  $q$  represents the particle position and  $F = -\nabla V$  is the deterministic force per mass unit derived from the interaction or external potential,  $V$ . The solution of this equation can be readily obtained by formal integration, to yield

$$v(t) = v_0 e^{-\gamma t} + \int_0^t e^{-\gamma(t-t')} F(x(t')) dt' + \int_0^t e^{-\gamma(t-t')} \delta R_G(t') dt', \quad (2.46a)$$

$$\begin{aligned} q(t) = & q_0 + \frac{v_0}{\gamma} (1 - e^{-\gamma t}) + \frac{1}{\gamma} \int_0^t [1 - e^{-\gamma(t-t')}] F(q(t')) dt' \\ & + \frac{1}{\gamma} \int_0^t [1 - e^{-\gamma(t-t')}] \delta R_G(t') dt', \end{aligned} \quad (2.46b)$$

where  $v_0 = v(0)$  and  $q_0 = q(0)$ . As can be seen, for  $\delta R_G = 0$ , (2.46) are the formal solutions of purely deterministic equations of motion. Therefore, without loss of generality, they can be expressed as

$$v(t) = v_d(t) + v_s(t), \quad (2.47a)$$

$$q(t) = q_d(t) + q_s(t), \quad (2.47b)$$

where  $d$  refers to the deterministic terms of the solutions and  $s$  to those associated with the stochastic force. Nevertheless, note that when  $\delta R_G(t) \neq 0$  the deterministic

part will also present some stochastic features due to the evaluation of  $F(q)$  along the trajectory  $q(t)$ , which is a stochastic process.

Taking advantage of properties 1 and 2 for a Gaussian white noise, the main average quantities can be written as (see Appendix B)

$$\langle v(t) \rangle = \bar{v}_d(t), \quad (2.48a)$$

$$\langle v^2(t) \rangle = \bar{v}_d^2(t) + \langle v_s^2(t) \rangle, \quad (2.48b)$$

$$\langle q(t) \rangle = \bar{q}_d(t), \quad (2.48c)$$

$$\langle q^2(t) \rangle = \bar{q}_d^2(t) + \langle q_s^2(t) \rangle, \quad (2.48d)$$

where the “barred” magnitudes indicate the respective averages of the deterministic part of the solution and

$$\langle v_s^2(t) \rangle = e^{-2\gamma t} \int_0^t dt' e^{2\gamma t'} \int_{-t'}^{t-t'} e^{\gamma \tau} \mathcal{G}_G(\tau) d\tau, \quad (2.49a)$$

$$\langle q_s^2(t) \rangle = \frac{1}{\gamma^2} \int_0^t dt' \left[ 1 - e^{-\gamma(t-t')} \right] \int_{-t'}^{t-t'} \left[ 1 - e^{-\gamma(t-t'-\tau)} \right] \mathcal{G}_G(\tau) d\tau. \quad (2.49b)$$

The final form of these expressions thus reads as

$$\langle v_s^2(t) \rangle = \frac{1}{\alpha^2} \left( 1 - e^{-2\gamma t} \right), \quad (2.50a)$$

$$\langle q_s^2(t) \rangle = \frac{1}{\gamma^2 \alpha^2} \left[ 2\gamma t + 1 - (2 - e^{-\gamma t})^2 \right], \quad (2.50b)$$

with  $\alpha = \sqrt{m/k_B T}$ . For example, if  $V = 0$ , the system is initially thermalized (i.e., it follows a Maxwell–Boltzmann velocity distribution) and has a uniform probability distribution in positions around  $q = 0$ , then  $\bar{v}_0 = 0$ ,  $\bar{v}_0^2 = k_B T/m$ , and  $\bar{q}_0 = 0$ . This leads to

$$\langle v(t) \rangle = 0, \quad (2.51a)$$

$$\langle v^2(t) \rangle = \frac{k_B T}{m}, \quad (2.51b)$$

$$\langle q(t) \rangle = 0, \quad (2.51c)$$

$$\langle q^2(t) \rangle = \bar{q}_0^2 + \frac{k_B T}{m\gamma^2} \left[ 2\gamma t + 1 - (2 - e^{-\gamma t})^2 \right], \quad (2.51d)$$

as it was found by Wiener in his description of Brownian motion [35].

From (2.51), two dynamical regimes can be clearly distinguished depending on the value of  $\gamma t$ . For  $\gamma t \ll 1$ , collision events are rare and the particle shows an almost free motion with relatively long mean free paths. This is the *ballistic* or *free-diffusion regime*, characterized by the MSD



$$\langle q^2(t) \rangle \sim \frac{k_B T}{m} t^2. \quad (2.52)$$

On the other hand, for  $\gamma t \gg 1$ , there is no free diffusion, since the effects of the stochastic force (collisions) are dominant. This is the *diffusive regime*, where the MSD is linear with time,

$$\langle q^2(t) \rangle \sim \frac{2k_B T}{m\gamma} t = 2Dt. \quad (2.53)$$

This is the so-called *Einstein's law* for diffusion. As can be inferred from (2.53), by lowering the friction  $\gamma$  acting on the particle, a faster diffusion takes place (the diffusion coefficient  $D$  increases). Transport processes characterized by a MSD violating Einstein's law are generically called *anomalous transport processes* [37] (see Sect. 1.3.2).

### 2.3.2 Brownian Motion and the Liouville Equation

As mentioned above, one can also seek for a statistical description of the dynamics and study the evolution of (statistical) ensembles of stochastic trajectories. In Sect. 1.4.1, it was already briefly discussed how classical dynamics generate probability densities in phase space. This settled down the basis to define statistical ensembles. The time-evolution of these probability densities is governed by the Liouville equation. Similarly, the time-evolution of any general dynamical variable  $A$ , which is a function of the phase-space point at any time, is given by an analogous equation,

$$\frac{\partial A}{\partial t} = -\mathcal{L}A. \quad (2.54)$$

In order to describe experimental macroscopic quantities, a coarse graining in time or time-average of the dynamical variable of interest should be carried out. As seen in Sect. 1.3.1, if the equations of motion are fully deterministic (as it happens, for example, in Molecular Dynamics simulations), the cause leading to make time-averages equivalent to phase-space averages (ergodic hypothesis) and then justifying the calculation of thermodynamic properties, is the intrinsic dynamical instability or chaos. However, when talking about transport properties, the key element is the decay of correlation functions with time, where the Green–Kubo relations constitutes the ordinary link between Liouvillian dynamics and transport coefficients. Although ergodicity is an important condition, it is not very useful, since one cannot define a timescale based only on this property. Again, the intrinsic relaxation times of correlation functions are ruled by the dynamical instability, which also allows to obtain transport coefficients from it. Time-correlation functions are also of experimental relevance, since the spectra measured by various spectroscopic techniques are the power spectra of well-defined dynamical variables. As mentioned in Chap. 1, resonant behavior can be extracted from the complex frequency spectrum of such spectral functions.

The evolution of a Brownian particle can be described (in a Cartesian three-dimensional configuration space) by a dynamical equation [3]

$$\dot{\mathbf{r}} = \mathbf{v}(t), \quad (2.55)$$

where  $\mathbf{v}(t)$  is a velocity associated with the particle displacement  $\mathbf{r}(t)$ . Now, due to the type of motion,  $\mathbf{v}(t)$  is a stochastic process and, therefore,  $\mathbf{r}(t)$  will also be a stochastic process, which is obtained from  $\mathbf{r}(t)$  (of course, not in the usual way how the concept of time-derivative is understood). Thus, consider the microscopic density distribution function (or, more specifically, the probability density) is  $\rho(\mathbf{r}, t)$ . This quantity gives the probability that a Brownian particle can be found within a volume element  $d\mathbf{r}$  of the configuration space at a time  $t$ . By invoking the probability conservation property, it can be shown that  $\rho(\mathbf{r}, t)$  obeys a stochastic Liouville equation,

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -\mathcal{L}\rho(\mathbf{r}, t), \quad (2.56)$$

where the differential operator  $\mathcal{L}\rho(\mathbf{r}, t) \equiv -\nabla \cdot \{\mathbf{v}(t)\rho(\mathbf{r}, t)\}$  is itself a stochastic operator because  $\mathbf{v}(t)$  is a stochastic process. In the reciprocal  $\mathbf{k}$ -space, (2.56) becomes

$$\frac{\partial \tilde{\rho}(\mathbf{k}, t)}{\partial t} = -i\mathbf{k} \cdot \mathbf{v}(t)\tilde{\rho}(\mathbf{k}, t), \quad (2.57)$$

where  $\tilde{\rho}(\mathbf{k}, t)$  is the Fourier transform of  $\rho(\mathbf{r}, t)$ . The solution of (2.57) is readily obtained to yield

$$\tilde{\rho}(\mathbf{k}, t) = \tilde{\rho}(\mathbf{k}, 0)e^{-i \int_0^t \mathbf{k} \cdot \mathbf{v}(t') dt'}. \quad (2.58)$$

Since  $\mathbf{v}(t)$  is a stochastic process, the probability distribution in Fourier space is given by averaging over all possible paths,

$$I(\mathbf{k}, t) = \langle \tilde{\rho}(\mathbf{k}, t)\tilde{\rho}(\mathbf{k}, 0) \rangle \propto \langle e^{-i \int_0^t \mathbf{k} \cdot \mathbf{v}(t') dt'} \rangle. \quad (2.59)$$

This is the definition of the characteristic function (see Appendix B) for the stochastic variable or stochastic trajectory  $\mathbf{v}(t)$ , also called *intermediate scattering function* within the context of diffusion processes [38]. In the same context, the time Fourier transform of (2.59) is the so-called *scattering law* or *dynamic structure factor* (except for some normalization factor),

$$S(\omega, t) = \int e^{-i\omega t} I(\mathbf{k}, t) dt, \quad (2.60)$$

which is directly related to the observable in diffusion experiments.

Assuming that the position stochastic variable is Gaussian, (2.59) can be reexpressed as

$$I(\mathbf{k}, t) = e^{-\mathbf{k}^2 \langle v_{\mathbf{k}}^2 \rangle \int_0^t (t-\tau) \phi(\tau) d\tau}, \quad (2.61)$$

where  $\phi(t)$  is the normalized velocity autocorrelation function and  $v_{\mathbf{k}}$  stands for the velocity vector projected along  $\mathbf{k}$ . According to the discussion above, for the motion of the physical particle to behave as a Gaussian, Markovian process, a coarse graining in time should be imposed by taking the long-time limit. Now, if the correlation time is defined as

$$\tau_c = \int_0^\infty \phi(\tau) d\tau, \quad (2.62)$$

equation (2.61) is approximated by

$$I(\mathbf{k}, t) \sim e^{-\mathbf{k}^2 \langle v_{\mathbf{k}}^2 \rangle \tau_c t + \delta}, \quad (2.63)$$

with  $\delta = \mathbf{k}^2 \int_0^\infty \tau \phi(\tau) d\tau$ . The intermediate scattering function (2.63) is the solution of the differential equation

$$\frac{\partial I(\mathbf{k}, t)}{\partial t} = -\mathbf{k}^2 \langle v_{\mathbf{k}}^2 \rangle \tau_c I(\mathbf{k}, t). \quad (2.64)$$

If this equation is Fourier-transformed back to the configuration space, one obtains the standard diffusion equation,

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = D \nabla^2 P(\mathbf{r}, t). \quad (2.65)$$

In this equation,  $P(\mathbf{r}, t)$  is the normalized autocorrelation function of the microscopic number density  $\rho(\mathbf{r}, t)$ , with initial condition

$$P(\mathbf{r}, 0) = \delta(\mathbf{r} - \mathbf{r}_0), \quad (2.66)$$

and  $D = \tau_c \langle v_{\mathbf{k}}^2 \rangle$  is the diffusion coefficient. The solution of the diffusion equation (2.65) is given by

$$P(\mathbf{r}, t) = \left( \frac{1}{4\pi Dt} \right)^{3/2} e^{-(\mathbf{r}-\mathbf{r}_0)^2/4Dt}, \quad (2.67)$$

which means that, as time goes on, the probability distribution gradually broadens, leading to an irreversible motion.

So far diffusion has been described in the configuration space. Obviously, it also admits a description in the velocity space or in the phase space. In the velocity space, the diffusion equation is described by the *Fokker-Planck equation* [39–41],

$$\frac{\partial P(\mathbf{v}, t)}{\partial t} = \gamma \nabla_{\mathbf{v}} \cdot [\mathbf{v} P(\mathbf{v}, t)] + \frac{\gamma k_B T}{m} \nabla_{\mathbf{v}}^2 P(\mathbf{v}, t), \quad (2.68)$$

with  $\gamma$  and  $D = \gamma k_B T / m$  being the drift and diffusion coefficients, respectively. The probability density is again sharply peaked at  $v_0$  and, asymptotically in time, it approaches the stationary Maxwellian distribution at temperature  $T$ . Regarding the phase-space description, the corresponding diffusion equation is the so-called *Kramers–Chandrasekhar equation* [6, 42, 43]. Within a more general context, it can be shown [44] that all these diffusion equations can be obtained from the reduced Liouville equation for one particle.

In 1940, Kramers [42] proposed a one-dimensional diffusion model for chemical reactions based on the motion of a Brownian particle under the action of an external potential  $V$ . In particular, originally  $V$  had the form of an asymmetric double well potential. Within this model, the Langevin equation describing the evolution of the reaction coordinate reads as

$$dq = v dt, \quad (2.69a)$$

$$m dv = - \left( \frac{dV}{dq} + \gamma m v \right) dt + \sqrt{2m\gamma k_B T} dW(t). \quad (2.69b)$$

Kramers was interested in the escape rate of the particle from a well. Two different regimes were thus considered for the rate:

1. *Strong friction*, where the friction coefficient is greater than the barrier frequency and the rate is limited by a spatial diffusion, decreasing as  $\gamma^{-1}$ .
2. *Weak friction*, where, on the contrary, the rate is limited by an energy diffusion process and increases linearly with  $\gamma$ .

These two extreme behaviors imply a maximum in between, namely the *Kramers turnover problem* [45]. For example, in the strong friction regime, after a time of the order of  $\gamma^{-1}$  all inertial effects have died out. This means that the left-hand side of (2.69b) is equal to zero (i.e.,  $dv = 0$ ) and therefore (2.69a) can be approximated by

$$dq = - \frac{1}{m\gamma} \frac{dV}{dq} dt + \sqrt{\frac{2k_B T}{m\gamma}} dW(t). \quad (2.70)$$

The corresponding Fokker–Planck or Smoluchowski equation can then be expressed as

$$\frac{\partial P(q, t)}{\partial t} = - \frac{\partial}{\partial q} \left[ \frac{1}{m\gamma} \frac{dV}{dq} P(q, t) \right] + \frac{1}{2} \frac{\partial^2}{\partial q^2} \left[ \frac{2k_B T}{m\gamma} P(q, t) \right]. \quad (2.71)$$

In general, solving numerically the Langevin set of equations (2.69) turns out to be easier at any regime than dealing with partial differential equations, such as the Fokker–Planck equation (2.71). In general, the Fokker–Planck equation can be solved as an eigenvalue problem [21]. A quantum and classical theory of surface diffusion based on Kramers’ theory of activated escape over one-dimensional potential barriers was developed by Pollak et al. [46–48] and Mel’nikov [49, 50]. Applications to Na atom diffusion on (corrugated) Cu surfaces can be found in the literature [51–53].

In this case, the stochastic trajectories issued from the numerical resolution of Langevin equations similar to the system constituted by (2.69) were used to build the corresponding intermediate scattering function (2.59) and scattering law (2.60).

### 2.3.3 The System-plus-Bath Approach

The system-plus-bath approach is perhaps the most successful and useful way to deal with stochastic dynamics, since it starts from a total system (system-plus-bath) which is conservative. In the particular case of open quantum systems, it seems to be the most natural approach. Notice that the passage from the classical system to the quantum-mechanical one, i.e., the *quantization* of the classical system, can be done in a straightforward way, applying different standard methods available in quantum mechanics (e.g., via quantum-classical correspondence).

Within the system-plus-bath approach, the corresponding dynamics is commonly described by a total Hamiltonian which is split up into three different parts,

$$H = H_S + H_B + H_{SB}, \quad (2.72)$$

where  $H_S$  is the system Hamiltonian,  $H_B$  is the bath Hamiltonian, and  $H_{SB}$  is the term describing the system-bath interaction or coupling. As mentioned above, the system usually consists of a few degrees of freedom, while the environment is formed by a huge number of them (even infinity). Moreover, it is reasonable to assume that the coupling between them is a linear function of the bath coordinates. This property of linearity is very convenient, since it is then very easy to eliminate the bath coordinates in an exact way. In this regard, for extensive systems, like a reservoir, it is very common to assume a set of  $N$  harmonic oscillators,

$$H_B = \frac{1}{2} \sum_{i=1}^N \left( \frac{p_i^2}{m_i} + m_i \omega_i^2 q_i^2 \right), \quad (2.73)$$

where  $q_i$  and  $p_i$  are the position and momentum of the  $i$ th oscillator, and  $m_i$  and  $\omega_i$  its mass and frequency, respectively (this one-dimensional Hamiltonian can be extended straightforwardly to three dimensions). Very often, the dissipation mechanism is independent of the choice of this type of bath.

This kind of approach is widely used to describe stochastic processes where dissipation and damping play a fundamental role. Without loss of generality, consider the system is formed by only one degree of freedom and its Hamiltonian is written as

$$H_S = \frac{P^2}{2M} + V(Q), \quad (2.74)$$

where  $M$  is the particle mass and  $V(Q)$  is an external potential acting on the particle. The coupling between system and bath is generally expressed as a linear interaction term with the following expression

$$H_{SB} = \sum_{i=1}^N \left( \frac{c_i^2}{m_i \omega_i^2} Q^2 - 2c_i q_i Q \right), \quad (2.75)$$

$c_i$  being the strength of the linear coupling. The classical equations of motion for a global system described by the total Hamiltonian  $H$ , which in the field of condensed matter physics is known as the *Caldeira–Leggett model Hamiltonian* [46–48, 54], leads to a generalized Langevin equation for  $Q(t)$ ,

$$M \ddot{Q}(t) + M \int_0^t dt' \gamma(t-t') \dot{Q}(t') + \frac{\partial V(Q)}{\partial Q} = R_G(t). \quad (2.76)$$

Here, the memory kernel or time-dependent friction reads as

$$\gamma(t) = \sum_i \frac{c_i^2}{m_i \omega_i} \cos(\omega_i t) \quad (2.77)$$

and the external force  $R_G(t)$  as

$$R_G(t) = - \sum_i c_i \left\{ \left[ q_i(0) + \frac{c_i}{m_i \omega_i^2} Q(0) \right] \cos(\omega_i t) + \frac{p_i(0)}{m_i \omega_i} \sin(\omega_i t) \right\}. \quad (2.78)$$

Given a suitably defined thermal distribution of initial conditions, denoted by  $(Q(0), P(0))$  and  $(q_i(0), p_i(0))$ , the external force is Gaussian distributed with zero mean, obeying the classical fluctuation–dissipation theorem. The bath or reservoir at a given temperature  $T$  is thus a source of noise displaying memory effects. The friction, in this case, is not a constant, but a time-dependent function. Nonetheless, in many physical situations, the memory kernel is a  $\delta$ -function of time, which leads to a constant (Ohmic) friction. Then, as mentioned above, the system dynamics becomes Markovian, losing track of its past. As can be noticed, the generalized Langevin equation (2.76) is equivalent to (2.32) when all initial conditions are set to zero (no temperature) and the kernel (2.77) is similar to (2.33). Moreover, (2.76) reduces to a standard Langevin equation in the Markovian approximation,

$$\ddot{Q} + \frac{\partial V}{\partial Q} - \gamma Q = R_G(t), \quad (2.79)$$

with  $R_G(t) = 2\gamma \delta(t)$ .

Nonlinear functions in (2.75) can also be envisaged [23]. In such a case, the open classical system becomes a state-dependent dissipation process and the random force exhibits multiplicative noise (see Appendix B). This leads to noise-induced transitions. This situation will not be considered in this monograph, although it is

worth mentioning that nonlinear environments are the subject of intensive research at present, since many important physical processes are better described in this way.

Very recently, some of the classical scattering singularities (rainbow, glory and skipping effects) mentioned in Chap. 1 have been considered under a stochastic viewpoint. The corresponding analysis has been carried out for adsorbate diffusion [53] on surfaces as well as atom-surface scattering [55]. This analysis could be easily extended to any type of scattering. The main features observed and interpreted in terms of a stochastic analysis lead to broadenings and shiftings as a function of the surface temperature. Friction-induced energy loss spectra have also been predicted in atom-surface scattering [56].

## 2.4 The Stochastic Hamilton–Jacobi Equation

Even if the overall dynamics observed is conservative, one could consider the possibility to understand this “regularity” as the result of an underlying stochastic dynamics. The theory of open classical systems could be then applied to describe this underlying motion. Specifically, assuming the corresponding motions are Brownian-like, they could be described in terms of an *Itô stochastic differential equation* (see Appendix B). In this case, the associated Itô stochastic equation reads [36, 57, 58] as

$$d\mathbf{r}(t) = \mathbf{a}_+(\mathbf{r}, t)dt + b d\mathbf{W}(t), \quad (2.80)$$

where  $\mathbf{a}_+$  is the *mean forward derivative* of the particle position or displacement, and  $b$  accounts for the strength of the stochastic force. The diffusion equation for the corresponding probability distribution is described by the Fokker–Planck equation

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = -\nabla \cdot [\mathbf{a}_+(\mathbf{r}, t)P(\mathbf{r}, t)] + \frac{b^2}{2} \nabla^2 P(\mathbf{r}, t). \quad (2.81)$$

Under time-inversion, this Fokker–Planck equation can also be written as

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = -\nabla \cdot [\mathbf{a}_-(\mathbf{r}, t)P(\mathbf{r}, t)] - \frac{b^2}{2} \nabla^2 P(\mathbf{r}, t), \quad (2.82)$$

where  $\mathbf{a}_-$  now denotes the *mean backward derivative* of the particle position. From the definitions for two mean derivatives, the *particle mean derivative* is now defined as

$$\mathbf{v}(\mathbf{r}, t) = \frac{1}{2} (\mathbf{a}_+ + \mathbf{a}_-). \quad (2.83)$$

This allows to express the continuity equation for this process as

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} + \nabla \cdot [\mathbf{v}(\mathbf{r}, t)P(\mathbf{r}, t)] = 0 \quad (2.84)$$

after adding the Fokker–Planck equations (2.81) and (2.82). On the other hand, after subtraction of the two Fokker–Planck equations, an additional vector field can be defined, namely the *osmotic velocity*,

$$\mathbf{u}(\mathbf{r}, t) = \frac{1}{2} (\mathbf{a}_+ - \mathbf{a}_-) = \frac{b^2}{2} \nabla \ln P(\mathbf{r}, t), \quad (2.85)$$

with its time-derivative being

$$\frac{\partial \mathbf{u}}{\partial t} = -\frac{b^2}{2} \nabla (\nabla \cdot \mathbf{v}) - \nabla (\mathbf{v} \cdot \mathbf{u}). \quad (2.86)$$

It can be shown [36] that a mean acceleration in this kind of processes can also be defined as

$$\mathbf{a} = \frac{1}{2} \frac{\partial}{\partial t} (\mathbf{a}_+ + \mathbf{a}_-) + \frac{1}{2} \mathbf{a}_+ \cdot \nabla \mathbf{a}_- + \frac{1}{2} \mathbf{a}_- \cdot \nabla \mathbf{a}_+ - \frac{b^2}{4} \nabla^2 (\mathbf{a}_+ - \mathbf{a}_-). \quad (2.87)$$

Hence, taking into account the definitions given above for the mean velocity (2.83) and the osmotic velocity (2.86), the time-derivative resulting for  $\mathbf{v}$  reads as

$$\frac{\partial \mathbf{v}}{\partial t} = \mathbf{a} - \mathbf{v} \cdot \nabla \mathbf{v} + \mathbf{u} \cdot \nabla \mathbf{u} + \frac{b^2}{2} \nabla^2 \mathbf{u}. \quad (2.88)$$

The above elements provide a full general hydrodynamic description of Brownian motion. For an overall conservative dynamics—i.e., as arisen from a conservative Markovian diffusion process—, it is assumed that the Brownian particle is moving in an external potential  $V(\mathbf{r})$  and the stochastic mean acceleration is given as  $\mathbf{a} = -\nabla V(\mathbf{r})/m$ . Then the time-derivative of the mean velocity field (2.88) can be expressed as

$$\frac{\partial \mathbf{v}}{\partial t} = -\frac{1}{m} \nabla V(\mathbf{r}) - \mathbf{v} \cdot \nabla \mathbf{v} + \mathbf{u} \cdot \nabla \mathbf{u} + \frac{b^2}{2} \nabla^2 \mathbf{u}. \quad (2.89)$$

This equation provides now a complete general description of the hydrodynamics of Brownian motion under the action of an external potential  $V$ . Actually, one can further proceed. Thus, if the probability density is defined by a scalar field  $R(\mathbf{r}, t)$  as

$$P(\mathbf{r}, t) = e^{2R(\mathbf{r}, t)}, \quad (2.90)$$

then the osmotic velocity (2.85) is given by

$$\mathbf{u}(\mathbf{r}, t) = b^2 \nabla R(\mathbf{r}, t). \quad (2.91)$$

Similarly, the velocity field can also be defined in terms of the gradient of another scalar field  $S(\mathbf{r}, t)$ ,

$$\mathbf{v}(\mathbf{r}, t) = \frac{\nabla S(\mathbf{r}, t)}{m}. \quad (2.92)$$



As it can be noticed (see [Chap. 1](#)), this equation is analogous to the corresponding one for (classical) conservative systems, which establishes a relationship between the particle velocity and its associated action. Taking this into account, [\(2.84\)](#) and [\(2.89\)](#) can also be rewritten as

$$\frac{\partial R}{\partial t} + \frac{\nabla^2 S}{2m} + \frac{1}{m} \nabla R \cdot \nabla S = 0, \quad (2.93a)$$

$$\frac{\partial S}{\partial t} + \frac{(\nabla S)^2}{2m} + V - \frac{mb^4}{2} [(\nabla R)^2 + \nabla^2 R] = 0. \quad (2.93b)$$

The fields  $R$  and  $S$  can be determined except for a time-dependent phase. Equations [\(2.93\)](#) can be regarded as the hydrodynamic formulation of Newtonian mechanics and constitute respectively the stochastic mechanic counterpart of the classical continuity and Hamilton–Jacobi equations seen in [Chap. 1](#). Note that [\(2.93b\)](#) reduces to the classical Hamilton–Jacobi equation [\(1.15\)](#) for  $b = 0$ . Furthermore, it is worth stressing that, within this framework, a conservative diffusion process has been generated. As will be seen in [Chap. 6](#), similar coupled equations are also found in Bohmian mechanics.

## References

1. Razavy, M.: *Classical and Quantum Dissipative Systems*. Imperial College Press, London (2005)
2. Hänggi, P., Jung, P.: Colored noise in dynamical systems. *Adv. Chem. Phys.* **89**, 239–326 (1995)
3. Kubo, R., Toda, M., Hashitsume, N.: *Statistical Physics II. Nonequilibrium Statistical Mechanics*. Springer-Verlag, Berlin (1985)
4. Hansen, J.P., McDonald, I.R.: *Theory of Simple Liquids*. Academic Press, New York (1986)
5. Boon, J.P., Yip, S.: *Molecular Hydrodynamics*. Dover, New York (1991)
6. McQuarrie, D.A.: *Statistical Mechanics*. Harper and Row, New York (1976)
7. Lichtenberg, A.J., Lieberman, M.A.: *Regular and Chaotic Dynamics*, 2nd edn. Springer-Verlag, New York (1992)
8. Goldstein, H.: *Classical Mechanics*. Addison–Wesley Publishing Company, Reading, MA (1980)
9. Caldirola, P.: Forze non conservative nella meccanica quantistica. *Nuovo Cimento* **18**, 393–400 (1941)
10. Kanai, E.: On the quantization of the dissipative systems. *Prog. Theor. Phys.* **3**, 440–442 (1948)
11. Dekker, H.: Classical and quantum mechanics of the damped harmonic oscillator. *Phys. Rep.* **80**, 1–110 (1981)
12. Morse, P.M., Feshbach, H.: *Methods of Theoretical Physics*. McGraw-Hill, New York (1953)
13. Bateman, H.: On dissipative systems and related variational principles. *Phys. Rev.* **38**, 815–819 (1931)
14. Ullersma, P.: An exactly solvable model for Brownian motion: I Derivation of the Langevin equation. *Physica (Utrecht)* **32**, 27–55 (1966)
15. Ullersma, P.: An exactly solvable model for Brownian motion: II Derivation of the Langevin equation. *Physica (Utrecht)* **32**, 56–73 (1966)

16. Ullersma, P.: An exactly solvable model for Brownian motion: III Motion of a heavy mass in a linear chain. *Physica (Utrecht)* **32**, 74–89 (1966)
17. Ullersma, P.: An exactly solvable model for Brownian motion: IV Susceptibility and Nyquist's theorem. *Physica (Utrecht)* **32**, 90–96 (1966)
18. Frenkel, D., Smit, B.: *Understanding Molecular Simulation: From Algorithms to Applications*. Academic Press, New York (2002)
19. van Kampen, N.G.: *Stochastic Processes in Physics and Chemistry*. North-Holland, Amsterdam (1981)
20. Gardiner, C.W.: *Handbook of Stochastic Methods*. Springer-Verlag, Berlin (1983)
21. Risken, R.: *The Fokker–Planck Equation*. Springer-Verlag, Berlin (1984)
22. Pathria, R.K.: *Statistical Mechanics*. Pergamon Press, Oxford (1972)
23. Weiss, U.: *Quantum Dissipative Systems*. World Scientific, Singapore (1999)
24. Horsthemke, W., Lefever, R.: *Noise-Induced Transition*. Springer-Verlag, Berlin (1984)
25. Ingen-Housz, J.: *Vermischte Schriften physisch-medizinischen Inhalts*, vol. 2, pp. 123–126. Wappler, Vienna (1784)
26. Bywater, J.: *Physiological Fragments: To Which are Added Supplementary Observations, to Shew That Vital Energies are of the Same Nature, and Both Derived From Solar Light*, pp. 127–128. R. Hunter, London (1824)
27. Brow, R.: A brief account of microscopical observations made in the months of June, July and August 1827, on the particles contained in the poller of plants; and on the general existence of active molecules in organic and inorganic bodies. *Phys. Mag.* **4**, 161–173 (1828)
28. Brown, R.: Additional remarks on active molecules. *Phys. Mag.* **6**, 161–166 (1829)
29. Lauritzen, S.L.: *Thiele: Pioneer in Statistics*. Oxford University Press, Oxford (2002)
30. Bachelier, L.: *Théorie de la Spéculation*, *Annales Scientifiques de l'École Normale Supérieure*, vol. 3, pp. 21–86 (1900). Translated into English by Davis, M. Etheridge, A.: *Louis Bachelier's Theory of Speculation: The Origins of Modern Finance*. Princeton University Press, Princeton (2006)
31. Einstein, A.: Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. *Ann. Physik* **17**, 549–560 (1905)
32. Einstein, A.: *Investigations on the Theory of Brownian Movement*. Dover, New York (1956)
33. Smoluchowski, M.: Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen. *Ann. Physik* **21**, 756–780 (1906)
34. Langevin, P.: Sur la théorie du mouvement brownien. *Comptes Rendus* **146**, 530–532 (1908)
35. Wiener, N.: The average of an analytical functional and the Brownian movement. *Proc. Nat. Acad. Sci. U. S. A.* **7**, 294–298 (1921)
36. Wolfgang, P., Baschnagel, J.: *Stochastic Processes. From Physics to Finance*. Springer-Verlag, Berlin (1999)
37. Metzler, R., Klafter, J.: The random walk's guide to anomalous diffusion: a fractional dynamics approach. *Phys. Rep.* **339**, 1–77 (2000)
38. Lovesey, S.W.: *Theory of Neutron Scattering From Condensed Matter*. Clarendon Press, Oxford (1984)
39. Fokker, A.D.: Die mittlere Energie rotierender elektrischer Dipole im Strahlungsfeld. *Ann. Physik* **43**, 810–820 (1914)
40. Planck, M.: Über einen Satz der statistischen Dynamik und eine Erweiterung in der Quantumtheorie. *Sitzb. Akad. Berlin*, pp. 324–341 (1917)
41. Kolmogorov, A.N.: Über die analytischen Methoden in der Wahrscheinlichkeitsrechnung. *Math. Ann.* **104**, 415–458 (1931)
42. Kramers, H.A.: Brownian motion in a field of force and the diffusion model of chemical reactions. *Physica* **8**, 284–304 (1940)
43. Chandrasekhar, S.: Stochastic problems in physics and astronomy. *Rev. Mod. Phys.* **15**, 1–89 (1943)
44. Balazs, N.L.: On the quantum-mechanical Fokker–Planck and Kramers–Chandrasekhar equation. *Physica* **94A**, 181–191 (1978)

45. Hänggi, P., Talkner, P., Borkovec, M.: Reaction-rate theory: fifty years after Kramers. *Rev. Mod. Phys.* **62**, 251–341 (1990)
46. Pollak, E.: Theory of activated rate processes: a new derivation of Kramers' expression. *J. Chem. Phys.* **85**, 865–867 (1986)
47. Pollak, E., Grabert, H., Hänggi, P.: Theory of activated rate processes for arbitrary frequency dependent friction: solution of the turnover problem. *J. Chem. Phys.* **91**, 4073–4087 (1989)
48. Georgievskii, Y., Pollak, E.: Semiclassical theory of activated diffusion. *Phys. Rev. E* **49**, 5098–5102 (1994)
49. Mel'nikov, V.I., Meshkov, S.V.: Theory of activated rate processes: exact solution of the Kramers problem. *J. Chem. Phys.* **85**, 1018–1027 (1986)
50. Mel'nikov, V.I.: The Kramers problem: Fifty years of development. *Phys. Rep.* **209**, 1–71 (1991)
51. Vega, J.L., Guantes, R., Miret-Artés, S.: Mean first passage time and the Kramers turnover theory in activated atom-surface diffusion. *Phys. Chem. Chem. Phys.* **4**, 4985–4991 (2002)
52. Guantes, R., Vega, J.L., Miret-Artés, S., Pollak, E.: Kramers' turnover theory for diffusion of Na atoms on a Cu(001) surface measured by He scattering. *J. Chem. Phys.* **119**, 2780–2791 (2003)
53. Miret-Artés, S., Pollak, E.: The dynamics of activated surface diffusion. *J. Phys.: Condens. Matter* **17**, S4133–S4150 (2005)
54. Caldeira, A.O., Leggett, A.J.: Quantum tunneling in a dissipative system. *Ann. Phys.* **149**, 374–456 (1983)
55. Pollak, E., Miret-Artés, S.: Classical theory of atom surface scattering. The rainbow effect. *Surf. Sci. Rep.* (2012, to appear)
56. Moix, J.M., Pollak, E., Miret-Artés, S.: Friction-induced energy-loss rainbows in atom surface scattering. *Phys. Rev. Lett.* **104**, 116103(1–4) (2010)
57. Nelson, E.: Derivation of the Schrödinger equation from Newtonian mechanics. *Phys. Rev.* **150**, 1079–1085 (1966)
58. Bohm, D., Hiley, B.J.: Non-locality and locality in the stochastic interpretation of quantum mechanics. *Phys. Rep.* **172**, 93–122 (1989)

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