4

Langevin Molecular Dynamics

4.1 Introduction

In this chapter, we describe one of the simplest, but nevertheless robust, method for simulating a given number N_p of classical particles in a finite volume Ω for a temperature T, namely for computing physical quantities in the so-called *NVT* ensemble (Allen and Tildesley, 1987; Tuckerman, 2010). This is obtained by means of the *first-order* Langevin dynamics, which is defined by the solution of a set of stochastic differential equations:

$$\frac{d\mathbf{R}(t)}{dt} = \mathbf{f}[\mathbf{R}(t)] + \boldsymbol{\eta}(t), \tag{4.1}$$

where $\mathbf{R}(t)$ is a (time dependent) D dimensional vector with components R_α ($\alpha = 1, \ldots, D$, with $D = N_p \times d$, d being the spatial dimensionality). In other words, this D-dimensional vector is a concise notation for the positions of all the particles interacting via a classical potential $V(\mathbf{R})$, which defines the deterministic "force" with components $f_\alpha(\mathbf{R})$:

$$f_\alpha(\mathbf{R}) = -\frac{\partial V(\mathbf{R})}{\partial R_\alpha}; \tag{4.2}$$

finally, $\boldsymbol{\eta}(t)$ is a random vector with components $\eta_\alpha(t)$ ($\alpha = 1, \ldots, D$) that represents a random noise with a vanishing mean value and no correlations between components $\alpha \neq \beta$ and times $t \neq t'$, i.e., it is a so-called *white noise*:

$$\langle \eta_\alpha(t) \rangle = 0, \tag{4.3}$$

$$\langle \eta_\alpha(t)\eta_\beta(t') \rangle = 2T\delta_{\alpha,\beta}\delta(t - t'), \tag{4.4}$$

where $\langle \ldots \rangle$ indicates the expectation value. We would like to emphasize that the first-order Langevin equations (4.1) are substantially different from the Newton equation of motions, which are *second-order* (deterministic) differential equations connecting the actual force to the acceleration of the particles. The dynamics that

is generated by the Newton equations may be used to simulate a set of classical particles in a finite volume Ω at fixed energy E, namely within the so-called *NVE* ensemble (Allen and Tildesley, 1987; Tuckerman, 2010). From one side, the first-order Langevin equations can be seen as an *ad hoc* approach to generate configurations that are equilibrated according to the Boltzmann distribution (see below). On the other side, they can be obtained from a coarse-grained description of the Brownian motion; here, a small grain with mass m in a fluid experiences, besides an external force $\mathbf{f}(\mathbf{R})$, a friction force with coefficient γ and a random force, which is due to random density fluctuations in the fluid. This approach leads to the *second-order* Langevin dynamics:

$$m\frac{d\mathbf{V}(t)}{dt} = \mathbf{f}[\mathbf{R}(t)] - \gamma\mathbf{V}(t) + \boldsymbol{\eta}(t), \tag{4.5}$$

$$\frac{d\mathbf{R}(t)}{dt} = \mathbf{V}(t). \tag{4.6}$$

Then, the first-order Langevin equations are obtained in the limit of $m \to 0$ (in this limit, γ just sets the time scale). Usually, this limit is called *over-damped* regime of the second-order Langevin dynamics.

Contrary to ordinary differential equations, the stochastic differential equations do not provide a unique solution starting from a given initial condition, but the possible solutions acquire a statistical meaning: starting at $t = t_0$ from $\mathbf{R}_0 \equiv \mathbf{R}(t_0)$, several stochastic trajectories are possible depending on the particular realization of the noise. Thus, a meaningful quantity that is defined is the probability $\mathcal{P}(\mathbf{R}, t)$ to find a given configuration $\mathbf{R}$ at time t, with the initial condition:

$$\mathcal{P}(\mathbf{R}, t_0) = \delta(\mathbf{R} - \mathbf{R}_0). \tag{4.7}$$

In the following, we will show that, after an equilibration time, $\mathcal{P}(\mathbf{R}, t)$ converges to an equilibrium distribution that is independent from the initial condition $\mathbf{R}_0$. In particular, the equilibrium probability is given by the Boltzmann distribution:

$$\mathcal{P}_{\text{eq}}(\mathbf{R}) = \frac{1}{\mathcal{Z}} \exp\left[-\frac{V(\mathbf{R})}{T}\right], \tag{4.8}$$

where $\mathcal{Z}$ is the partition function, needed for the normalization condition of the probability:

$$\mathcal{Z} = \int d\mathbf{R} \exp\left[-\frac{V(\mathbf{R})}{T}\right]. \tag{4.9}$$

Then, the solution of the differential equations (4.1) can be used to sample a large number N of configurations $\mathbf{R}_n$ at discrete times t_n to represent the canonical distribution $\mathcal{P}_{\text{eq}}(\mathbf{R})$, which allows us to compute any correlation function $\mathcal{O}(\mathbf{R})$:

$$\int d\mathbf{R} \, \mathcal{O}(\mathbf{R}) \, \mathcal{P}_{\text{eq}}(\mathbf{R}) \approx \frac{1}{N} \sum_n \mathcal{O}(\mathbf{R}_n) \tag{4.10}$$

similarly to the ordinary Monte Carlo method discussed in section 3.1.

For a given system, there is no general rule telling whether it is more convenient to work with molecular dynamics or Monte Carlo approaches. However, in some cases, molecular dynamics represents the best choice. For example, in several *ab-initio* methods, the classical potential $V(\mathbf{R})$ is not given by a simple form, but it is the result of complicated algorithms (e.g., when it represents the ion-ion interaction that comes from a density-functional theory in the Born-Oppenheimer approximation). Here, a similar amount of computer time is taken to compute all components of the forces or to employ a single calculation of the energy necessary for a Metropolis acceptance step. In such a situation molecular dynamics is typically more convenient than Monte Carlo, because with the same computational effort all the positions of the atoms are changed at once. Moreover, it is not necessary to employ local moves limited to a single or a few atoms to remain with a good acceptance rate. By contrast, the advantage of the Monte Carlo method is that there is no other bias than the statistical one, whereas in molecular dynamics it is always necessary to introduce a time discretization, which implies a systematic, but controllable, error (as we will discuss in the following).

4.2 Discrete-Time Langevin Dynamics

In a computer simulation, a time discretization is necessary to obtain the solution of differential equations. Therefore, in order to define an appropriate algorithm for the simulation of classical particles at finite temperature, we integrate both sides of Eq. (4.1) over a finite interval (t_n, t_{n+1}), where $t_n = t_0 + \Delta n$ are discretized times (t_0 is the initial time and Δ represents the discrete time step). In this way, we obtain (at the lowest-order approximation in Δ):

$$\mathbf{R}_{n+1} - \mathbf{R}_n = \int_{t_n}^{t_{n+1}} dt \, \{\mathbf{f}[\mathbf{R}(t)] + \boldsymbol{\eta}(t)\} = \Delta \mathbf{f}_n + \int_{t_n}^{t_{n+1}} dt \, \boldsymbol{\eta}(t), \tag{4.11}$$

where $\mathbf{R}_n = \mathbf{R}(t_n)$ and $\mathbf{f}_n = \mathbf{f}[\mathbf{R}(t_n)]$; here, we have approximated the integral of the force in this interval with the lowest-order approximation $\Delta \mathbf{f}_n$, because the force is approximately constant within the small time interval, see Eqs. (4.15) and (4.16). Notice that this is the only approximation done in the above integrations. The time-integral in the r.h.s. of Eq. (4.11) can be estimated by noticing that a sum of many random variables (and, therefore, also an integral) is a Gaussian random number (see section 2.7). In particular, by introducing a random vector $\mathbf{z}_n$, which is normally (Gaussian) distributed with zero mean and unit variance, we have:

$$\int_{t_n}^{t_{n+1}} dt\, \boldsymbol{\eta}(t) = \sqrt{2T\Delta}\, \mathbf{z}_n, \tag{4.12}$$

where the coefficient in the r.h.s. gives the correct variance of the integral:

$$\langle z_{\alpha,n} z_{\beta,n} \rangle = \frac{1}{2T\Delta} \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t_{n+1}} dt'\, \langle \eta_\alpha(t) \eta_\beta(t') \rangle = \frac{\delta_{\alpha,\beta}}{\Delta} \int_{t_n}^{t_{n+1}} dt = \delta_{\alpha,\beta}, \tag{4.13}$$

where we have used Eq. (4.4). Moreover, we have that $\langle z_{\alpha,n} z_{\beta,m} \rangle = 0$ for $n \neq m$, since the integrand is always zero in such cases.

By collecting all these results, we can write down the final expression for the discretized-time Langevin equation:

$$\mathbf{R}_{n+1} = \mathbf{R}_n + \Delta \mathbf{f}_n + \sqrt{2T\Delta}\, \mathbf{z}_n, \tag{4.14}$$

which defines an iteration scheme that gives the new coordinates $\mathbf{R}_{n+1}$, at time t_{n+1}, in terms of the old ones $\mathbf{R}_n$, at time t_n, the discretized force $\mathbf{f}_n$, and a set of Gaussian variables $\mathbf{z}_n$. This iteration represents just a Markov process, which can be implemented by a simple iterative algorithm, since it is only required to have an algorithm that evaluates the force for any given positions $\mathbf{R}_n$ of the N classical particles. It is important to emphasize that, for $\Delta \to 0$, the noise (which is proportional to $\sqrt{\Delta}$) dominates over the deterministic force (which is linear in Δ). Notice that the presence of the noisy term $\boldsymbol{\eta}(t)$ makes the solution of the Langevin equation non-continuous and non-differentiable, since:

$$\frac{\mathbf{R}_{n+1} - \mathbf{R}_n}{\Delta} = O\left(\frac{1}{\sqrt{\Delta}}\right), \tag{4.15}$$

which justifies the approximation in the integral of the deterministic force in Eq. (4.11):

$$\int_{t_n}^{t_{n+1}} dt\, \mathbf{f}[\mathbf{R}(t)] = \Delta \mathbf{f}_n + O(\Delta^{3/2}). \tag{4.16}$$

As a consequence of Eq. (4.15), the actual trajectory for $\Delta \to 0$ is not defined. Nevertheless, we will show that the time discretization of Eq. (4.14) allows us to determine the evolution of the probability distribution $\mathcal{P}(\mathbf{R}, t)$ with no uncertainty in the limit $\Delta \to 0$. We finally mention that, in the limit of zero temperature $T = 0$, the noisy term disappears from the equations of motion and, therefore, the algorithm becomes deterministic. In particular, it turns into the steepest descent method (Press et al., 2007), yielding the minimum (or, more generally, a local minimum) of the potential $V(\mathbf{R})$ in a deterministic way for $n \to \infty$ and Δ small enough.

4.3 From the Langevin to the Fokker-Planck Equation

Here, we derive the Master equation for the discretized Langevin dynamics of Eq. (4.14) that defines the evolution of the probability $\mathcal{P}_n(\mathbf{R})$ of the classical variables $\mathbf{R}$ for a finite time step Δ. Most importantly, the limit $\Delta \to 0$ can be performed, leading to the so-called Fokker-Planck equation that represents the Master equation of the Langevin equation (4.1).

Since the discretized Langevin dynamics defines a Markov process, the probability $\mathcal{P}_n(\mathbf{R})$ is fully determined in terms of the conditional probability $K(\mathbf{R}'|\mathbf{R})$ associated to the Markov step:

$$\mathcal{P}_{n+1}(\mathbf{R}') = \int \mathbf{dR}\, K(\mathbf{R}'|\mathbf{R})\mathcal{P}_n(\mathbf{R}). \tag{4.17}$$

The conditional probability can be determined by noticing that, in Eq. (4.14), only the variable $\mathbf{z}_n$ is stochastic, while the force is fully deterministic. Therefore, given $\mathbf{R}$, the new variable $\mathbf{R}'$ is given by the deterministic part $\mathbf{R} + \Delta\mathbf{f}(\mathbf{R})$ plus a random noise that is normally distributed with zero mean and variance equal to $2T\Delta$. Then:

$$K(\mathbf{R}'|\mathbf{R}) = \prod_\alpha \int \frac{dz_\alpha}{\sqrt{2\pi}} e^{-z_\alpha^2/2} \delta\left(R'_\alpha - R_\alpha - \Delta f_\alpha - \sqrt{2T\Delta}z_\alpha\right), \tag{4.18}$$

which is clearly normalized with $\int \mathbf{dR}'K(\mathbf{R}'|\mathbf{R}) = 1$. By replacing this form of the conditional probability in the Master equation, we obtain:

$$\mathcal{P}_{n+1}(\mathbf{R}') = \prod_\alpha \int \frac{dz_\alpha}{\sqrt{2\pi}} e^{-z_\alpha^2/2} \int dR_\alpha \delta\left(R'_\alpha - R_\alpha - \Delta f_\alpha - \sqrt{2T\Delta}z_\alpha\right) \mathcal{P}_n(\mathbf{R}). \tag{4.19}$$

Now, we carry out the integral over the R_α's. Thus, we are led to find the zeros of the argument of the δ-function in Eq. (4.19), for fixed $\mathbf{R}'$ and $\mathbf{z}$:

$$\mathbf{R}' - \mathbf{R} - \Delta\mathbf{f}(\mathbf{R}) - \sqrt{2T\Delta}\,\mathbf{z} = 0, \tag{4.20}$$

which represents a set of D non-linear equations in D unknown (the R_α's). This problem is apparently difficult to solve; however, the solution can be found by performing a systematic expansion for small Δ:

$$\mathbf{R} = \mathbf{R}' - \sqrt{2T\Delta}\,\mathbf{z} - \Delta\mathbf{f}(\mathbf{R}') + O\left(\Delta^{3/2}\right). \tag{4.21}$$

In this way, we can carry out the integration over the R_α's in the Master equation (4.19) and obtain:

$$\mathcal{P}_{n+1}(\mathbf{R}') = \prod_\alpha \int \frac{dz_\alpha}{\sqrt{2\pi}} \frac{e^{-z_\alpha^2/2}}{|1 + \Delta f'_\alpha(\mathbf{R}')|} \mathcal{P}_n(\mathbf{R}' - \Delta\mathbf{f}(\mathbf{R}') - \sqrt{2T\Delta}\,\mathbf{z}), \tag{4.22}$$

where $f'_\alpha(\mathbf{R}') = \partial f_\alpha / \partial R'_\alpha$, computed in $\mathbf{R}'$; this relation is valid up to order $O(\Delta^{3/2})$. By further expanding it to leading order in Δ, we get:

$$\mathcal{P}_{n+1}(\mathbf{R}') = \prod_\alpha \int \frac{dz_\alpha}{\sqrt{2\pi}} e^{-z_\alpha^2/2} \left[1 - \Delta \sum_\beta \frac{\partial f_\beta(\mathbf{R}')}{\partial R'_\beta} \right]$$
$$\times \mathcal{P}_n(\mathbf{R}' - \Delta \mathbf{f}(\mathbf{R}') - \sqrt{2T\Delta}\,\mathbf{z}); \qquad (4.23)$$

finally, we can expand the probability distribution:

$$\mathcal{P}_n(\mathbf{R}' - \Delta\mathbf{f}(\mathbf{R}') - \sqrt{2T\Delta}\mathbf{z}) \approx \mathcal{P}_n(\mathbf{R}')$$
$$- \sum_\beta \left[\Delta f_\beta(\mathbf{R}') + \sqrt{2T\Delta}z_\beta \right] \frac{\partial \mathcal{P}_n(\mathbf{R}')}{\partial R'_\beta} + T\Delta \sum_{\alpha,\beta} z_\alpha z_\beta \frac{\partial^2 \mathcal{P}_n(\mathbf{R}')}{\partial R'_\alpha \partial R'_\beta}. \qquad (4.24)$$

In principle, the validity of the Taylor expansion is not justified for large values of z_α, however, this is not a problem because all the integrals in $\{z_\alpha\}$ are dominated in the region where $|z_\alpha| < 1$. By substituting the above expansion in Eq. (4.23) and carrying out the Gaussian integrations over $\{z_\alpha\}$, we get (changing $\mathbf{R}' \to \mathbf{R}$):

$$\mathcal{P}_{n+1}(\mathbf{R}) = \mathcal{P}_n(\mathbf{R}) + \Delta \sum_\alpha \left[T\frac{\partial^2 \mathcal{P}_n(\mathbf{R})}{\partial R_\alpha^2} - \frac{\partial f_\alpha(\mathbf{R})}{\partial R_\alpha}\mathcal{P}_n(\mathbf{R}) - f_\alpha(\mathbf{R})\frac{\partial \mathcal{P}_n(\mathbf{R})}{\partial R_\alpha} \right]. \qquad (4.25)$$

Now, the limit $\Delta \to 0$ can be obtained. Indeed, for small values of Δ:

$$\mathcal{P}_{n+1}(\mathbf{R}) - \mathcal{P}_n(\mathbf{R}) \approx \Delta \frac{\partial \mathcal{P}(\mathbf{R},t)}{\partial t}, \qquad (4.26)$$

which brings us to the Fokker-Planck equation for the probability density $\mathcal{P}(\mathbf{R},t)$:

$$\frac{\partial \mathcal{P}(\mathbf{R},t)}{\partial t} = T \sum_\alpha \frac{\partial^2 \mathcal{P}(\mathbf{R},t)}{\partial R_\alpha^2} - \sum_\alpha \frac{\partial}{\partial R_\alpha} \left[\mathcal{P}(\mathbf{R},t)f_\alpha(\mathbf{R}) \right]. \qquad (4.27)$$

It is easy to show that the Boltzmann distribution of Eq. (4.8) is a stationary solution of the Fokker-Planck equation; indeed, we can rewrite Eq. (4.27) as:

$$\frac{\partial \mathcal{P}(\mathbf{R},t)}{\partial t} = \sum_\alpha \frac{\partial}{\partial R_\alpha} \left[T\frac{\partial \mathcal{P}(\mathbf{R},t)}{\partial R_\alpha} - \mathcal{P}(\mathbf{R},t)f_\alpha(\mathbf{R}) \right], \qquad (4.28)$$

whose r.h.s. is vanishing for the Boltzmann distribution. Another important property of the Fokker-Planck equation is that the r.h.s. is a total divergence. This

is just the consequence that the normalization of the probability $\int \mathbf{dR}\, \mathcal{P}(\mathbf{R}, t) = N(t) = 1$, which represents a constant of motion of the equation. Indeed, by integrating both sides of the equation over a given volume and applying the Gauss theorem for the r.h.s., we get:

$$\frac{\partial N(t)}{\partial t} = \int \mathbf{dS}\, \mathbf{A}(\mathbf{R}, t) \cdot \mathbf{n}(\mathbf{R}), \tag{4.29}$$

where

$$A_\alpha(\mathbf{R}, t) = T\frac{\partial \mathcal{P}(\mathbf{R}, t)}{\partial R_\alpha} - \mathcal{P}(\mathbf{R}, t) f_\alpha(\mathbf{R}), \tag{4.30}$$

and $\mathbf{n}(\mathbf{R})$ is the unit vector perpendicular to the surface $\mathbf{S}$. Then, $\mathbf{A}(\mathbf{R}, t)$ vanishes at infinity (since the probability vanishes at infinity), implying that $N(t)$ is independent from t.

4.4 Fokker-Planck Equation and Quantum Mechanics

Here, we show how the Fokker-Planck equation allows us to compute the probability $\mathcal{P}(\mathbf{R}, t)$ at any given time, once the initial condition $\mathcal{P}(\mathbf{R}, t_0)$ is given. Moreover, we also show that $\mathcal{P}(\mathbf{R}, t)$ approaches the equilibrium distribution for large time t in an exponential way, starting from any initial probability.

There is a deep relationship between the Fokker-Planck equation and the Schrödinger equation in imaginary time (Nelson, 1966; Parisi and Wu, 1981). This is obtained by writing the solution of Eq. (4.27) in the following way:

$$\mathcal{P}(\mathbf{R}, t) = \Upsilon_0(\mathbf{R})\Phi(\mathbf{R}, t) \tag{4.31}$$

where $\Upsilon_0(\mathbf{R}) = \sqrt{\mathcal{P}_{\text{eq}}(\mathbf{R})}$ represents a normalized quantum state:

$$\int \mathbf{dR}\, \Upsilon_0^2(\mathbf{R}) = 1. \tag{4.32}$$

By substituting the above definition of $\mathcal{P}(\mathbf{R}, t)$ into the Fokker-Planck equation (4.27), we obtain that $\Phi(\mathbf{R}, t)$ satisfies the Schrödinger equation in imaginary time:

$$-\frac{\partial \Phi(\mathbf{R}, t)}{\partial t} = \mathcal{H}_{\text{eff}}\Phi(\mathbf{R}, t), \tag{4.33}$$

where $\mathcal{H}_{\text{eff}}$ is an effective Hamiltonian given by:

$$\mathcal{H}_{\text{eff}} = -T\sum_\alpha \frac{\partial^2}{\partial R_\alpha^2} + V_{\text{eff}}(\mathbf{R}); \tag{4.34}$$

here, the inverse (classical) temperature plays the role of the mass of the particles. Moreover, $V_{\text{eff}}(\mathbf{R})$ is an effective potential that depends upon the classical potential $V(\mathbf{R})$:

$$V_{\text{eff}}(\mathbf{R}) = \frac{1}{2} \sum_{\alpha} \left\{ \frac{1}{2T} \left[\frac{\partial V(\mathbf{R})}{\partial R_\alpha} \right]^2 - \frac{\partial^2 V(\mathbf{R})}{\partial R_\alpha^2} \right\}. \tag{4.35}$$

Notice that, in the limit of zero temperature, the minima of the original potential $V(\mathbf{R})$ are also minima of $V_{\text{eff}}(\mathbf{R})$; indeed, the first term of the above equation (which dominates for $T \to 0$) vanishes at the minima of the original potential $V(\mathbf{R})$. The effective potential can be rewritten as:

$$V_{\text{eff}}(\mathbf{R}) = \frac{T}{\Upsilon_0(\mathbf{R})} \sum_{\alpha} \frac{\partial^2 \Upsilon_0(\mathbf{R})}{\partial R_\alpha^2}. \tag{4.36}$$

Now, $\Upsilon_0(\mathbf{R})$ is an eigenstate of $\mathcal{H}_{\text{eff}}$, as verified by a direct inspection of Eqs. (4.34) and (4.36), with energy $E_0 = 0$. Since it has no nodes (e.g., $\mathcal{P}_{\text{eq}}(\mathbf{R})$ is positive for all the configurations $\mathbf{R}$), it is also the actual ground state of the effective Hamiltonian. Then, the solution of the Schrödinger equation, and the corresponding Fokker-Planck equation, can be formally given in closed form by expanding the initial condition in terms of the eigenstates $\Upsilon_n(\mathbf{R})$ of $\mathcal{H}_{\text{eff}}$:

$$\mathcal{P}(\mathbf{R}, t_0) = \Upsilon_0(\mathbf{R}) \sum_n a_n \Upsilon_n(\mathbf{R}), \tag{4.37}$$

where

$$a_n = \int d\mathbf{R} \, \frac{\Upsilon_n(\mathbf{R})}{\Upsilon_0(\mathbf{R})} \mathcal{P}(\mathbf{R}, t_0), \tag{4.38}$$

which implies that $a_0 = 1$ from the normalization condition on $\mathcal{P}(\mathbf{R}, t_0)$. We thus obtain the full evolution of the probability $\mathcal{P}(\mathbf{R}, t)$ as:

$$\mathcal{P}(\mathbf{R}, t) = \Upsilon_0(\mathbf{R}) \sum_n a_n e^{-E_n t} \Upsilon_n(\mathbf{R}). \tag{4.39}$$

Therefore, for large times t, $\mathcal{P}(\mathbf{R}, t)$ converges *exponentially* to the stationary equilibrium distribution $\Upsilon_0^2(\mathbf{R}) = \mathcal{P}_{\text{eq}}(\mathbf{R})$. The characteristic time τ for equilibration is given by the inverse gap to the first excitation, i.e., $\tau = 1/E_1$.

Let us finish this section by showing that the evolution generated by the Fokker-Planck equation satisfies the detailed balance condition. The formal solution of the Schrödinger equation is given by:

$$\Phi(\mathbf{R}', t) = \int d\mathbf{R} \, \langle \mathbf{R}' | e^{-\mathcal{H}_{\text{eff}} t} | \mathbf{R} \rangle \, \Phi(\mathbf{R}, 0). \tag{4.40}$$

Therefore, by using Eq. (4.31), the evolution of the probability density can be written as:

$$\mathcal{P}(\mathbf{R}', t) = \int d\mathbf{R}\, K_t(\mathbf{R}'|\mathbf{R})\mathcal{P}(\mathbf{R}, 0)$$

$$= \int d\mathbf{R}\, \langle \mathbf{R}' | e^{-\mathcal{H}_{\text{eff}}t} | \mathbf{R} \rangle \sqrt{\frac{\mathcal{P}_{\text{eq}}(\mathbf{R}')}{\mathcal{P}_{\text{eq}}(\mathbf{R})}} \mathcal{P}(\mathbf{R}, 0), \qquad (4.41)$$

which implies that the conditional probability is given by:

$$K_t(\mathbf{R}'|\mathbf{R}) = \langle \mathbf{R}' | e^{-\mathcal{H}_{\text{eff}}t} | \mathbf{R} \rangle \sqrt{\frac{\mathcal{P}_{\text{eq}}(\mathbf{R}')}{\mathcal{P}_{\text{eq}}(\mathbf{R})}}. \qquad (4.42)$$

Since $\mathcal{H}_{\text{eff}}$ is symmetric, i.e., $\langle \mathbf{R}'|e^{-\mathcal{H}_{\text{eff}}t}|\mathbf{R}\rangle = \langle \mathbf{R}|e^{-\mathcal{H}_{\text{eff}}t}|\mathbf{R}'\rangle$, we have that:

$$\frac{K_t(\mathbf{R}'|\mathbf{R})}{K_t(\mathbf{R}|\mathbf{R}')} = \frac{\mathcal{P}_{\text{eq}}(\mathbf{R}')}{\mathcal{P}_{\text{eq}}(\mathbf{R})}, \qquad (4.43)$$

which shows that the detailed balance condition is indeed satisfied. We would like to emphasize that the time discretization introduces an error that spoils the detailed balance condition. In this sense, for any finite values of the discrete time step Δ, the equilibrium distribution is not given by the Boltzmann one (4.8), but reduces to it when $\Delta \to 0$.

4.4.1 Exact Solution for the Harmonic Case

To have some insight on how time discretization affects the dynamics, let us consider a generic quadratic potential of the type:

$$V(\mathbf{R}) = \frac{1}{2} \sum_{\alpha,\beta} K_{\alpha,\beta}(R_\alpha - R_{\text{eq},\alpha})(R_\beta - R_{\text{eq},\beta}), \qquad (4.44)$$

where $\mathbf{R}_{\text{eq}}$ are the equilibrium positions. The force-constant matrix $\mathbf{K}$ is symmetric and, therefore, can be diagonalized by a unitary matrix $\mathbf{U}$:

$$\bar{\mathbf{K}} = \mathbf{U}\mathbf{K}\mathbf{U}^\dagger, \qquad (4.45)$$

and its eigenvalues will be denoted by $\bar{K}_\alpha$, with $\bar{K}_1 \leq \bar{K}_2 \leq \cdots \leq \bar{K}_D$, i.e., the diagonal elements of the diagonal matrix $\bar{\mathbf{K}}$. The effective potential considered in Eq. (4.35) can be explicitly given in this case and the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ remains harmonic with:

$$V_{\text{eff}}(\mathbf{R}) = \frac{1}{2} \sum_{\alpha,\beta} K^{\text{eff}}_{\alpha,\beta}(R_\alpha - R_{\text{eq},\alpha})(R_\beta - R_{\text{eq},\beta}) - \frac{1}{2} \sum_\alpha K_{\alpha,\alpha}, \qquad (4.46)$$

where the effective harmonic coupling is:

$$K_{\alpha,\beta}^{\text{eff}} = \frac{1}{2T} \sum_{\gamma} K_{\alpha,\gamma} K_{\gamma,\beta} = \frac{1}{2T} \left[K^2 \right]_{\alpha,\beta}. \tag{4.47}$$

Since the effective Hamiltonian is quadratic, we obtain a harmonic problem with the above force-constant matrix and the mass $m = 1/2T$ for all degrees of freedom. Thus, according to standard calculations, the eigenvalues of the dynamical matrix $\mathbf{K}$ provide the eigenmodes of the harmonic problem (up to an energy shift):

$$E(\{n_\alpha\}) = \sum_{\alpha} \bar{K}_\alpha \left(n_\alpha + \frac{1}{2} \right) - \frac{1}{2} \sum_{\alpha} \bar{K}_\alpha = \sum_{\alpha} \bar{K}_\alpha n_\alpha, \tag{4.48}$$

where n_α are non-negative integers (the ground state corresponding to $n_\alpha = 0$ for all values of α). Here, we have used that the constant term in Eq. (4.46) is the trace of the matrix $\mathbf{K}$, which is the sum of its eigenvalues. The correlation time in this case can be explicitly given by:

$$\tau = \frac{1}{\bar{K}_1}, \tag{4.49}$$

where $\bar{K}_1$ is the minimum eigenvalue of the harmonic potential. Remarkably the correlation time τ does not depend on the temperature T.

The discretized version of the Langevin equation (4.14) can be solved explicitly in the harmonic case, as it will be explained in the following. In fact, by multiplying both sides of Eq. (4.14) by $\mathbf{U}$ and introducing normal-mode coordinates $\mathbf{Q} = \mathbf{U}(\mathbf{R} - \mathbf{R}_{\text{eq}})$, the discretized Langevin dynamics becomes:

$$Q_{\alpha,n+1} = \left(1 - \Delta \bar{K}_\alpha \right) Q_{\alpha,n} + \sqrt{2T\Delta} y_{\alpha,n}, \tag{4.50}$$

where $\mathbf{y}_n = \mathbf{U}\mathbf{z}_n$ are normal distributed random variables satisfying:

$$\langle y_{\alpha,n} y_{\beta,n} \rangle = \delta_{\alpha,\beta}. \tag{4.51}$$

Since normal modes do not couple, we can deal with each mode separately. The Master equation corresponding to Eq. (4.50) depends on the conditional probability $K(Q_\alpha'|Q_\alpha)$ that, in this case, can be explicitly derived:

$$K(Q_\alpha'|Q_\alpha) = \frac{1}{\sqrt{4\pi T\Delta}} \exp\left\{ -\frac{1}{4T\Delta} \left[Q_\alpha' - (1 - \Delta\bar{K}_\alpha)Q_\alpha \right]^2 \right\}. \tag{4.52}$$

Then, we have that the probability distribution:

$$\mathcal{P}_{\text{eq},\alpha}(Q_\alpha) = \frac{1}{\mathcal{Z}} \exp\left[-\frac{K_\alpha' Q_\alpha^2}{2T} \right], \tag{4.53}$$

with

$$K'_\alpha = \left(1 - \frac{\Delta \bar{K}_\alpha}{2}\right)\bar{K}_\alpha, \tag{4.54}$$

satisfies the detailed balance condition:

$$\frac{K(Q'_\alpha|Q_\alpha)}{K(Q_\alpha|Q'_\alpha)} = \frac{\mathcal{P}_{\text{eq},\alpha}(Q'_\alpha)}{\mathcal{P}_{\text{eq},\alpha}(Q_\alpha)}. \tag{4.55}$$

Indeed, by using Eq. (4.52), we find:

$$\frac{K(Q'_\alpha|Q_\alpha)}{K(Q_\alpha|Q'_\alpha)} = \exp\left\{\frac{1}{4T\Delta}\left[(\Delta\bar{K}_\alpha)^2 - 2\Delta\bar{K}_\alpha\right]\left[(Q'_\alpha)^2 - Q^2_\alpha\right]\right\}, \tag{4.56}$$

which is consistent with the distribution (4.53) with K'_α given by Eq. (4.54). Thus, collecting all modes together, the equilibrium distribution is given by:

$$\mathcal{P}_{\text{eq}}(Q_\alpha) = \frac{1}{\mathcal{Z}}\exp\left[-\frac{1}{2T}\sum_\alpha\left(1 - \frac{\Delta\bar{K}_\alpha}{2}\right)\bar{K}_\alpha Q^2_\alpha\right]. \tag{4.57}$$

An important remark about this result is that $\mathcal{P}_{\text{eq}}(Q_\alpha)$ is only defined when:

$$1 - \frac{\Delta\bar{K}_\alpha}{2} \geq 0, \tag{4.58}$$

for all α, otherwise the Langevin iteration will produce unbounded values of the coordinates Q_α. Therefore, we arrive to the condition that the time step Δ must satisfy the following condition:

$$\Delta < \frac{2}{\bar{K}_D}, \tag{4.59}$$

where $\bar{K}_D$ is the maximum eigenvalue of the force-constant matrix **K**. Indeed, this represents a very general result for the Langevin molecular dynamics, which is stable only for a small enough time step.

In summary, it is important to make the following remarks:

- The error in the discretization of the Langevin equation scales correctly to zero for $\Delta \to 0$ since the exact distribution is obtained in this limit as $K'_\alpha \to \bar{K}_\alpha$ for $\Delta \to 0$. Notice that the relative error in the determination of the equilibrium distribution, namely the error in the spring constant $\bar{K}_\alpha$, does not depend on the temperature T; therefore, the time step Δ can be kept independent from the temperature for given target accuracy.
- At finite values of Δ, the error in the discretization determines a (slightly) different equilibrium distribution that, however, remains of the same Gaussian form. Only for a single mode (i.e., for $D = 1$), this change can be interpreted as a renormalization of the effective temperature, $T \to T/(1 - \frac{\bar{K}_1\Delta}{2})$.

- The number of iterations n_{corr} that are needed to generate an independent configuration $\mathbf{R}'$ from a given one $\mathbf{R}$ is then given by:

$$n_{\text{corr}} = \frac{\tau}{\Delta} \geq \frac{\bar{K}_D}{\bar{K}_1} \equiv \bar{K}_{\text{cond}}, \tag{4.60}$$

where the correlation time τ is determined by Eq. (4.49) and $\bar{K}_{\text{cond}}$ is the *condition number* of the matrix $\mathbf{K}$, namely the ratio between its largest and smallest (non-zero) eigenvalues. Notice that, for the harmonic potential, n_{corr} does not depend on the temperature.

4.5 Accelerated Langevin Dynamics

When the condition number $\bar{K}_{\text{cond}}$ is large, the matrix is ill conditioned, implying that the number of iterations to generate a new independent configuration is extremely large. Therefore, the method is inefficient and some trick is necessary to speed up the algorithm (Parisi, 1984). One simple idea is to introduce in the Langevin equation (4.1) an acceleration matrix $\mathbf{S}$ such that:

$$\frac{d\mathbf{R}(t)}{dt} = \mathbf{S}^{-1}\mathbf{f}[\mathbf{R}(t)] + \boldsymbol{\eta}(t), \tag{4.61}$$

where the noise satisfies the following conditions:

$$\langle \eta_\alpha(t) \rangle = 0, \tag{4.62}$$
$$\langle \eta_\alpha(t)\eta_\beta(t') \rangle = 2TS^{-1}_{\alpha,\beta}\delta(t - t'). \tag{4.63}$$

The modified algorithm gives a substantial improvement with respect to the original one of Eqs. (4.1), (4.3), and (4.4) when $\mathbf{S}$ is chosen as close as possible to the Hessian matrix:

$$H_{\alpha,\beta}(\mathbf{R}) = \frac{1}{2}\frac{\partial^2 V(\mathbf{R})}{\partial R_\alpha \partial R_\beta}. \tag{4.64}$$

In the following, we consider the case in which the matrix $\mathbf{S}$ does not depend upon the coordinates $\{\mathbf{R}\}$, although a generalization in this sense is possible (Mazzola and Sorella, 2017). The advantage of considering the scheme of Eq. (4.61) can be understood by exploiting the limit of small temperatures. Indeed, for $T \to 0$, the standard Langevin equation (4.1) reduces to the steepest descent method that, starting from a given initial point $\mathbf{R}$, gives a practical way to find the closest minimum of the potential $V(\mathbf{R})$ (Press et al., 2007). The number of steps that are necessary to convergence is related to the condition number. Instead, by using the Newton-Raphson method, we can reach the target with one step in the harmonic case, no matter how large is the condition number. Therefore, by considering $\mathbf{S}$ that closely

approximates the Hessian matrix, the dynamics generated by Eq. (4.61) represents the generalization at finite temperatures of the Newton-Raphson approach, which minimizes the thermalization/correlation time.

Following the same steps as in section 4.2, we can arrive at the discretized version of the Langevin equation:

$$\mathbf{R}_{n+1} = \mathbf{R}_n + \Delta \mathbf{S}^{-1}\mathbf{f}_n + \sqrt{2T\Delta}\, \mathbf{z}_n, \tag{4.65}$$

with

$$\langle z_{\alpha,n} z_{\beta,n} \rangle = S_{\alpha,\beta}^{-1}. \tag{4.66}$$

The previous relations imply that the following modified Fokker-Planck equation holds in the limit $\Delta \to 0$:

$$\frac{\partial \mathcal{P}(\mathbf{R},t)}{\partial t} = \sum_\alpha \frac{\partial}{\partial R_\alpha} \left\{ \sum_\beta S_{\alpha,\beta}^{-1} \left[T \frac{\partial \mathcal{P}(\mathbf{R},t)}{\partial R_\beta} - \mathcal{P}(\mathbf{R},t) f_\beta(\mathbf{R}) \right] \right\}, \tag{4.67}$$

which has the same equilibrium distribution as before, i.e., the Boltzmann one given in Eq. (4.8).

The efficiency of this acceleration scheme can be appreciated by considering the harmonic case, which is a good approximation for low enough temperatures, where the thermal fluctuations are limited to configurations close to the minimum of the potential. In this case:

$$\mathbf{f}[\mathbf{R}(t)] = -\mathbf{K}[\mathbf{R}(t) - \mathbf{R}_{\text{eq}}]. \tag{4.68}$$

Hence, by choosing $\mathbf{S} = \mathbf{K}$, we get:

$$\mathbf{S}^{-1}\mathbf{f}_n = -(\mathbf{R}_n - \mathbf{R}_{\text{eq}}); \tag{4.69}$$

then, by taking $\Delta = 1$ (as in the Newton-Raphson method), Eq. (4.65) drastically simplifies into:

$$\mathbf{R}_{n+1} = \mathbf{R}_{\text{eq}} + \sqrt{2T}\, \mathbf{z}_n, \tag{4.70}$$

which represents a very efficient method for generating new configurations with very short correlation time, i.e., $n_{\text{corr}} = 1$; indeed, the above equation sets a new independent configuration according to:

$$\mathcal{P}_{\text{eq}}(\mathbf{R}) = \frac{1}{\mathcal{Z}} \exp\left[-\frac{1}{4T} \sum_{\alpha,\beta} K_{\alpha,\beta}(R_\alpha - R_{\text{eq},\alpha})(R_\beta - R_{\text{eq},\beta}) \right]; \tag{4.71}$$

notice that this equilibrium distribution corresponds to the correct (Gaussian) results for the harmonic potential of Eq. (4.44), apart from the presence of an extra
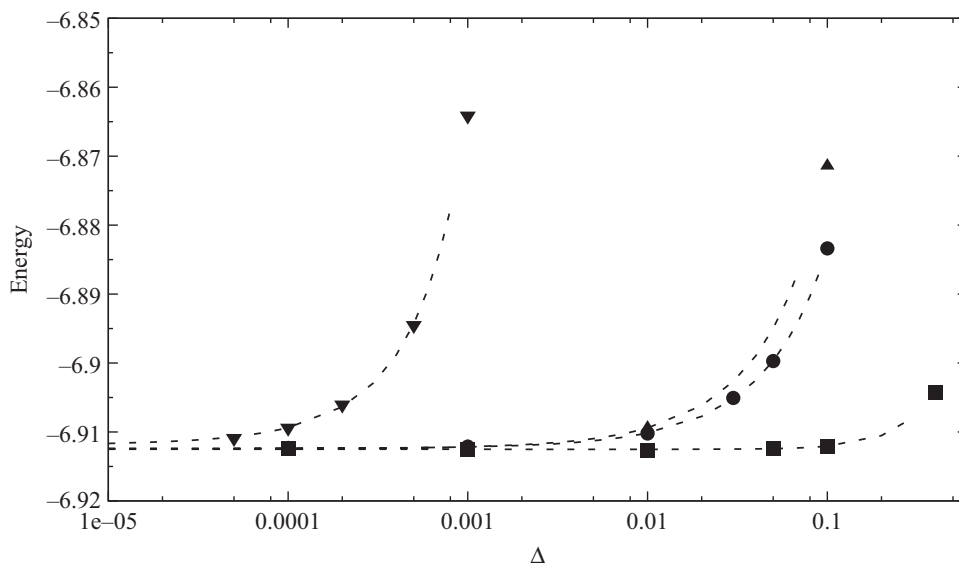
Figure 4.1 The convergence of the total energy as a function of the discretization step Δ that is used to integrate the Langevin equations is shown for a classical system with 64 particles interacting through a Lennard-Jones potential. The side of the cubic box is $L = 7.8$ and the temperature is $T = 0.4$. The standard scheme of Eq. (4.14) (downward triangles), the accelerated dynamics of Eq. (4.65) (upward triangles), and the one of Eq. (4.76) with $A = 1$ (full circles) and $A = 4$ (full squares) are reported.

factor 2 multiplying the temperature, which is due to the $\sqrt{2T}$ term in Eq. (4.70). This fact is a drawback of the approximation introduced by the time discretization. Nevertheless, for general cases, when the potential is not harmonic, this method is able to reduce substantially the correlation time and represents a very efficient and simple method that could be taken in mind before starting a molecular dynamics simulation with the first-order Langevin dynamics. An example of the accelerated Langevin dynamics for a classical systems of 64 particles, interacting through a Lennard-Jones potential, is reported in Fig. 4.1, for a sufficiently low temperature inside the solid phase.

An improvement in the discretization of the accelerated Langevin equation of Eq. (4.61) can be performed by assuming that the chosen acceleration matrix $\mathbf{S}$ gives a good approximation of the Hessian at equilibrium $\mathbf{K} \approx A\mathbf{S}$, apart from an overall constant A that can be empirically tuned to achieve the smallest possible error in the time discretization. Thus, we can consider that, even when the potential is not harmonic:

$$\mathbf{S}^{-1}\mathbf{f}[\mathbf{R}(t)] = -A\mathbf{R}(t) + \mathbf{C}[\mathbf{R}(t)], \tag{4.72}$$

where $\mathbf{C}[\mathbf{R}(t)]$ is weakly dependent on $\mathbf{R}(t)$, once we neglect non-harmonic contributions at equilibrium; then, a good approximation is given by taking $\mathbf{C}[\mathbf{R}(t)] = A\mathbf{R}_{eq}$. Therefore, we are led to consider:

$$\frac{d\mathbf{R}(t)}{dt} = -A[\mathbf{R}(t) - \mathbf{R}_{eq}] + \boldsymbol{\eta}(t). \tag{4.73}$$

Since this differential equation is linear, it can be integrated *exactly* (i.e., without any error in Δ) by considering the new variable $\mathbf{R}'(t)$, such that $\mathbf{R}(t) = \mathbf{X}(t)\mathbf{R}'(t)$, where $\mathbf{X}(t)$ is a suitable time-dependent matrix:

$$\frac{d\mathbf{X}(t)}{dt} = -A\mathbf{X}(t), \tag{4.74}$$

$$\mathbf{X}(t)\frac{d\mathbf{R}'(t)}{dt} = A\mathbf{R}_{eq} + \boldsymbol{\eta}(t). \tag{4.75}$$

Then, the result in the interval (t_n, t_{n+1}) is given by:

$$\mathbf{R}_{n+1} = \mathbf{R}_n - A\Delta_A(\mathbf{R}_n - \mathbf{R}_{eq}) + \sqrt{2\Delta_{2A}T}\,\mathbf{z}_n, \tag{4.76}$$

where

$$\Delta_A = \frac{1 - e^{-A\Delta}}{A}, \tag{4.77}$$

$$\langle z_{\alpha,n}z_{\beta,n}\rangle = S_{\alpha,\beta}^{-1}. \tag{4.78}$$

This scheme represents a more accurate integration of the accelerated dynamics, which for large values of Δ gives the exact dynamics of the harmonic potential of Eq. (4.44). Indeed, for $\Delta \to \infty$, we have:

$$\mathbf{R}_{n+1} = \mathbf{R}_{eq} + \sqrt{\frac{T}{A}}\,\mathbf{z}_n, \tag{4.79}$$

which leads to the correct Boltzmann distribution at temperature T (since $\langle z_{\alpha,n}z_{\beta,n}\rangle = AK_{\alpha,\beta}^{-1}$):

$$\mathcal{P}_{eq}(\mathbf{R}) = \frac{1}{\mathcal{Z}}\exp\left[-\frac{1}{2T}\sum_{\alpha,\beta}K_{\alpha,\beta}(R_\alpha - R_{eq,\alpha})(R_\beta - R_{eq,\beta})\right]. \tag{4.80}$$

In the general non-harmonic case, we can replace the second term in the r.h.s. of Eq. (4.76) by $\Delta_A\mathbf{S}^{-1}\mathbf{f}_n$ and obtain the iterative integration scheme:

$$\mathbf{R}_{n+1} = \mathbf{R}_n + \Delta_A\mathbf{S}^{-1}\mathbf{f}_n + \sqrt{2\Delta_{2A}T}\,\mathbf{z}_n, \tag{4.81}$$

which becomes exact if non-harmonic terms can be neglected and $\mathbf{K}$ is exactly given by $A\mathbf{S}$. Notice that Eq. (4.81) is equivalent to change $\Delta \to \Delta_A$ and $T \to T\Delta_{2A}/\Delta_A$ in Eq. (4.65). In practice, given an approximation of the Hessian matrix $\mathbf{S}$, we can

empirically select the value of A to minimize the time step error and work with a large value of Δ. Although the error for a generic potential $V(\mathbf{R})$ remains linear in Δ, it is usually quite small as it depends only on the non-harmonic terms for an accurate approximation of the Hessian.

The results obtained with this approach for a classical systems of 64 particles interacting through a Lennard-Jones potential are reported in Fig. 4.1. We notice that the optimal choice for A is not given by $A = 1$, which corresponds to the exact Hessian. This is because the non-harmonic terms are quite strong in this case and a rescaled Hessian is more accurate to describe the overall shape of the potential.