Chapter 4

Stochastic Equations

4.1 Langevin equation

To explain the idea of introduction of the Langevin equation, let us consider the concrete example taken from surface physics: motion of an atom (adatom) adsorbed on a crystal surface. The role of the substrate in this case may be reduced to the following four factors.

(a) First of all, the surface atoms of the substrate produce some potential $V(\vec{r})$ which plays the role of the external potential for the adatom. At the same time we have to take into account that the coordinates of substrate atoms are not rigidly fixed, the surface atoms can "adjust" themselves to the adatom position by shifting in such a way that to lower the total potential energy of the system (the so-called "polaronic effect"). Such "adiabatic" potential $V(\vec{r})$ may be introduced in a rigorous way only when the adatom velocity is much lower than a characteristic velocity of substrate atoms. In the opposite case we have to take into account the retarded effects of the substrate response, and the potential $V(\vec{r})$ will depend on the whole previous trajectory of the adatom.

(b) When $T \neq 0$, the substrate atoms oscillate near their equilibrium positions. Owing to this, the potential produced by the substrate atoms is "smoothed", the corresponding "effective" potential $V_{\text{eff}}(\vec{r})$ differs from the "bare" potential $V(\vec{r})$ by the Debye-Waller factor.

(c) There always exists an energy exchange between the adatom and the substrate, in a result of which the moving adatom may lose a part of its kinetic energy for excitation of various substrate degrees of freedom (phonons, plasmons, electron-hole pairs, *etc.*). This effect may be approximately described with the help of a friction force $\vec{F}^{f}(t)$ applying to the adatom. When the adatom velocity is small, this force may be approximated by the linear expression,

$$\vec{F}^f(t) = -m\eta \dot{\vec{r}}_a(t), \qquad (4.1)$$

where η is the viscous friction coefficient.

(d) Besides the energy flux from the adatom to the substrate, at $T \neq 0$ there always exists the reverse flux from the substrate to the adatom. Namely, the surface atoms of the substrate due to their thermal vibrations "push" the adatom in random directions. This effect may be modeled by introduction of some random force $\vec{F}^r(t)$ acting on the adatom. Evidently, the following equation should be satisfied,

$$\langle \vec{F}^r(t) \rangle = 0, \qquad (4.2)$$

because in the opposite case we may redefine the "regular" force

$$\vec{F}(t) = -\left[\frac{\partial V_{\text{eff}}(\vec{r})}{\partial \vec{r}}\right]_{\vec{r}=\vec{r}_a(t)}.$$
(4.3)

In the simplest approximation the random force is assumed to correspond to the Gaussian white noise, so that its correlator is taken to be

$$\langle F_{\alpha}^{r}(t) F_{\beta}^{r}(t') \rangle = A \,\delta_{\alpha\beta} \,\delta(t-t') \,, \tag{4.4}$$

where α and β are the Cartesian coordinates, and

$$A = 2\eta m k_B T. \tag{4.5}$$

The coefficient A is determined uniquely by the condition that the system must tend to thermal equilibrium as $t \to \infty$ (the so-called *fluctuation-dissipation theorem*, see [76]).

In a general case, the friction force may be non-Markovian as well as nonlinear with respect to particle's velocity. For example, the non-Markovian friction force $\vec{\mathcal{F}}^f(t)$ is introduced with the help of the following expression,

$$\mathcal{F}^{f}_{\alpha}(t) = -m \sum_{\beta=1}^{\nu} \int_{0}^{\infty} d\tau \,\mathcal{N}_{\alpha\beta}(\tau) \,\dot{r}_{\beta}(t-\tau) \,, \qquad (4.6)$$

where $\mathcal{N}_{\alpha\beta}(\tau)$ is known as the response tensor, or the memory kernel. In this case the random force $\vec{\mathcal{F}}^r$ will be non-Gaussian: according to the fluctuation-dissipation theorem, its correlator should be equal to

$$\langle \mathcal{F}_{\alpha}^{r}(t) \mathcal{F}_{\beta}^{r}(t') \rangle = \mathcal{N}_{\alpha\beta}(|t-t'|) m k_{B} T.$$
(4.7)

Equations (4.6) and (4.7) reduce to Eqs. (4.1), (4.4) and (4.5), if we put

$$\mathcal{N}_{\alpha\beta}(t) = 2\,\eta\,\delta_{\alpha\beta}\,\delta(t)\,.\tag{4.8}$$

Note also that in a general case the friction coefficient depends on the adatom coordinate, $\eta \to \eta (\vec{r}_a(t))$, so that in the case of using of a constant friction coefficient we should assume that η is some effective friction averaged over the trajectory of adatom motion.

Of course, in order to calculate the functions $V_{\text{eff}}(\vec{r})$ and $\mathcal{N}_{\alpha\beta}(\tau)$, we must solve the full system of Newtonian motion equations for the adatom and all substrate atoms with the help of the MD method as it was described above in Sec. 3.3. Often, however, these functions may be properly modeled. For example, for the adatom problem described above, $V_{\text{eff}}(\vec{r})$ is a periodic function along the surface which is characterized by the symmetry determined by the corresponding crystallographic face of the substrate (if the surface is not reconstructed). The amplitude of the function $V_{\text{eff}}(\vec{r})$ determines the activation energy of diffusion of a single adatom, ε_a , while the shape of $V_{\text{eff}}(\vec{r})$ may be approximated if the frequencies ω_{α} of the adatom vibrations at the minimum of the substrate potential well are known. Besides, the value of the friction coefficient η is coupled with the width of vibrational line Γ . Thus, all necessary parameters in Eqs. (4.1) to (4.3) may be properly approximated if we know the parameters ε_a , ω_{α} and Γ from independent experiments.

So, instead of the consideration of motion of the whole system "adatom plus substrate", we may consider the motion of the singled out subsystem, for example, the adatom only as we have done above. Thus, the adatom motion is modeled by the following equations,

$$\begin{cases} m\ddot{\vec{r}}_{a}(t) + m\eta\dot{\vec{r}}_{a}(t) + \partial V_{\text{eff}}(\vec{r}_{a})/\partial\vec{r}_{a} = \vec{F}^{r}(t), \\ \langle \vec{F}^{r}(t) \rangle = 0, \\ \langle F_{\alpha}^{r}(t) F_{\beta}^{r}(t') \rangle = 2\eta m k_{B}T \,\delta_{\alpha\beta} \,\delta(t-t'). \end{cases}$$

$$(4.9)$$

The set of equations (4.9) is called the *Langevin equation*. It must be emphasized from the very beginning that this equation is the *stochastic equation*, not an ordinary differential equation (see below Sec. 4.4).

In some particular cases, Eq. (4.9) has an analytical solution. For example, when the external potential is absent, $V_{\text{eff}}(\vec{r}) \equiv 0$, the solution of Eq. (4.9) is

$$\vec{v}(t) = \vec{v}(t_0) e^{-\eta(t-t_0)} + \frac{1}{m} \int_{t_0}^t dt' e^{-\eta(t-t')} \vec{F}^r(t') , \qquad (4.10)$$

where t_0 is the initial time moment.

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The memory on the initial velocity is lost for a time $\sim \eta^{-1}$, therefore at $t - t_0 \gg \eta^{-1}$ the first term in the right-hand side of Eq. (4.10) may be neglected. Then, the velocity autocorrelation function may be written in the following way,

$$K_{\alpha\beta}(\tau) \equiv \langle v_{\alpha}(t+\tau) v_{\beta}(t) \rangle$$

= $m^{-2} \int_{-\infty}^{t+\tau} dt' \int_{-\infty}^{t} dt'' e^{-\eta(t+\tau-t'+t-t'')} \langle F_{\alpha}^{r}(t') F_{\beta}^{r}(t'') \rangle$
= $\delta_{\alpha\beta} (2\eta k_{B}T/m) \left(\int_{-\infty}^{t} dt'' e^{2\eta t''} \right) e^{-\eta(2t+\tau)}$
= $\delta_{\alpha\beta} (k_{B}T/m) e^{-\eta\tau},$ (4.11)

where we assumed $\tau > 0$. Thus, the correlation function decays exponentially, and it holds the relationship $\frac{1}{2}m\langle \vec{v}^2 \rangle = \nu \frac{1}{2}k_BT$.

From Eq. (4.11) we can easily find the mean-square displacement of the particle,

$$\langle \left[\vec{r}(t) - \vec{r}(t_0) \right]^2 \rangle = \sum_{\alpha=1}^{\nu} \langle \left(\int_{t_0}^t dt' \, v_\alpha(t') \right)^2 \rangle$$

$$= \nu \int_{t_0}^t dt' \int_{t_0}^t dt'' \langle v_\alpha(t') \, v_\alpha(t'') \rangle$$

$$= 2\nu \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' K_{\alpha\alpha}(t' - t'')$$

$$= 2\nu (k_B T / m \eta) t .$$

$$(4.12)$$

Thus, the Langevin equation for the particle subjected to a viscous medium describes its Brownian motion with the diffusion coefficient

$$D = D_f \equiv k_B T / m \,\eta \,. \tag{4.13}$$

Besides, the solution of the Langevin equation for the harmonic potential $V_{\text{eff}}(\vec{r}) \propto \vec{r}^2$ is known too. Namely, for the one-dimensional equation

$$\ddot{x}(t) + \eta \, \dot{x}(t) + \omega_0^2 \, x(t) = \frac{1}{m} \, F^r(t) \tag{4.14}$$

for times $t \gg \eta^{-1}$, when a memory on the initial state is lost, the solution has the following form,

$$x(t) = \int^{t} dt' R(t - t') F^{r}(t'), \qquad (4.15)$$

where

$$R(t) = \frac{1}{m\,\omega_*} \,\exp\left(-\frac{1}{2}\,\eta\,t\right) \sin(\omega_* t) \tag{4.16}$$

and $\omega_*^2 = \omega_0^2 - \eta^2/4$. If $\omega_0 < \eta/2$, we have to make the substitutions $\omega_* = i \, \omega'_*$ and $\sin \omega_* t = i \sinh \omega'_* t$ in Eq. (4.16), where $\omega'_* = \eta^2/4 - \omega_0^2$. With the help of Eqs. (4.15) and (4.16) we may calculate the correlation functions of coordinates or velocities. The Fourier transform of the correlation function gives the following expression:

$$K(\omega) = \int_{-\infty}^{\infty} dt \, e^{-i\omega t} K(t) \propto \frac{(\omega_0^2 - \omega^2) - i\eta \, \omega}{(\omega_0^2 - \omega^2)^2 + (\eta \, \omega)^2} \,. \tag{4.17}$$

Thus, Eq. (4.14) leads to the Lorentz shape of the vibrational line with the half-width $\Gamma = \eta$ (the socalled "full width at half maximum", or FWHM). Recall that in real physical systems the inhomogeneous broadening (leading to the Gaussian line shape) as well as the broadening owing to dephasing effects are presented additionally.

In a general case the Langevin equation (4.9) may be solved by numerical methods.

4.2 Numerical solution of the Langevin equation

In order to solve the Langevin equation with a computer, first of all we need of a subroutine that produces the normal random numbers, i.e. the sequence $\{\xi_n\}$ of random numbers with Gaussian distribution,

$$\operatorname{Prob}\left(\xi_{n}\right) = (2\pi)^{-1/2} \exp\left(-\xi_{n}^{2}/2\right), \qquad (4.18)$$

which also satisfy the conditions

$$\langle \xi_n \rangle = 0 \text{ and } \langle \xi_n \xi_m \rangle = \delta_{nm}.$$
 (4.19)

Such random numbers may be obtained from the standard random numbers $\{\gamma_m\}$, i.e., the random numbers uniformly distributed in the interval (0,1), with the help of the formula

$$\xi_n = \left(\sum_{m=1}^{12} \gamma_m\right) - 6\,,\tag{4.20}$$

i.e. we obtain one normal random number from twelve standard random numbers (see details below in Sec. 5.1.2).

The further integration of the stochastic equation is carried out practically in the same way as it does in the case of an ordinary differential equation [106]. The only difference is that we have to choose a Runge-Kutta scheme with the constant time step Δt , and then at each time step $t_n = n \Delta t$ we should add the random force

$$F_n^r = B\,\xi_n\tag{4.21}$$

to the sum of the regular force $F_n = F(t_n)$ and the friction force $F_n^f = F^f(t_n)$. The coefficient B in Eq. (4.21) is defined by the integration of Eq. (4.4),

$$\int_{-\infty}^{\infty} dt \left\langle F^{r}(t) F^{r}(t') \right\rangle = 2 \eta m k_{B} T; \qquad (4.22)$$

with accounting of Eqs. (4.19) and (4.21) that gives the expression

$$B = (2\eta m k_B T / \Delta t)^{1/2}.$$
(4.23)

The appearance of the time step Δt in the expression for the random force is caused by the fact that the Langevin equation is the stochastic one. Emphasize that Δt in Eq. (4.23) corresponds to the time between the consequential calls of the subroutine which calculates the forces. Therefore, if we use the forth-order RK method (which calls the "force subroutine" 4 times in one step) with the time step τ , then we must take $\Delta t = \tau/4$ in Eq. (4.23). Note also that the described method works as well if the damping coefficient η depends on the coordinates of moving particles. However, when η depends on the velocities, the problem becomes more involved [193].

To control the work of the computer program, one may test, for example, the condition of the equally distribution of the kinetic energy among all degrees of freedom in the stationary regime.

In a result of the numerical solution of the Langevin equation we obtain one particular realization of the temporal trajectory of system motion. When we are studying the stationary state of the system, we have to remove some initial part of the trajectory, and then to use the remainder for calculation of different averages similarly as it was done in the MD method. Note that the equilibrium solution of the Langevin equation does not depend on the friction coefficient η , thus the value of η may be chosen appropriately in order to accelerate the approaching to equilibrium (usually $\eta \sim \omega_0$ is taken). In investigation of nonstationary (e.g., relaxation) processes, the whole trajectory is used, and sometimes we have to make the averaging over the initial states of the system. Besides, to get reliable results, it is always useful to carry out also the averaging over an ensemble of different realizations of the trajectory, i.e. to average over the set of trajectories calculated with different sequences of random numbers.

4.3 Generalized Langevin equation

In a general case, the idea of simulation with the help of stochastic equations consists in the separation of the whole system into two parts, the "main" one and the "thermostat". A part of the whole system that is the most interesting one for the problem under investigation, is singled out as the main part, and its evolution is modeled with the help of rigorous solution of motion equations. The remainder of the whole system is related to the thermostat, and it is assumed that the influence of the thermostat on the main part reduces to creation of some external potential, and to arising of the energy exchange (dissipation of the kinetic energy) and the corresponding random force. Of course, we have to be sure that a "developed chaos" really exist in the remainder which we have modeled as the thermostat. A rigorous introducing of the Langevin equation is possible only in the case when there exists a hierarchy of times in the system. This means that a characteristic time τ_A of motion of the singled out subsystem (e.g., the adatom in the example described above) must essentially exceed the characteristic time τ_S of the thermostat (e.g., the substrate). As the time τ_A of the main subsystem we may take, for example, the period of its characteristic oscillations, while as the time τ_S of the thermostat, the time of decay of temporal fluctuations. In the case $\tau_A \gg \tau_S$ the fluctuations in the thermostat are fast, and the action of the thermostat on the main subsystem may be approximately described by the δ -correlated random force. Otherwise, in the case of $\tau_A < \tau_S$, the employing of Gaussian random force is not rigorous, and we have to use Eqs. (4.6) to (4.8) corresponded to non-Markovian dynamics.

The simplest way to carry out the described program is to assume that the motion of atoms situated at the boundary between the main subsystem and the thermostat, undergoes the Langevin motion equations instead of Newtonian ones. A more rigorous approach developed by Adelman and Doll [107] and Tully [108], is based on the Zwanzig-Mori-Kubo technique [109, 110, 111]. Namely, let the whole system consists of Natoms, and N_A atoms belong to the singled out subsystem **A**, while N_S atoms, to the thermostat **S**. Let \vec{x} denote the array (vector) of coordinates of all atoms, \vec{x}_A denote the coordinates of the main subsystem, and \vec{x}_S denote the thermostat coordinates. Introduce also the projection operators \mathcal{P} and \mathcal{Q} which separate the atoms of the main subsystem and the thermostat respectively, i.e. $\vec{x}_A = \mathcal{P} \vec{x}$ and $\vec{x}_S = \mathcal{Q} \vec{x}$. To reduce notations, let us introduce the displacements \vec{u} of atoms from the equilibrium positions $\vec{x}^{(0)}$, the latter correspond to the absolute minimum of the potential energy $V(\vec{x})$ of the system. Then, the rigorous motion equations may be written in the following form,

$$\ddot{\vec{u}} = \vec{\mathcal{F}}(\vec{x}) = - \stackrel{\leftrightarrow}{\Omega}^2 (\vec{x}^{(0)}) \ \vec{u} + \delta \vec{\mathcal{F}}(\vec{x}) , \qquad (4.24)$$

where $\vec{\mathcal{F}} = -\partial V / \partial \vec{x}$, and $\stackrel{\leftrightarrow}{\Omega}^2$ is the dynamical matrix which describes the system evolution in the harmonic approximation. If we neglect all nonlinear effects in the thermostat, Eq. (4.24) may be rewritten in the following form,

$$\ddot{\vec{u}}_A = - \overleftrightarrow{\Omega}_A^2 \vec{u}_A - \overleftrightarrow{\Omega}_{AS}^2 \vec{u}_S + \delta \vec{\mathcal{F}}_A(\vec{x}_A, \vec{x}_S^{(0)}), \qquad (4.25)$$

$$\ddot{\vec{u}}_S = - \stackrel{\leftrightarrow}{\Omega}_S^2 \vec{u}_S - \stackrel{\leftrightarrow}{\Omega}_{SA}^2 \vec{u}_A , \qquad (4.26)$$

where $\stackrel{\leftrightarrow}{\Omega}_{A}^{2} = \mathcal{P} \stackrel{\leftrightarrow}{\Omega}^{2} \mathcal{P}, \quad \stackrel{\leftrightarrow}{\Omega}_{S}^{2} = \mathcal{Q} \stackrel{\leftrightarrow}{\Omega}^{2} \mathcal{Q}, \quad \stackrel{\leftrightarrow}{\Omega}_{AS}^{2} = \mathcal{P} \stackrel{\leftrightarrow}{\Omega}^{2} \mathcal{Q}, \text{ and } \stackrel{\leftrightarrow}{\Omega}_{SA}^{2} = \mathcal{Q} \stackrel{\leftrightarrow}{\Omega}^{2} \mathcal{P}.$ A formal solution of the linear equation (4.26) is

$$u_{S}(t) = \cos(\Omega_{S}t) u_{S}(0) + \Omega_{S}^{-1} \sin(\Omega_{S}t) \dot{u}_{S}(0) -\Omega_{S}^{2} \Omega_{SA}^{2} u_{A}(t) + \Omega_{S}^{-2} \cos(\Omega_{S}t) \Omega_{SA}^{2} u_{A}(0) + \int^{t} dt' \Omega_{S}^{-2} \cos[\Omega_{S}(t-t')] \Omega_{SA}^{2} \dot{u}_{A}(t') .$$
(4.27)

The substitution of Eq. (4.27) into Eq. (4.25) gives the generalized Langevin equation (GLE) which describes the evolution of N_A atoms of the singled out subsystem only:

$$\ddot{\vec{u}}_A(t) = - \overleftrightarrow{\Omega}_{\text{eff}}^2 \vec{u}_A(t) - \overleftrightarrow{\mathcal{N}}(t) \vec{u}_A(0) - \int^t dt' \,\, \overleftrightarrow{\mathcal{N}}(t-t') \,\, \dot{\vec{u}}_A(t)$$

$$+\vec{\mathcal{F}}^{r}(t) + \delta\vec{\mathcal{F}}_{A}\left(\vec{x}_{A}(t), \vec{x}_{S}^{(0)}\right), \qquad (4.28)$$

where

$$\widehat{\Omega}_{\text{eff}}^2 = \widehat{\Omega}_A^2 - \widehat{\mathcal{N}}(0) = \widehat{\Omega}_A^2 - \widehat{\Omega}_{AS}^2 \widehat{\Omega}_S^2 \widehat{\Omega}_{SA}^{-2} ,$$

$$(4.29)$$

$$\vec{\mathcal{N}}(t) = \vec{\Omega}_{AS} \cos\left(\vec{\Omega}_{S} t\right) \, \vec{\Omega}_{S}^{-2} \, \vec{\Omega}_{SA}^{-2} \,, \tag{4.30}$$

$$\vec{\mathcal{F}}^{r}(t) = - \overleftrightarrow{\Omega}^{2}_{AS} \cos\left(\overleftrightarrow{\Omega}_{S} t\right) \vec{u}_{S}(0) - \overleftrightarrow{\Omega}^{2}_{AS} \sin\left(\overleftrightarrow{\Omega}_{S} t\right) \dot{\vec{u}}_{S}(0), \qquad (4.31)$$

and, as it should be according to the fluctuation-dissipation theorem,

$$\langle \vec{\mathcal{F}}^r(t) \, \vec{\mathcal{F}}^r(0) \rangle = k_B T \, \overleftrightarrow{\mathcal{N}}(t) \,. \tag{4.32}$$

The generalized Langevin equation (4.28) is the matrix equation for N_A atoms only. But this equation includes the response matrix $\stackrel{\leftrightarrow}{\mathcal{N}}(t)$, and to calculate the latter, the full system of N motion equations must be solved. The idea of simulation with the help of the GLE consists in the following trick: let us take artificially for $\stackrel{\leftrightarrow}{\mathcal{N}}(t)$ some simple expression which (we hope) describes the thermostat dynamics quite well. For example, we may assume that the thermostat consists of a set of Brownian harmonic oscillators, that leads analogously to Eqs. (4.14–4.16) to the approximation

$$\vec{\mathcal{N}}(t) = \vec{\mathcal{N}}_0 \exp\left(-\frac{1}{2} \, \vec{\eta} \, t\right) \left[\cos\left(\vec{\omega}_* t\right) + \frac{1}{2} \, \vec{\eta} \, \vec{\omega}_*^{-1} \sin\left(\vec{\omega}_* t\right)\right]. \tag{4.33}$$

At the same time, $\stackrel{\leftrightarrow}{\mathcal{N}}(t)$ satisfies the differential equation

$$\ddot{\vec{\mathcal{N}}}(t) = - \overleftrightarrow{\omega}_0^2 \overleftrightarrow{\mathcal{N}}(t) - \overleftrightarrow{\eta} \overleftrightarrow{\vec{\mathcal{N}}}(t), \qquad (4.34)$$

where

$$\dot{\omega}_0^2 = \dot{\omega}_*^2 + \frac{1}{4} \dot{\eta}^2 . \tag{4.35}$$

The approximation (4.33) depends on three matrices, $\stackrel{\leftrightarrow}{\mathcal{N}}_0$, $\stackrel{\leftrightarrow}{\eta}$, and $\stackrel{\leftrightarrow}{\omega}_*$, each of them has the dimension $\nu N_A \times \nu N_A$. They should be chosen in such a way that, for example, to describe correctly the vibrational spectrum of the thermostat.

The employing of the non-Markovian random force (4.32) in computations is not convenient. Using Eq. (4.34), the set of equations (4.28), (4.29), (4.32) and (4.33) may be reduced to the set of Markovian stochastic equations but, however, already for $2N_A$ particles (N_A atoms of the main subsystem and N_A "fictitious" atoms with the coordinates $\vec{s}(t)$):

$$\ddot{\vec{u}}_A(t) = \vec{\mathcal{F}}_A(\vec{x}_A(t), \vec{x}_S^{(0)}) + \overset{\leftrightarrow}{\mathcal{N}}_0^{1/2} \overset{\leftrightarrow}{\omega}_0 \vec{s}(t) , \qquad (4.36)$$

$$\ddot{\vec{s}}(t) = \overset{\leftrightarrow}{\mathcal{N}}_{0}^{1/2} \overset{\leftrightarrow}{\omega}_{0} \vec{u}_{A}(t) - \overset{\leftrightarrow}{\omega}_{0}^{2} \vec{s}(t) - \overset{\leftrightarrow}{\eta} \dot{\vec{s}}(t) + \vec{F}^{r}(t) , \qquad (4.37)$$

where the random force $\vec{F}^r(t)$ is now Markovian,

$$\langle \vec{F}^r(0) \, \vec{F}^r(t) \rangle = 2 \, k_B T \stackrel{\leftrightarrow}{\eta} \delta(t) \,. \tag{4.38}$$

Methods of numerical solution of the system of stochastic equations (4.36) to (4.38) are described, e.g., in the works [112] and [113].

Note also that the separation of the whole system into the main part and the thermostat may be changed during the system evolution. For example, if we included into the main part the adatom together with a few nearest neighboring atoms of the substrate, then during the adatom diffusion on the surface, its surrounding will change, i.e. some surface atoms will "pass out" into the thermostat, while the others that occur to be in the nearest surrounding of the adatom at the given instant, should "pass into" from the thermostat to the main subsystem. The method of accounting of such an effect was described by Tully [108].

4.4 Fokker-Planck-Kramers equation

Emphasize ones more that the Langevin equation is the stochastic one, it differs from an ordinary differential equation by the existence of random force. The stochastic equation may be reduced to a differential equation, but the latter will be the differential equation with partial derivatives called the *Fokker-Planck* (FP) equation. In the present section we deduce the FP equation from the Langevin one (for a more detailed description of the theory of stochastic processes see, for example, the monograph [114]).

Temporarily, let us turn from the continuous time t to the discrete time variable $t_n = n \Delta t$. Then, the stochastic equation for some measurable quantity q(t) in a general case may be written in the following way,

$$\Delta q(t_n) \equiv q(t_n) - q(t_{n-1}) = K(q(t)) \ \Delta t + G(q(t)) \ \Delta w(t_n), \qquad (4.39)$$

where the first term in the right-hand side of Eq. (4.39) called the *drift term* describes the action of the regular force, and the second term called the *diffusion term*, the action of the random force. According to its definition, the quantity $\Delta w(t_n)$ must satisfy the following two conditions,

$$\begin{cases} \langle \Delta w(t_n) \rangle = 0, \\ \langle \Delta w(t_n) \Delta w(t_m) \rangle = \delta_{nm} \Delta t, \end{cases}$$
(4.40)

where δ_{nm} is Kronecker's delta symbol.

Note, however, that the functions K and G in Eq. (4.39) depend on the coordinates which in turn are the functions of time. Therefore, the question arises, at which time instant t they should be calculated. There may be two variants:

(a) In the so-called *Ito's calculus*, one takes $t = t_{n-1}$. In this case the calculation of different averages is significantly simplified, because, for example,

$$\langle G(q(t_{n-1})) \Delta w(t_n) \rangle = \langle G(q(t)) \rangle \langle \Delta w(t) \rangle = 0.$$
(4.41)

(b) In the Stratonovich calculus the time instant t is taken at the middle between the n-th and (n-1)-th steps, $t = \frac{1}{2}(t_n + t_{n-1})$. This calculus is convenient by that differentiation and integration operations are carried out with the same rules as in the ordinary differential and integral calculi.

Returning to the continuous time, $\Delta t \rightarrow dt$, Eqs. (4.39) and (4.40) are rewritten in the following form,

$$\begin{cases} dq(t) = K(q) dt + G(q) dw, & (a) \\ \langle dw \rangle = 0, & (b) \\ \langle dw(t) dw(t) \rangle = dt. & (c) \end{cases}$$
(4.42)

From Eq. (4.42c) one can see that the stochastic equation differs from a differential one by existence of the diffusion term such that $\langle dw \rangle \sim \sqrt{dt}$.

When we solved the Langevin equation, we calculated the trajectory of system motion which then was used for calculation of temporal averages. For stochastic processes, however, it is more natural to use a distribution function $f(q, t|q_0, t_0)$ which is the conditional probability that the system is in the state q at the instant t, if at the previous time moment t_0 it was in the state q_0 . Let us deduce now an equation for the distribution function $f(q, t|q_0, t_0)$. For this, we take an arbitrary function u(q) which depends on the coordinates, and write down its average (over the ensemble) quantity $\langle u \rangle$ at time t as

$$\langle u \rangle = \int dq \, u(q) \, f(q, t|q_0, t_0) \,.$$
 (4.43)

Then the derivative of u(q) with respect to time is equal to

$$\frac{d}{dt}\langle u\rangle = \int dq \, u(q) \, \frac{\partial f(q,t|q_0,t_0)}{\partial t} \,. \tag{4.44}$$

On the other hand, the differential of the function u(q) with an accuracy up to dt, with the help of Eq. (4.42a) may be written in the form

$$du = (\partial u/\partial q) dq + \frac{1}{2} (\partial^2 u/\partial q^2) dq dq = (\partial u/\partial q) [K(q) dt + G(q) dw(t)] + \frac{1}{2} (\partial^2 u/\partial q^2) G^2(q) dw(t) dw(t) , \qquad (4.45)$$

where the appearance of the second derivatives is caused by the fact that in the stochastic equation $\langle dw \rangle \sim \sqrt{dt}$.

Averaging Eq. (4.45) over time with the help of the Ito calculus, dividing both sides of the equation by dt, and taking into account Eqs. (4.42b,c), we obtain

$$\frac{\langle du \rangle}{dt} = \left\langle \frac{\partial u}{\partial q} K(q) \right\rangle + \frac{1}{2} \left\langle \frac{\partial^2 u}{\partial q^2} G^2(q) \right\rangle.$$
(4.46)

The first term in the right-hand side of Eq. (4.46) may be rewritten as

$$\left\langle \frac{\partial u}{\partial q} K(q) \right\rangle = \int dq \, f(q, t|q_0, t_0) \, K(q) \, \frac{\partial u}{\partial q} = -\int dq \, u(q) \, \frac{\partial}{\partial q} [K(q) \, f(q, t|q_0, t_0)], \qquad (4.47)$$

where we also have carried out the integration by parts. Analogously, the second term in the right-hand side of Eq. (4.46) may be transformed, if we carry out the integration by parts two times. Then, comparing the obtained expression for $\langle du \rangle/dt$ with Eq. (4.44) and taking into account that the function u(q) is an arbitrary one, we obtain that the distribution function $f(q,t|\cdots)$ must satisfy the following equation,

$$\frac{\partial f(q,t|\cdots)}{\partial t} = -\frac{\partial}{\partial q} [K(q) f(q,t|\cdots)] + \frac{1}{2} \frac{\partial^2}{\partial q \partial q} [G^2(q) f(q,t|\cdots)].$$
(4.48)

Eq. (4.48) is called the *Fokker-Planck* (FP) equation.

The described deduction may easily be generalized for a system of many variables, $q \rightarrow \vec{q} \equiv \{q_l\}$. The stochastic equation in this case takes the following form,

$$\begin{cases} dq_l(t) = K_l(q) dt + \sum_m G_{lm}(q) dw_m(t), \\ \langle dw_m(t) \rangle = 0, \\ \langle dw_l(t) dw_m(t) \rangle = \delta_{lm} dt, \end{cases}$$

$$(4.49)$$

and the Fokker-Planck equation, the form

$$\frac{\partial f(\vec{q},t|\cdots)}{\partial t} = -\sum_{l} \frac{\partial}{\partial q_{l}} [K_{l}(\vec{q}) f(\vec{q},t|\cdots)] + \frac{1}{2} \sum_{kl} \frac{\partial^{2}}{\partial q_{k} \partial q_{l}} \left(\sum_{m} G_{km} G_{lm} f(\vec{q},t|\cdots) \right).$$
(4.50)

As an example, let us consider the Langevin equation (4.9). For a single degree of freedom x(t), Eq. (4.9) may be rewritten as the set of equations

$$\begin{cases} \dot{x} = v, \\ \dot{v} = -\eta \, v - V_{\text{eff}}'(x)/m + F^r(t). \end{cases}$$
(4.51)

Putting $q_1 = x$ and $q_2 = v$, one can see that the system (4.51) takes the form of the stochastic equations (4.49) with the following parameters,

$$K_{1} = v, \quad K_{2} = -\eta \, v - V'_{\text{eff}}(x)/m,$$

$$G_{11} = 0, \quad G_{12} = 0, \quad G_{21} = 0,$$

$$G_{22} = (2 \, \eta \, k_{B} T/m)^{1/2}.$$
(4.52)

4.5. KRAMERS THEORY

Thus, in this case the FP equation for the function f(x, v, t) has the form

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial x} - \frac{1}{m} V'_{\text{eff}}(x) \frac{\partial f}{\partial v} = \eta \frac{\partial}{\partial v} \left[\left(v + \frac{k_B T}{m} \frac{\partial}{\partial v} \right) f \right].$$
(4.53)

Equation (4.53) is known as the *Fokker-Planck-Kramers* (FPK) *equation*. The generalization for the system with many degrees of freedom in the present case looks as

$$\frac{\partial f}{\partial t} + \vec{v} \frac{\partial f}{\partial \vec{x}} - \frac{1}{m} \frac{\partial V}{\partial \vec{x}} \frac{\partial f}{\partial \vec{v}} = \frac{\partial}{\partial \vec{v}} \left[\overleftarrow{\eta} \left(\vec{v} + \frac{k_B T}{m} \frac{\partial}{\partial \vec{v}} \right) f \right].$$
(4.54)

Note that if the left-hand side of Eq. (4.54) is put to zero,

$$\frac{\partial f}{\partial t} + \vec{v} \frac{\partial f}{\partial \vec{x}} - \frac{1}{m} \frac{\partial V}{\partial \vec{x}} \frac{\partial f}{\partial \vec{v}} = 0, \qquad (4.55)$$

then we obtain nothing else that the Liouville equation, but for the "singled out" subsystem only which undergoes the Newtonian motion equations. Thus, the right-hand side of Eq. (4.54) describes the influence of the thermostat on the "main" subsystem.

In the case of strong friction, $\eta \gg \omega_0$, where ω_0 is a characteristic frequency of system vibrations, we may neglect by the first (inertial) term in the Langevin equation. Then, comparing the equation

$$m\eta \dot{x} + V_{\text{eff}}'(x) = F^r(t) \tag{4.56}$$

with the stochastic equation (4.42), we see that now $K(x) = -V'_{\text{eff}}(x)/m\eta$ and $G = (2 k_B T/m\eta)^{1/2}$, so that the FP equation takes the form

$$\frac{\partial f(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(\frac{V_{\text{eff}}'(x)}{m \eta} f(x,t) \right) + \left(\frac{\partial^2}{\partial x^2} f(x,t) \right) \frac{k_B T}{m \eta} \,. \tag{4.57}$$

Equation (4.57) is called the *Smoluchowsky equation*.

Thus, on the one hand, the stochastic dynamics may be investigated with the help of solution of the Langevin equation using the random number generator and calculating as large as possible number of trajectories. On the other hand, we may solve the FPK equation, i.e. the equation with partial derivatives. Both the approaches are mathematically equivalent, and they must lead to the same final results.

For solution of the FP equation, a number of approximate methods have been developed which are described, e.g., in Risken's monograph [115]. As an example, in the next section we describe the results of numerical solution of the FPK equation.

4.5 Kramers theory

4.5.1 The problem

Perhaps, the most known application of stochastic equations is connected with the theory of thermally activated processes firstly developed by Kramers [116].

Let $V(x_1, \ldots, x_N)$ denote the potential energy of the system with N degrees of freedom, and let the function $V(x_1, \ldots, x_N)$ has minima (the absolute minimum as well as relative, or local minima), maxima and saddle points. If this system is in contact with a thermostat having a temperature T, then it will stay mainly near one of the minima of V, the absolute minimum (the ground state of the system) or a local minimum (a metastable state). However, when $T \neq 0$, then, owing to action of random (fluctuating) forces, the system may pass from a given minimum **A** to a nearest neighboring minimum **B** as shown in Fig. 4.1. Thus, it emerges the question about the probability R of such a transition per unit of time.

Approximately we may suppose that the transition from \mathbf{A} to \mathbf{B} is carried out along the adiabatic trajectory. To construct it, first we have to find the saddle trajectory, i.e. the trajectory which connects the



Figure 4.1: Escape of an atom from a potential well.

points of the minima **A** and **B** on the surface $y = V(x_1, \ldots, x_N)$ in the (N + 1)-dimensional space passing through a nearest saddle point **S**. The saddle trajectory is determined by solution of the equation

$$\frac{\partial \vec{x}}{\partial \tau} = -\frac{\partial V}{\partial \vec{x}} \tag{4.58}$$

(where τ is a parameter varying along the trajectory), i.e. it is the curve of steepest descent, and it describes non-inertial (i.e. with the infinitely large friction) motion of the system from the saddle point **S** to the nearest minima **A** and **B**. If there are several saddle trajectories, as the adiabatic trajectory we have to select that saddle trajectory which is characterized by the minimum energy barrier. Motion along the adiabatic trajectory will occur with the lowest energy losses and, therefore, it will take place with the highest probability. Along the adiabatic trajectory we may introduce a coordinate ξ (which is a curved coordinate in a general case), so that the potential energy becomes the function of a single variable, $V(\xi)$, and the problem reduces to one-dimensional one.

Thus, the problem under investigation is reduced approximately to solution of the one-dimensional Langevin equation or the corresponding FPK equation for the potential $V(\xi)$ schematically shown in Fig. 4.1. As an initial condition we may assume that at the initial instant t = 0 the system is near the minimum **A** in the "thermal equilibrium" state, i.e. that

$$f(\xi, \dot{\xi}, t = 0) = \frac{m\omega_A}{2\pi k_B T} \exp\left(-\frac{m\dot{\xi}^2/2 + V_A(\xi)}{k_B T}\right),$$
(4.59)

where m is the reduced mass, and the function

$$V_A(\xi) = \frac{1}{2} m \,\omega_A^2 (\xi - \xi_A)^2 \tag{4.60}$$

approximates $V(\xi)$ near the minimum point $\xi = \xi_A$. To define the probability R of the transition $\mathbf{A} \rightarrow \mathbf{B}$ per time unit, we have to calculate the flux of particles through the saddle point $\xi = \xi_S$ from the left-hand to the right-hand side,

$$j(t) = \int_0^\infty d\dot{\xi} \,\dot{\xi} \,f(\xi_S, \dot{\xi}, t) \,. \tag{4.61}$$



Figure 4.2: The initial state probability density function P(x, v, t) at t = 0, the Maxwell-Boltzmann distribution with $\varepsilon_A/k_BT = 4$ and corresponding to the equilibrium state if only the left minimum of the potential V(x) in Fig. 4.1 were present (from [119]).

Then, taking into account the normalization of the function (4.59), we find

$$R \approx j(t) \quad \text{for} \quad t \sim \omega_A^{-1}.$$
 (4.62)

The approximate solution obtained by Kramers for the case of $\varepsilon_A \equiv V(\xi_S) - V(\xi_A) \gg k_B T$, has the Arrhenius form,

$$R = R_0 \exp(-\varepsilon_A / k_B T), \qquad (4.63)$$

where

$$R_0 \approx \begin{cases} (\omega_A/2\pi)(\eta/\eta^*) & \text{for } \eta \ll \eta^* \equiv (\omega_A/2\pi)(k_B T/\varepsilon_A) \,, & \text{(a)} \\ (\omega_A/2\pi) & \text{for } \eta^* \ll \eta < \omega_S \,, & \text{(b)} \\ (\omega_0/2\pi)(\omega_S/\eta) & \text{for } \eta > \omega_S \,, & \text{(c)} \end{cases}$$

and the value ω_S determines the curvature of the barrier near the saddle point, $V(\xi) \approx -\frac{1}{2}m \omega_S^2(\xi - \xi_S)^2$ at $\xi \approx \xi_S$. Thus, the rate of escape from the potential well reaches the maximum and approximately does not depend on the friction η in the case of intermediate friction (4.64b). Note that this case corresponds to the region where the Eyring absolute rate theory [117] may be applied, and that namely this case corresponds to a majority of real situations in physics and chemistry. In the case of small friction, $\eta \ll \eta^*$, the rate of the process is slowed, because in order to overcome the barrier, the system must (fluctuationally) get from the thermostat an energy which exceeds the activation barrier ε_A , and this process is carried out during too long time in the case of small η . On the other hand, in the case of strong friction, $\eta > \omega_S$, the rate of the escape from the potential well is small due to a small velocity of the system motion in the configuration space when it overcomes the saddle point.

However, the solution obtained by Kramers is an approximate one. It was checked and made more precise in a number of works (e.g., see the survey [118]). Below we describe the results of one of such works, where the computer simulation was used.



Figure 4.3: The time evolution of the probability density function P(x, v, t) in the phase space as determined from the Fokker-Planck-Kramers equation for the potential (4.65) and from the initial state in Fig. 4.2 as calculated by Cartling [119]. The damping constant $\eta = 0.01$ and the sequence of times is: (a) 4, (b) 10, (c) 40, and (d) 200.



Figure 4.4: As in Fig. 4.3, but for the damping constant $\eta = 0.4$ and the sequence of times: (a) 4, (b) 10, (c) 20, and (d) 100 (after [119]).



Figure 4.5: As in Fig. 4.3, but for the damping constant $\eta = 10.0$ and the sequence of times: (a) 20 and (b) 100 (after [119]).

4.5.2 Numerical solution of the FPK equation

To check the Kramers theory, Cartling [119] solved numerically the FPK equation for the potential

$$V(x) = \begin{cases} \frac{1}{2}(x+2)^2 & \text{if } x < -1, \\ 1 - \frac{1}{2}x^2 & \text{if } |x| \le 1, \\ \frac{1}{2}(x-2)^2 & \text{if } x > 1, \end{cases}$$
(4.65)

i.e. it was chosen m = 1, $x_A = -2$, $x_B = 2$, $x_S = 0$, $\varepsilon_A = 1$, and $\omega_A = \omega_S = 1$. The region of variation of the variables was restricted to the rectangle $|x| \leq 5$, $|v| \leq 3$, and at the border of the rectangle, the function f(x, v, t) was put to zero. The transformation of the differential FPK equation to the difference equation was carried out by standard numerical method with the help of introducing a mesh (e.g., see [120]). The mesh step was taken as $h_x = h_v = 0.02$, and the time step was chosen as $\Delta t = 0.025$. As an initial condition, it was taken the Maxwell-Boltzmann distribution (4.59) shown in Fig. 4.2. Evolution of the function f(x, v, t)for different friction coefficients η (the small friction $\eta = 0.01$, the intermediate friction $\eta = 0.4$, and the strong friction $\eta = 10$) for the temperature $k_B T = 0.25$ is shown in Figs. 4.3 to 4.5. To determine the rate R, there were calculated the probabilities to find the particle at each of the minima, at the left minimum Q_L and the right one Q_R ,

$$Q_L(t) = \int_{-\infty}^{\infty} dv \, \int_{-\infty}^{0} dx \, f(x, v, t), \qquad Q_R(t) = \int_{-\infty}^{\infty} dv \, \int_{0}^{\infty} dx \, f(x, v, t), \tag{4.66}$$

so that $Q_L(t) + Q_R(t) = 1$, and then the transition rates $R_{L\to R}$ and $R_{R\to L}$ were found with the help of the kinetic equation,

$$\frac{dQ_L(t)}{dt} = R_{L \to R}Q_L(t) - R_{R \to L}Q_R(t).$$

$$(4.67)$$

The simulation has shown that the approximate Kramers expressions (4.63), (4.64) describe the numerical results with a sufficient accuracy.