

Surface Diffusion

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Chapter 1

Introduction

Surface diffusion deals with very interesting physics, namely:

- surface diffusion may be considered as motion in an external (substrate) potential; thus, here we meet with low-dimensional (two-dimensional) physics, or even with one-dimensional situation as for diffusion in channels of furrowed surfaces like W(112);
- “transparent” – atomic motion on a plane may easily be visualized; surface diffusion may be studied by direct experimental methods (although experimental techniques are not too simple – a surface should be specially prepared to have a well-defined structure without defects or with controlled defects, one should use high vacuum to avoid impurities, the technique should be with high spatial resolution, one should take care to prevent evaporation or absorption into the bulk);
- explores the very wide concentration interval from $\theta = 0$ to 1 or even more.

Surface diffusion is very important practically, namely:

- growing of crystals;
- emission electronics;
- catalysis;
- corrosion;
- soldering, welding, powder metallurgy.

Theoretically the problem reduces to motion of atoms in an external (periodic) potential when the interaction between the atoms must be taken into account.

What will not be described in this book: diffusion on disordered lattices (see excellent survey of Haus and Kehr (1987)). However, a role of defects will be considered briefly.

Chapter 2

Diffusion of a Single Atom

2.1 Diffusion: what is it?

Classical diffusion (or Brownian motion, or random walk) is defined as such a motion of a particle that its mean-square displacement from an initial point is proportional to time,

$$\langle (r(t) - r(0))^2 \rangle = 2\nu Dt, \quad t \rightarrow \infty. \quad (2.1)$$

Here $\langle \dots \rangle$ stands for the averaging over the *equilibrium* state of the system, and $\nu = 1$ for the 1D system, $\nu = 2$ for the 2D (surface) diffusion, and $\nu = 3$ for the 3D (bulk) diffusion. Using Eq. (2.1), the diffusion coefficient D may be defined as

$$D = \frac{1}{2\nu} \lim_{t \rightarrow \infty} \left\langle \frac{d}{dt} (r(t) - r(0))^2 \right\rangle = \frac{1}{\nu} \lim_{t \rightarrow \infty} \langle v(t) (r(t) - r(0)) \rangle = \frac{1}{\nu} \lim_{t \rightarrow \infty} \left\langle \int_0^t dt' v(t)v(t') \right\rangle, \quad (2.2)$$

so that

$$D = \frac{1}{\nu} \int_0^\infty d\tau \langle v(0)v(\tau) \rangle. \quad (2.3)$$

It is natural to generalize this definition and to introduce the tensor diffusion coefficient,

$$D_{\alpha\beta}(\omega) = \int_0^\infty d\tau e^{i\omega\tau} \langle v_\alpha(0)v_\beta(\tau) \rangle, \quad (2.4)$$

so that $D = \frac{1}{\nu} \sum_{\alpha=1}^{\nu} D_{\alpha\alpha}(0)$.

To use Eqs. (2.3) or (2.4), first we have to know a corresponding motion equation as well as its solution.

In statistical mechanics the system state is described by the distribution function $f(r, p; t)$, which depends on the coordinate r and the momentum $p = mv$ of a particle of mass m , and in the absence of a time-dependent external perturbation the system must approach to the equilibrium state, $f(r, p; t \rightarrow \infty) \rightarrow f_0(r, p)$, which corresponds to the Maxwell-Boltzmann distribution

$$f_0(r, p) = \mathcal{N} \left(\frac{1}{\sqrt{2\pi m k_B T}} \right)^\nu \exp \left\{ -\frac{1}{k_B T} \left[\frac{1}{2m} p^2 + \varphi(r) \right] \right\}, \quad (2.5)$$

where $\varphi(r)$ is the potential energy the particle; the function $\varphi(r)$ should be 2D-periodic along the surface. \mathcal{N} is an appropriate normalization; usually it is convenient to normalize on one particle per unit of volume (or area in the case of surface diffusion, or length for the 1D diffusion). For example, for the 1D potential with the period a_s the normalization factor is

$$\mathcal{N}^{-1} = \frac{1}{a_s} \int_0^{a_s} dx \exp \left(-\frac{\varphi(x)}{k_B T} \right). \quad (2.6)$$

Evolution of the distribution function may often be described by the equation

$$\dot{f} = Lf. \quad (2.7)$$

Different methods of deduction of Eq. (2.7) are described, e.g., in []. (Zaslavsk)

For a Hamiltonian system, the operator L corresponds to the Liouville operator,

$$L_H = -v \frac{\partial}{\partial x} - \dot{p} \frac{\partial}{\partial p} = - \sum_{\alpha} \left(v_{\alpha} \frac{\partial}{\partial x_{\alpha}} + F_{\alpha} \frac{\partial}{\partial p_{\alpha}} \right), \quad (2.8)$$

where $F_{\alpha} = -\partial\varphi(r)/\partial x_{\alpha}$ is the force acting on the particle.

The motion equation allows us to couple the diffusion coefficient D with the mobility coefficient B . The latter describes a linear response of the system being in the equilibrium state, to an action of infinitesimal external force $\delta F(x, t)$. Namely, the external perturbation leads to the change of the distribution function on

$$\Delta f = f - f_0, \quad |\Delta f| \ll |f_0|. \quad (2.9)$$

According to (2.7), the deviation Δf should satisfy the linearized equation ($Lf_0 = 0$)

$$\frac{\partial}{\partial t} (\Delta f) = (L + \Delta L)(f_0 + \Delta f) \approx L \Delta f + \Delta L f_0, \quad (2.10)$$

a solution of which may formally be written in the form

$$\Delta f(t) = \int^t dt' \exp [L(t - t')] \delta L(t') f_0. \quad (2.11)$$

A deviation of the distribution function from the equilibrium one leads to appearance of the flux of particles with the density

$$\langle j(x, t) \rangle = \int dp \frac{p}{m} \Delta f(x, p; t). \quad (2.12)$$

Substituting (2.11) into (2.12) and using $\delta L(t) = -\delta F(x, t) \frac{\partial}{\partial p}$ which follows from Eq. (2.8), and incorporating also the equation $\partial f_0 / \partial p = -f_0 v / k_B T$ which follows from (2.5), we obtain

$$\langle j_{\alpha}(x, t) \rangle = (k_B T)^{-1} \int^t dt' \left\{ \int dp f_0(x, v) v_{\alpha} e^{L(t-t')} v_{\beta} \right\} \delta F_{\beta}(x, t'). \quad (2.13)$$

Defining now the mobility tensor by the relation

$$\langle j_{\alpha}(x, t) \rangle = \int^t dt' B_{\alpha\beta}(t - t') \delta F_{\beta}(x, t'), \quad (2.14)$$

we obtain for it the expression

$$B_{\alpha\beta}(\tau) = \begin{cases} (k_B T)^{-1} \langle v_{\alpha}(0) v_{\beta}(\tau) \rangle & \text{if } \tau > 0, \\ 0 & \text{if } \tau < 0. \end{cases} \quad (2.15)$$

Fourier transform of Eq. (2.15) yields

$$B_{\alpha\beta}(\omega) = (k_B T)^{-1} \int_0^{\infty} dt e^{i\omega t} \langle v_{\alpha}(0) v_{\beta}(t) \rangle. \quad (2.16)$$

Comparing (2.3) and (2.16), we get the Einstein relation

$$D_{\alpha\beta}(\omega) = k_B T B_{\alpha\beta}(\omega). \quad (2.17)$$

Emphasize that the coefficients $B_{\alpha\beta}(\omega)$ or $D_{\alpha\beta}(\omega)$ contain the full information on the equilibrium state of the system. Besides, the functions $B_{\alpha\beta}(\omega)$ and $D_{\alpha\beta}(\omega)$ are complex, and owing to the causality principle their real and imaginary parts are coupled by the (dispersion) Kramers-Kronig relation. Note also that the energy absorption is proportional to $\text{Re } B(\omega)$.

2.2 Langevin and Fokker-Planck-Kramers equations

In the first-order approximation, the role of crystalline substrate reduces to producing of a stationary external potential $\varphi(r)$, in the field of which an atom moves. When the potential $\varphi(r)$ is one-dimensional, the corresponding Hamiltonian motion equation is always integrable and the motion is regular, $\langle x(t) \rangle \propto t$. However, already for a 2D potential $\varphi(r)$ because of the coupling of the two degrees of freedom the system integrability is destroyed, and in a general case the atom motion becomes stochastic (Lichtenberg), the motion follows the law

$$\langle x^2(t) \rangle \propto t^{1+\varepsilon}, \quad t \rightarrow \infty, \quad (2.18)$$

where the parameter ε depends on the shape of potential $\varphi(r)$ as well as on the energy of the atom. Stochastic motion of the adsorbed atom due to coupling of the modes was studied in (ZETF Chirikov), and that due to coupling of the parallel and perpendicular to the surface motion of the adatom, in (my Radiophysics).

Besides the adatom's degrees of freedom, there are degrees of freedom corresponding to the motion of substrate atoms. From a general theory of dynamical systems (Lichtenberg) it is known that with increasing of the number of degrees of freedom in a nonlinear system, the chaos becomes more and more "developed", and the character of the motion, more diffusional (i.e. $\varepsilon \rightarrow 0$ in Eq. (2.18)). However, the complete description of motion of a Hamiltonian system with more than two degrees of freedom is too complicated. Therefore, usually the motion of substrate atoms is treated phenomenologically by introducing a "viscous" friction with a coefficient η (or the tensor $\eta_{\alpha\beta}$ in a general case) which is equal to the rate of energy exchange between the adatom and substrate (my SS, Uspechi). Simultaneously, we have to introduce an external force $\delta F(t)$ acting on the adatom, such that

$$\langle \delta F(t) \rangle = 0, \quad (2.19)$$

while the average kinetic energy of the adatom has to be equal to $\frac{1}{2}k_B T$ for every system's degree of freedom. Usually it is assumed that the external force $\delta F(t)$ corresponds to white noise, i.e. it is random with the Markov correlator

$$\langle \delta F_\alpha(t) \delta F_\beta(t') \rangle = \delta_{\alpha\beta} 2\eta m k_B T \delta(t - t'), \quad (2.20)$$

so that the motion equation reduces to the stochastic equation,

$$m\ddot{r}_\alpha + m\eta\dot{r}_\alpha + \frac{\partial\varphi(r)}{\partial r_\alpha} = \delta F_\alpha(t). \quad (2.21)$$

Equations (2.19) to (2.21) are the well-known Langevin equation. They correspond to the kinetic equation (2.7) with the operator

$$L = L_H + L_\eta, \quad L_\eta = \sum_{\alpha\beta} \frac{\partial}{\partial p_\alpha} \eta_{\alpha\beta} \left[p_\beta + (m k_B T) \frac{\partial}{\partial p_\beta} \right]. \quad (2.22)$$

A deduction of Eq. (2.7), (2.22)s known as the Fokker-Planck-Kramers equation, from the Langevin equation (2.21), as well as the approximations made at this deduction could be found, e.g., in (Gardiner) or [Haken]. Namely, for the FKP equation to operate we need:

(1) a corresponding Langevin equation, i.e. the stochastic force $\delta F(t)$ should be Markovian and the fluctuations should be Gaussian, and

(2) it should exist such a time interval Δt where $x(t)$ is varying slowly while δF changes fast, as it is for, e.g., a heavy particle in a gas of light atoms.

At high enough friction, $\eta \gg \omega_0$, where ω_0 is a characteristic frequency of vibrations of the atom at a minimum of the potential $\varphi(r)$, we may neglect by the inertial term in Eq. (2.21), and the Langevin equation simplifies to the form

$$m\eta\dot{r}_\alpha + \frac{\partial\varphi(r)}{\partial r_\alpha} = \delta F_\alpha(t). \quad (2.23)$$

This equation corresponds to the so-called Smoluchowsky equation (e.g., see [Gardiner]):

$$\dot{\rho} = L_{\text{sm}}\rho, \quad L_{\text{sm}} = \sum_{\alpha=1}^3 \left(-\frac{1}{m\eta} \frac{\partial}{\partial x_\alpha} F_\alpha(x) + \frac{k_B T}{m\eta} \frac{\partial^2}{\partial x_\alpha^2} \right), \quad (2.24)$$

where the distribution function $\rho(x, t) = \int dp f(x, v; t)$ corresponds to the standard density of particles.

The operator L_{sm} is the first term in series expansion of L over η^{-1} . The whole series is described in [d'Agliaio, Risken, Gardiner]. Physically it corresponds to elimination of fast variables (here v is fast and x is slow). The Smoluchowsky equation is valid when a variation of the external potential, $\delta\varphi \sim \varphi'' l^2$, on a distance of free path length, $l \sim (k_B T/m)^{1/2} / \eta$, does not exceed the thermal energy $k_B T$, so that the Maxwell equilibrium distribution for velocities can be achieved. From this reason we obtain the following restriction for validity of the Smoluchowsky equation:

$$\eta \gtrsim \max(\omega_0, \omega_s), \quad (2.25)$$

where $\omega \dots$

It is easy to see that Eq. (2.24) is the classical diffusion equation, i.e. it describes a local conservation of the number of atoms (the so-called continuity equation),

$$\dot{\rho} + \nabla \cdot J = 0, \quad (2.26)$$

when the total flux J of particles (Ω is a small volume),

$$\begin{aligned} J(x) &= \frac{d}{dt} \langle x \rangle_\Omega = \frac{d}{dt} \int_\Omega dx x \rho(x, t) = \int_\Omega dx x L_{\text{sm}} \rho \\ &= \int_\Omega dx x \frac{\partial}{\partial x} \left(D_f \frac{\partial}{\partial x} - B_f F(x) \right) \rho = \int_\Omega dx \left(-D_f \frac{\partial}{\partial x} + B_f F(x) \right) \rho, \end{aligned} \quad (2.27)$$

is the sum of the diffusion flux

$$J_d = -D_f \nabla \rho, \quad D_f = \frac{k_B T}{m\eta} \quad (2.28)$$

and the drift flux

$$J_\mu = \rho j_\mu, \quad j_\mu = B_f F(x), \quad B_f = \frac{1}{m\eta} = \frac{D_f}{k_B T}. \quad (2.29)$$

In the opposite case of a very small friction, $\eta \rightarrow 0$, we may make a transform to the variables (x, ε) , where ε is the energy of the atom. In this case ε is a slow variable, while x is fast so that we may make an averaging over it, and the FPK equation reduces again to the diffusion equation, but now in the energy space.

Until now we assumed (and, due to complexity of the FPK equation, will have to assume in next sections too) that the friction coefficient η is constant. However, we may neglect by a

dependence of η on time only if a response of the substrate on the adatom motion is instantaneous, i.e. if $\omega_0 \ll \omega_m$, where ω_m is the maximum frequency of vibrations of the substrate atoms (e.g., the Debye frequency). This is valid for the motion of a heavy atom with mass $m_a \gg m_s$ (m_s is the mass of the substrate atom). But usually the condition $\omega_0 \gtrsim \omega_m$ is valid, so that the adparticle motion should be described by the generalized Langevin equation

$$m\ddot{r}(t) + m \int^t dt' \mathcal{N}(t-t') \dot{r}(t') + \frac{\partial \varphi(r)}{\partial r} = \delta F(t), \quad (2.30)$$

where the stochastic force $\delta F(t)$ must now have the non-Markov correlator,

$$\langle \delta F(t) \delta F(0) \rangle = mk_B T \mathcal{N}(t). \quad (2.31)$$

The simplest approximation for $\mathcal{N}(t)$ is $\mathcal{N}(t) \propto \exp(-t/\tau)$ with $\tau \sim \omega_m^{-1}$. A more rigorous method to calculate the function $\mathcal{N}(t)$ or its Fourier transform,

$$\eta(\omega) = \int_0^\infty dt e^{i\omega t} \mathcal{N}(t) \quad (2.32)$$

for adsystems is described in [my SS, Uspechi]. Results:

- (1) for $\omega < \omega_m$, $\eta(\omega) \lesssim \omega_m$ is determined by the one-phonon mechanism;
- (2) for $\omega_m < \omega < (2 \div 3)\omega_m$ the main contribution to the damping is due to decay of the local vibration into the substrate phonons with $\eta(\omega) \sim (10^{-1} \div 10^{-2}) \omega_m$ and strongly depends on temperature,

$$\eta(T) \approx \begin{cases} \exp(\dots) & \text{if } T < \dots \\ T & \text{if } T > \dots \end{cases} \quad (2.33)$$

- (3) for $\omega \gg \omega_m$ the main is the electron-hole decay mechanism with $\eta \lesssim 10^{-2} \omega_0$.

The non-Markovian Langevin equation (2.30) was studied in a number of works [Grote and Hynes 1980; Leiber, Marchesoni, Risken 1987; Jung and Hänggi 1988; Wanhström; see also the review of Hanggi]. The result is rather evident: if we need to describe the shape of the vibrational line for atomic vibration in a potential well with the frequency $\omega \sim \omega_0$, we have to take $\eta \approx \eta(\omega_0)$; if we want to describe the diffusion, i.e. an overcoming the barrier characterized by the saddle frequency ω_s , we have to take $\eta \approx \eta(\omega_s)$.

When an adatom moves in the potential relief $\varphi(r)$, the rate of energy exchange η depends also on the position of the adatom with respect to the substrate atoms, i.e. $\eta = \eta(x)$. This dependence might be strong enough for the one-phonon friction mechanism [Wangstrom]. For the e-h friction η also depends on x [my SS], although not so strong. If we need to know the whole dependence $B(\omega)$, we must take into account the dependence $\eta(x)$ [Wangstrom]. But if we need only $B(0)$, we may take some η_{eff} averaged over a trajectory.

Due to complexity of solution of the FPK equation, in what follows we shall assume that the friction coefficient is constant. However, we have to remember that in fact η is some effective coefficient which may depend essentially on temperature of the system.

The Langevin equation is the classic-mechanical one. It is clear that at low temperatures, $k_B T < \hbar \omega_0$, we have to take into account quantum-mechanical corrections. Besides, in principle the quantum diffusion – the underbarrier tunnel motion of the adatom – may take place. In bulk, it was observed in ... and theoretically described by [Yu.Kagan]. But for adsystems, probably, the quantum diffusion is negligible because of relatively large mass of adatoms and too high barriers of $\varphi(r)$.

The FPK equation is rigorously deduced for $m_a \gg m_s$. However, it works as well (?) for $m_a < m_s$ too. Why? Probably because the substrate atoms are coupled in the lattice so that their displacements are small. But it should be $\omega_a \ll \omega_D$?

...

2.3 Solution: one-dimensional system

2.3.1 Conventional diffusion equation

In the simplest case, taking into account

(1) the conservation law, $\dot{\rho} = -\nabla \cdot j$ (this law is exact!), and

(2) the phenomenological Fick law, $j = -D \nabla \rho$,

we obtain the parabolic equation for the distribution function $\rho(x; t)$,

$$\frac{\partial \rho}{\partial t} = D \Delta \rho. \quad (2.34)$$

In the most simple case of the absence of the external potential at all, $\varphi(x) = 0$, the Smoluchowsky equation takes the form

$$\dot{\rho} = D_f \Delta \rho. \quad (2.35)$$

In mathematical physics, a general form of the parabolic (diffusion) equation is:

$$\frac{\partial \rho}{\partial t} = D \Delta \rho + g(x, t), \quad (2.36)$$

where $g(x, t)$ is the “source” term which describes creation or annihilation of new particles. For a complete formulation of the problem, this equation needs either initial or boundary conditions.

A general method of solution of Eq. (2.36) is provided by the Green function technique. First, we have to find the so-called *fundamental* solution of the following equation,

$$\dot{G} = D \Delta G, \quad G(x, 0) = \delta(x), \quad (2.37)$$

where $x \in (-\infty, +\infty)$ and $t \geq 0$. Then, introducing the Laplace transform over time and the Fourier transform over spatial coordinates,

$$G(q, \lambda) = \int_0^\infty dt e^{-\lambda t} \int dr e^{-iqr} G(r, t), \quad (2.38)$$

and applying this transformation to both sides of Eq. (2.37), we obtain finally

$$-1 + \lambda G(q, \lambda) + D_f q^2 G(q, \lambda) = 0, \quad (2.39)$$

so that the solution of Eq. (2.37) is

$$G(q, \lambda) = \left(\lambda + D_f q^2 \right)^{-1}, \quad (2.40)$$

or, for the Fourier transform over time, it is

$$G(q, \omega) = \frac{1}{\pi} \frac{Dq^2}{\omega^2 + (Dq^2)^2} = \frac{1}{\pi} \left(\frac{1}{\pm i\omega + Dq^2} + ? \right). \quad (2.41)$$

The back Fourier transforms give

$$G(q, t) = \exp(-q^2 D_f t) \quad (2.42)$$

and

$$G(r, t) = \left(\frac{1}{\sqrt{4\pi D_f t}} \right)^\nu \exp\left(-\frac{r^2}{4D_f t} \right). \quad (2.43)$$

The function (2.43) is normalized on one particle in the system, $\int dx G(x, t) = 1$.

Finally, the solution of the Cauchy problem (2.36) with an initial condition $\rho(x, 0) = \rho_{\text{ini}}(x)$ is the following:

$$\rho(x, t) = \int_{-\infty}^{+\infty} dx' G(x - x', t) \rho_{\text{ini}}(x') + \int_0^t dt' \int_{-\infty}^{+\infty} dx' G(x - x', t - t') g(x', t'). \quad (2.44)$$

Remark: if $\rho_{\text{ini}}(x) = ax$, then $\rho(x, t) = ax$ too, i.e. this is a steady (but unnormalized) state.

Thus, if at the beginning we had the atom at the origin of coordinates, $\rho_{\text{ini}}(r) = \delta(r)$, then $\langle r^2 \rangle = \int dr r^2 \rho(r, t) = 2\nu D_f t$, so that $D_s = D_f \equiv k_B T / m\eta$. Moreover, substituting the expression for the velocity from the Eq. (??) into the definition (??) and using (??), we see that the generalized diffusion coefficient does not depend on frequency, i.e. $D(\omega) \equiv D_f$ (as it should be, because the Smoluchowsky equation does not include inertia effects).

2.3.2 The FPK equation in the absence of the substrate potential

Consider now the Langevin equation (2.21) in the absence of the external potential. It is easy to check that the solution has the form

$$v(t) = v_{\text{ini}} e^{-\eta t} + \frac{1}{m} \int_0^t dt' e^{-\eta(t-t')} \delta F(t'). \quad (2.45)$$

Therefore, we have

$$\begin{aligned} \langle [x(t) - x_{\text{ini}}]^2 \rangle &= \left\langle \left[\int_0^t dt' v(t') \right]^2 \right\rangle \\ &= \left(v_{\text{ini}}^2 - \frac{k_B T}{m} \right) \frac{1}{\eta^2} (1 - e^{-\eta t})^2 + \left(\frac{2k_B T}{m\eta} \right) t - \left(\frac{2k_B T}{m\eta^2} \right) (1 - e^{-\eta t}) \end{aligned} \quad (2.46)$$

$$\approx \begin{cases} (v_{\text{ini}} t)^2 & \text{if } t \ll \eta^{-1}, \\ 2D_f t & \text{if } t \gg \eta^{-1}. \end{cases} \quad (2.47)$$

Thus, the diffusion law (2.1) works for times $t \gg \eta^{-1}$ only, and the diffusion coefficient D_s is again determined by the expression (2.28). On the other hand, substituting (??) into (??) and using (??), we obtain

$$D(\omega) = \frac{k_B T}{m} \frac{i}{\omega + i\eta}, \quad (2.48)$$

and $D(0) = D_f$.

Expression (2.48) may be compared with the solution of Langevin equation for the harmonic oscillator, $\varphi(x) = \frac{1}{2} m \omega_0^2 x^2$, which is:

$$D_{\text{harm}}(\omega) = \frac{k_B T}{m} \frac{i\omega}{\omega^2 - \omega_0^2 + i\eta\omega}. \quad (2.49)$$

As seen, the function $D_{\text{harm}}(\omega)$ has a peak at $\omega = \omega_0$, while at $\omega \rightarrow 0$ we have $D(\omega) \rightarrow 0$ as it should be, although at $\omega_0 \rightarrow 0$ the expression (2.49) reduces to (2.48).

Thus, in a general case one may expect that with presence of the substrate potential but at high temperatures, $k_B T \gg \varepsilon_a$, when we may neglect by the substrate relief, expression (2.48) should work, while at low temperatures, $k_B T \ll \varepsilon_a$, the function $D(\omega)$ has to have two maxima, one at $\omega = 0$ describing the diffusion (jump) motion, and another at $\omega = \omega_0$ corresponded to vibration at minima of the external potential, the width of both peaks being determined by the value η . Exact solution of the FPK confirms this expectation (see Fig. ??).

2.3.3 General case

Let us consider now the Langevin equation at low temperatures, $\varepsilon_a \gtrsim k_B T$. In a general case the Fokker–Planck equation can be presented in the following form,

$$\dot{f}(z, t) = L(z)f(z, t), \quad (2.50)$$

where $z \equiv x$ for the Smoluchowski equation (2.24) and $z \equiv (x, p)$ for the Langevin equation (2.22). Formal solution of Eq. (2.50) is

$$f(z, t) = e^{Lt}f(z, 0). \quad (2.51)$$

Because the linear operator $L(z)$ does not depend on time, it is convenient to make the Laplace transform

$$f(z, t) = \int_0^\infty d\lambda e^{-\lambda t} f_\lambda(z). \quad (2.52)$$

Substituting (2.52) into (2.50), we obtain an eigenvalue equation

$$L(z)f_\lambda(z) = -\lambda f_\lambda(z). \quad (2.53)$$

The solution of Eq. (2.53) with $\lambda = 0$ is the stationary solution $f_0(z)$ with zero atomic flux $j = 0$. Note that the existence of the stationary solution is the consequence of detailed balance.

Usually it is convenient to make the unitary transformation

$$\tilde{L} = f_0^{-1/2} L f_0^{+1/2}, \quad (2.54)$$

$$\tilde{f} = f_0^{-1/2} f, \quad (2.55)$$

so that the form of the eigenvalue equation (2.53) remains the same,

$$\tilde{L}(z)\tilde{f}_\lambda(z) = -\lambda\tilde{f}_\lambda(z). \quad (2.56)$$

To solve this equation, introduce the Green function $G(z, t|z', 0)$, which is a solution of Eq. (2.50), $\dot{G} = LG$, with the initial condition

$$G(z, t|z', 0)|_{t=0} = \delta(z - z'). \quad (2.57)$$

The function $G(z, t|z', 0)$ is known also as the transition probability.

Using the formal solution (2.51) with the initial condition (2.57), the correlation function for any function $A(z)$ may be calculated as

$$\langle A(z(0)) A(z(t)) \rangle = \int dz f_0(z) A(z) e^{Lt} A(z) = \int dz dz' A(z) G_2(z, t|z', 0) A(z'), \quad (2.58)$$

where the joint probability G_2 is defined as

$$G_2(z, t|z', 0) = f_0(z) G(z, t|z', 0). \quad (2.59)$$

To find the diffusion coefficient, we have to calculate the correlation function for the velocity, $A(z) = v = \dot{x} = p/m$.

A general method of numerical solution of the FP equation (2.50) is described in a series of papers of Risken *et al.*, see also book ... It consists in expansion of functions depended on z over some complete orthonormal basis $\{\psi_\alpha(z)\}$. For the periodic external potential $\varphi(x)$ we may take

the plane waves $\psi_q(x) = (2\pi)^{-1/2} \exp(iqx)$ as the basis. For the FPK equation we need also to have the basic functions depended on momentum; it is natural to take the Hermite polynomials

$$\psi_n(\tilde{v}) = \frac{1}{\sqrt{n!}} \left(\frac{1}{2}\tilde{v} - \frac{\partial}{\partial \tilde{v}} \right)^n \psi_0(\tilde{v}), \quad \psi_0(\tilde{v}) = (2\pi)^{-1/4} \exp\left(-\frac{1}{4}\tilde{v}^2\right), \quad (2.60)$$

where $\tilde{v} = p/\sqrt{mk_B T}$.

The main condition which should be used in choosing the basis $\{\psi_\alpha(z)\}$, is that the matrix elements of the FP operator,

$$L_{\alpha\beta} = \int dz \psi_\alpha^*(z) L(z) \psi_\beta(z) \quad (2.61)$$

should have a simple form. Thus, the partial differential equation (2.50) reduces finally to the matrix equation.

It is clear that in numerical calculation we have to restrict the number Q of basic functions. The value Q depends on the shape of the potential $\varphi(x)$ as well as on the accuracy required. For example, to find the eigenvalues of Eq. (2.53) with the accuracy 10^{-3} at $\varepsilon_a/k_B T = 4$ the value $Q \geq 12$ should be used (Risken 1982 mol). The value of Q grows with the increase of the ratio $\varepsilon_a/k_B T$.

The matrix equation has also the exact solution in a form of continued fraction. Again, in its calculation we have to break up the fraction at some step Q . The value of Q depends on the friction coefficient η . For example, for $\eta/\omega_0 = 5$ we may take $Q = 8$, while for a small friction $\eta/\omega_0 = 0.01$ the value of Q increases up to $Q = 256$ to achieve the same accuracy 10^{-3} . Thus, the matrix continued fraction may be used successfully for not too small values of the friction coefficient and not too high amplitude of the external potential (or not too low temperature),

$$\begin{aligned} \varepsilon_a/k_B T &\lesssim 10, \\ \eta/\omega_0 &\gtrsim 2.5 \cdot 10^{-2}. \end{aligned} \quad (2.62)$$

Note that for typical adsystems such set of parameters is quite common.

2.3.4 Smoluchowski equation

To describe different methods of solution of the FP equation, let us consider first a simple one-dimensional Smoluchowski equation (2.24),

$$\frac{\partial \rho(x, t)}{\partial t} = D_f \left[\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial U}{\partial x} \frac{\partial \rho}{\partial x} + \frac{\partial^2 U}{\partial x^2} \rho \right] = \frac{\partial J}{\partial x}, \quad (2.63)$$

where we have defined

$$U(x) = \frac{\varphi(x)}{k_B T}, \quad J = -D_f \left(\frac{\partial \rho}{\partial x} + \rho \frac{\partial U}{\partial x} \right). \quad (2.64)$$

Recall that the equilibrium solution of Eq. (2.63) is $\rho_0(x) = \mathcal{N} \exp[-U(x)]$. The transform (2.54) leads to the operator

$$\tilde{L}_{\text{sm}} = D_f \left[\frac{\partial^2}{\partial x^2} - \tilde{U}(x) \right] \quad (2.65)$$

with

$$\tilde{U}(x) = \left[\frac{\partial \left(\frac{1}{2} U \right)}{\partial x} \right]^2 - \frac{\partial^2 \left(\frac{1}{2} U \right)}{\partial x^2}. \quad (2.66)$$

The operator (2.65) is Hermitian, thus Eq. (2.63) is the Schrödinger equation for the periodic “potential” $\tilde{U}(x)$, all eigenvalues of Eq. (2.63) are real, and the system dynamics corresponds to pure relaxation.

There are the following methods of solution of Eq. (2.63).

A constant external field

Let us add to the periodic potential $\varphi(x)$ the potential $\delta\varphi = -x\delta F$ corresponded to a d.c. external force δF , and look for a stationary periodic solution $\rho(x+a) = \rho(x)$ of the Smoluchowski equation (2.63) characterized by a constant flux J . It is easy to check that such a solution may be obtained by periodic repetition of the following function defined on the interval $(x_0, x_0 + a)$ (Ambegaokar, Ivanchenko):

$$\rho(x) = \mathcal{N} e^{-U(x)} \left[e^{-U(x_0)} \int_{x_0}^x dx' e^{+U(x')} + e^{-U(x_0+a)} \int_x^{x_0+a} dx' e^{+U(x')} \right], \quad (2.67)$$

where

$$U(x) = [\varphi(x) - x\delta F] / k_B T. \quad (2.68)$$

If the normalization is defined by Eq. (2.6), then the density (2.67) leads to the constant flux

$$J = -D_f \mathcal{N} \left\{ e^{-U(x_0)} - e^{-U(x_0+a)} \right\}. \quad (2.69)$$

Defining the static mobility as $B = J/\delta F$, taking the limit $\delta F \rightarrow 0$, and using the Einstein relation (2.17), we obtain (x_0 is arbitrary)

$$D_s = a^2 / 2T_*, \quad (2.70)$$

where

$$T_* = I_1' I_2 = \frac{1}{2D_f} \left[\int_{x_0}^{x_0+a} dx e^{-U(x)} \right] \left[\int_{x_0}^{x_0+a} dx' e^{+U(x')} \right]. \quad (2.71)$$

Using the quadratic approximation and putting $x_0 = x_s$ for I_1' and $x_0 = 0$ for I_2 , we obtain

$$D_s = \frac{\omega_0 \omega_s}{2\pi\eta} a^2 e^{-\Delta U}. \quad (2.72)$$

Band theory

The eigenvalue equation (2.56) for the Smoluchowski operator (2.65) takes the form

$$\left[-\frac{\partial^2}{\partial x^2} + \tilde{U}(x) \right] \tilde{\rho}_\lambda(x) = \frac{\lambda}{D_f} \tilde{\rho}_\lambda(x). \quad (2.73)$$

The potential $\tilde{U}(x)$ is the periodic function with the period a . Equation (2.73) is the Schrödinger equation for a “quantum” motion of an “electron” with the effective mass $m = \frac{1}{2}\hbar^2$ in the potential $\tilde{U}(x)$. Therefore, we may use standard methods of band theory (e.g., Kittel). As is well known, the eigenvalues $\mu_n(q) = \lambda_n(q)/D_f$ and the corresponding eigen-functions $\psi_q^{(n)}(x)$ of Eq. (2.73) are numerated by two quantum numbers, the band number n and the reduced wavevector q (q belongs to the first Brillouen zone, $|q| \leq \pi/a$). According to Bloch theorem, the eigen-functions have the form

$$\tilde{\rho}_{n,q}(x) = e^{iqx} u_n(x), \quad (2.74)$$

where $u_n(x)$ is a periodic function, so that only the eigenfunction with $q = 0$ has the period a required for the stationary solution.

connection D_s with $\lambda_n(q)$ see in Risken end part XI and refs therein

Evolution of a state $\psi_q^n(x)$, according to Eqs. (2.50) and (2.73), takes now the form

$$\psi(x, t) = e^{\tilde{L}t} \psi_q^n(x) = e^{-\lambda_n(q)t} \psi_q^n(x). \quad (2.75)$$

To find D_s which determines the system behavior at $t \rightarrow \infty$, it is enough to know the minimum eigenvalue only, thus we may restrict ourselves by the first Brillouen zone, $n = 1$.

Let us construct from the Bloch functions $\psi_q(x)$ of the first Brillouen zone the Wannier functions

$$\varphi(x + ra) = M^{-1/2} \sum_q e^{iqra} \psi_q(x), \quad (2.76)$$

$$\psi_q(x) = M^{-1/2} \sum_r e^{-iqra} \varphi(x + ra), \quad (2.77)$$

where M is the number of adsites. The function $\varphi(x + ra)$ is centered at the site r . Then, let us prepare an initial state as the Wannier function centered at $x = 0$, i.e. $\tilde{\rho}_{\text{ini}}(x) \propto \varphi(x)$, or

$$\rho_{\text{ini}}(x) = \mathcal{N} \rho_0^{1/2}(x) \int_{-\pi/a}^{+\pi/a} dq \psi_q(x), \quad (2.78)$$

where the normalization factor \mathcal{N} corresponds to one atom in the system,

$$\mathcal{N}^{-1} = \int_{-\infty}^{+\infty} dx \rho_{\text{ini}}(x). \quad (2.79)$$

Evolution of this state, according to Eq. (2.75), is described by the equation

$$\rho(x, t) = \mathcal{N} \rho_0^{1/2}(x) \int_{-\pi/a}^{+\pi/a} dq e^{-\lambda_1(q)t} \psi_q(x) \approx \rho_{\text{ini}}(x) - t \mathcal{N} \rho_0^{1/2}(x) \int_{-\pi/a}^{+\pi/a} dq \lambda_1(q) \psi_q(x) + \dots \quad (2.80)$$

This series is correct in the $\lambda_1(q) \rightarrow 0$ limit only. Now we can find the mean-square displacement of the atom,

$$\langle x^2(t) \rangle = \int_{-\infty}^{+\infty} dx x^2 \rho(x, t) = 2D_s t, \quad (2.81)$$

where

$$D_s = -\frac{1}{2} \mathcal{N} \int_{-\infty}^{+\infty} dx x^2 \rho_0^{1/2}(x) \int_{-\pi/a}^{+\pi/a} dq \lambda_1(q) \psi_q(x). \quad (2.82)$$

Substituting (2.77) into (2.82), changing integration over x by that over y introduced as $y = x - ra$, and taking into account that $\rho_0(x)$ is periodic with the period a , we obtain

$$D_s = -\frac{1}{2} \int_{-\pi/a}^{+\pi/a} dq \lambda_1(q) \frac{1}{\sqrt{M}} \sum_r e^{-iqra} (ra)^2 \left[\mathcal{N} \int_{-\infty}^{+\infty} dy \rho_0^{1/2}(y) \varphi(y) \right]. \quad (2.83)$$

According to Eq. (2.79), the expression in the square brackets is equal to one.

Then, differentiating the equality

$$M^{-1} \sum_{r=-\frac{1}{2}M+1}^{\frac{1}{2}M} e^{-iqra} = \delta_{q,0} \quad (2.84)$$

over q twice, we get

$$M^{-1} \sum_r e^{-iqra} (ra)^2 = -\frac{d^2}{dq^2} \delta_{q,0}. \quad (2.85)$$

Finally, substituting (2.85) into (2.83) and integrating by parts two times, we obtain

$$D_s = \frac{1}{2} \lim_{q \rightarrow 0} \frac{d^2}{dq^2} \lambda_1(q). \quad (2.86)$$

Examples:

For free atoms we have $\mu(q) = q^2$, thus $D_s = D_f$.

Strong coupling: $\mu(q) = -M_0 - 2M_1 \cos(qa)$, thus $D_s = a^2 M_1 D_f$, where

$$M_r = - \int dx \phi^*(x+ra) \left(-\frac{\partial^2}{\partial x^2} + \tilde{U}(x) \right) \phi(x). \quad (2.87)$$

Variational method, WKB, perturbation methods, etc.

Mean-first-passage time

If an atom was injected into the system at a point x_1 , then an average time needed for the atom to achieve another point x_2 , is called the mean-first-passage time (MFPT) (Gardiner p.185)

$$T_{\text{MFPT}}(x_1 \rightarrow x_2) = \frac{1}{D_f} \int_{x_1}^{x_2} dx \exp[U(x)] \int^x dy \exp[-U(y)]. \quad (2.88)$$

Let $x_1 = 0$ corresponds to a minimum of the potential $\varphi(x)$ and $x_2 = a$, to the nearest neighboring equivalent minimum. Then from Eq. (2.88) we have

$$D_s = a^2 / 2T_{\text{MFPT}}(0 \rightarrow a). \quad (2.89)$$

Let the potential $\varphi(x)$ has a single maximum between two nearest minima, which is located at the $x = x_s$ and has the height $\varepsilon_a = \varphi(x_s) - \varphi(0)$. Then the integral (2.88) can simply be found in the following two cases.

First, if

$$\Delta U \equiv \varepsilon_a / k_B T \gg 1, \quad (2.90)$$

then the function $\exp[+U(x)]$ has a sharp maximum at $x = x_s$, while the function $\int^x dy \exp[-U(y)]$ varies slowly at $x \sim x_s$ because the value of $\exp[-U(y)]$ is very small at $y \approx a_s$. Therefore, in the second integral in Eq. (2.88) we may put $x = x_s$ and take the resulting constant factor out of the first integral, so that

$$T_{\text{MFPT}}(0 \rightarrow a) \approx I_1 I_2 / D_f, \quad (2.91)$$

where

$$I_1 = \int_0^{x_s} dx \exp[-U(x)] \quad (2.92)$$

is proportional to the probability that the atom lies in the first well of the potential relief, while the value

$$I_2 = \int_0^{a_s} dx \exp[+U(x)] \quad (2.93)$$

is proportional to the flux over the barrier. Investigation of the function $T(a) = T_{\text{MFPT}}(0 \rightarrow a)$ shows that most of time the atom spends overcoming the barrier, i.e. for diffusion in the coordinate space.

Second, if

$$k_B T \ll 12 [\varphi''(\omega_{0,s})]^2 / \varphi'v(\omega_{0,s}), \quad (2.94)$$

then the potential $\varphi(x)$ near the extrema in a layer $\sim k_B T$ may be described by quadratic approximation,

$$\begin{aligned} \varphi(x) &\approx \frac{1}{2} m \omega_0^2 x^2 && \text{near } x = 0, \\ \varphi(x) &\approx \varepsilon_a - \frac{1}{2} m \omega_0^2 x^2 && \text{near } x = x_s. \end{aligned} \quad (2.95)$$

Substituting (2.95) into (2.92) and (2.93) and extending the integration limits to $\pm\infty$, we approximately obtain

$$I_1 \approx \frac{1}{2} \omega_0^{-1} \sqrt{2\pi m k_B T / m}, \quad I_2 \approx \exp(\Delta U) \omega_s^{-1} \sqrt{2\pi m k_B T / m}, \quad (2.96)$$

so that

$$T_{\text{MFPT}}(0 \rightarrow a) \approx (\pi\eta / \omega_0 \omega_s) \exp(\Delta U) \quad (2.97)$$

and

$$D_s \approx \frac{\omega_0 \omega_s}{2\pi\eta} a^2 \exp(-\Delta U). \quad (2.98)$$

Emphasize that the expression (2.98) is valid for a strong enough friction, $\eta \gtrsim \omega_{0,s}$, and at simultaneous validity of both conditions (2.90) and (2.94). For “non smooth” potentials $\varphi(x)$ such as, for example, the triangular or square-shape potentials, the condition (2.94) is not valid, so that the integrals (2.92) and (2.93) should be calculated exactly, and the pre-exponential factor will depend on the temperature T .

Thus, in the Smoluchowski (overdamped) case, the Arrhenius law

$$D = D_0 \exp(-\Delta U) \quad (2.99)$$

works only if $\Delta U \gg 1$ and also the potential is parabolic near the extrema; otherwise D_0 depends on T . Besides, $D(\omega \rightarrow \infty) = D_f$, and

$$D_s < D(\omega) < D_f \quad (2.100)$$

see Fig 2.6 from Dieterich p.539.

2.3.5 Low-friction limit

In the low-friction case it is convenient to pass from the variable $p \in (-\infty, +\infty)$ to the variable $\varepsilon \in (0, +\infty)$ defined by

$$\varepsilon = \frac{1}{2m} p^2 + \varphi(x) \quad (2.101)$$

(here we assumed $\varphi(0) = 0$). Because now one value of the new variable ε corresponds to two values $\pm p$ of the old variable, we have to introduce, instead of the distribution function, two new distribution functions $f_{\pm}(x, \varepsilon, t) \equiv f(x, \pm v(x, \varepsilon), t)$, or their symmetric and anti-symmetric combinations

$$f_{s,a}(x, \varepsilon, t) = f(x, +v(x, \varepsilon), t) \pm f(x, -v(x, \varepsilon), t), \quad (2.102)$$

where

$$v(x, \varepsilon) = \left| \sqrt{2(\varepsilon - \varphi(x)) / m} \right|. \quad (2.103)$$

Taking into account that $\frac{\partial}{\partial p} = \pm v(x, \varepsilon) \frac{\partial}{\partial \varepsilon}$ for $p \gtrless 0$, we obtain that the new distribution functions satisfy the following FP equations:

$$\frac{1}{v(x, \varepsilon)} \frac{\partial f_{\pm}}{\partial t} = \mp \left[\frac{\partial f_{\pm}}{\partial x} + F(x) \frac{\partial f_{\pm}}{\partial \varepsilon} \right] + m\eta \frac{\partial}{\partial \varepsilon} \left[v(x, \varepsilon) \left(1 + k_B T \frac{\partial}{\partial \varepsilon} \right) f_{\pm} \right], \quad (2.104)$$

$$\frac{1}{v(x, \varepsilon)} \frac{\partial f_{s,a}}{\partial t} = - \left[\frac{\partial f_{a,s}}{\partial x} + F(x) \frac{\partial f_{a,s}}{\partial \varepsilon} \right] + m\eta \frac{\partial}{\partial \varepsilon} \left[v(x, \varepsilon) \left(1 + k_B T \frac{\partial}{\partial \varepsilon} \right) f_{s,a} \right]. \quad (2.105)$$

An average value of a function $A(x, v)$ can now be calculated as

$$\langle A \rangle = \int_{x_1(\varepsilon)}^{x_2(\varepsilon)} dx \int \frac{d\varepsilon}{v(x, \varepsilon)} \left\{ \frac{1}{2} [A(x, +v(\dots)) + A(x, -v(\dots))] f_s(x, \varepsilon, t) + \frac{1}{2} [A(x, +v(\dots)) - A(x, -v(\dots))] f_a(x, \varepsilon, t) \right\}. \quad (2.106)$$

Putting $A = 1$ in Eq. (2.106), we get the normalization condition

$$1 = \iint \frac{dx d\varepsilon}{v(x, \varepsilon)} f_s(x, \varepsilon, t), \quad (2.107)$$

while putting $A = p/m$, we obtain the flux density

$$j = \iint dx d\varepsilon f_a(x, \varepsilon, t). \quad (2.108)$$

Let, for the sake of simplicity, the periodic function $\varphi(x)$ have one minimum (equal zero) at $x = 0$ and only one maximum at $x = \pi$ over the period 2π . In this case we have $x_1 = -\pi$ and $x_2 = +\pi$ for $\varepsilon > \varepsilon_a$, while for $0 < \varepsilon < \varepsilon_a$ the values $x_1(\varepsilon)$ and $x_2(\varepsilon)$ are determined by the roots of the equation $\varphi(x_{1,2}) = \varepsilon$. Then, let us explore the constant-field method, putting $\varphi(x) \rightarrow \varphi(x) - x\delta F$, and look for a stationary periodic solution, $f_{s,a}(x, \varepsilon) = f_{s,a}(x + 2\pi, \varepsilon)$, so that for $\varepsilon > \varepsilon_a$ we have

$$f_{s,a}(-\pi, \varepsilon) = f_{s,a}(+\pi, \varepsilon), \quad (2.109)$$

while for $0 < \varepsilon < \varepsilon_a$

$$f_a(x_1(\varepsilon), \varepsilon) = f_a(x_2(\varepsilon), \varepsilon) = 0. \quad (2.110)$$

At $\eta \rightarrow 0$ the variable ε is slow and x is fast, so in the first approximation we may put $f_{s,a}(x, \varepsilon) \approx f_{s,a}(\varepsilon)$. Then from (2.102) for $0 < \varepsilon < \varepsilon_a$ we obtain $f_a(\varepsilon) = 0$, and the equation (2.105) is satisfied if

$$\left(1 + k_B T \frac{\partial}{\partial \varepsilon} \right) f_s(\varepsilon) = 0, \quad (2.111)$$

which has the solution

$$f_s(\varepsilon) = 2\mathcal{N} e^{-\varepsilon/k_B T}. \quad (2.112)$$

For $\varepsilon > \varepsilon_a$, averaging Eq. (2.105) over x , we get

$$\delta F f_{a,s}(\varepsilon) = m\eta \left[\bar{v}(\varepsilon) \left(1 + k_B T \frac{\partial}{\partial \varepsilon} \right) f_{s,a}(\varepsilon) \right], \quad (2.113)$$

where

$$\bar{v}(\varepsilon) = \int_{-\pi}^{+\pi} dx v(x, \varepsilon). \quad (2.114)$$

The solution of Eq. (2.113) which matches with (2.112) at $\varepsilon = \varepsilon_a$, is:

$$f_a(\varepsilon) = 2\mathcal{N}e^{-\varepsilon/k_B T} \sinh \left[\frac{\delta F}{m\eta} \frac{g(\varepsilon)}{k_B T} \right], \quad (2.115)$$

$$f_s(\varepsilon) = 2\mathcal{N}e^{-\varepsilon/k_B T} \cosh \left[\frac{\delta F}{m\eta} \frac{g(\varepsilon)}{k_B T} \right], \quad (2.116)$$

where

$$g(\varepsilon) = \int_{\varepsilon_a}^{\varepsilon} \frac{d\varepsilon'}{v(\varepsilon')}. \quad (2.117)$$

In the limit $\delta F \rightarrow 0$ from (2.107) we get

$$\mathcal{N}^{-1} = \iint dx dp \exp \left\{ \left[-\frac{p^2}{2m} - \varphi(x) \right] / k_B T \right\} = \sqrt{2\pi m k_B T} \int_{-\pi}^{+\pi} dx e^{-\varphi(x)/k_B T}, \quad (2.118)$$

and for the flux we obtain the relation

$$j = 2\pi \int_{\varepsilon_a}^{\infty} d\varepsilon (2\mathcal{N}) e^{-\varphi(x)/k_B T} \frac{\delta F}{m\eta} \frac{1}{k_B T} g(\varepsilon). \quad (2.119)$$

For the sinusoidal substrate potential this approximation gives (Risken and Vollmer)

$$D_s = \frac{\pi \varepsilon_a}{\eta m} \exp \left(-\frac{\varepsilon_a}{k_B T} \right). \quad (2.120)$$

For $\eta \rightarrow 0$ we obtain the exact solution (Risken Vollmer 1979b)

$$D_s = D_f \frac{(\pi m k_B T / 2)^{-1/2} \int_{\varepsilon_a}^{\infty} d\varepsilon \langle v(\varepsilon) \rangle^{-1} \exp(-\varepsilon/k_B T)}{a^{-1} \int_0^a dx \exp(-\varphi(x)/k_B T)}, \quad (2.121)$$

where

$$\langle v(\varepsilon) \rangle = \frac{1}{a} \int_0^a dx |v(x, \varepsilon)|. \quad (2.122)$$

2.3.6 Intermediate friction

At low temperatures, $k_B T \lesssim \varepsilon_a$, the diffusion coefficient approximately takes the form

$$D_s = Rl^2, \quad (2.123)$$

where R is the probability of escaping of the adatom from a minimum of $\varphi(r)$ over one unit of time, and l is the free path length, i.e. the distance passed by the adatom after it overcame the barrier until it gets lost the kinetic energy and becomes trapped in another minimum of the potential relief. According to the Kramers theory, the escaping rate has the Arrhenius form,

$$R = R_0 \exp \left(-\frac{\varepsilon}{k_B T} \right), \quad (2.124)$$

where the pre-exponent $R_0 = R_{\text{ART}} B(\eta)$ depends on the rate of energy exchange with the substrate,

$$R_{\text{ART}} = \frac{\omega_0}{2\pi}, \quad (2.125)$$

and $B(\eta)$ is the following: for intermediate or high values of the friction coefficient, when

- (1) there is an equilibrium at the bottom of the potential well, and
- (2) the potential is parabolic at the bottom as well as at the saddle point, we have

$$B(\eta) = \sqrt{\tau^2 + 1} - \tau, \quad \tau = \eta/2\omega_s. \quad (2.126)$$

Thus, at intermediate friction the ART operates,

$$B(\eta) \approx 1. \quad (2.127)$$

At large friction, the friction restricts the rate of transition over the barrier (the saddle configuration),

$$B(\eta) \approx \frac{\omega_*}{\eta}. \quad (2.128)$$

The value ω_* which separates these two limiting cases, may be estimated in the following way. Near the barrier $\varphi(x) \approx \varepsilon_a - \frac{1}{2}m\omega_s^2x^2$, the adatom velocity is $v(x) \approx \omega_s x$, so that during the transition the adatom loses an energy $\Delta\varepsilon = \int dx F = m \int dx \eta v = m \int dx x \eta \omega_s \sim m \eta \omega_s x^2$. Thus, the rate of the transition over the barrier is slowed down if $\Delta\varepsilon(x) > m\omega_s^2x^2$, or $\omega_* = \omega_s$.

At small friction [Melnikov] the distribution at the well's bottom is nonequilibrium, and therefore

$$B(\eta) \approx \frac{\eta}{\eta_*}, \quad \eta_* = \frac{\omega_0 k_B T}{2\pi \varepsilon_a}, \quad (2.129)$$

so that $l > a$. The value of η_* can be estimated as follows. Overcoming the barrier, the adatom has an energy $\sim \varepsilon_a + k_B T$ and moves with a velocity $v \sim (\varepsilon_a/m)^{1/2}$, so that it passes the distance a for a time $\tau \sim a/v$. During the transition the atom loses an energy $\Delta\varepsilon \sim (\varepsilon_a + k_B T)(1 - e^{-\eta\tau}) \sim \varepsilon_a \eta \tau \sim \varepsilon_a \eta a/v \sim a \eta (m\varepsilon_a)^{1/2}$. Long jumps appear when $\Delta\varepsilon < k_B T$, so that $\eta_* \sim \frac{k_B T}{a(m\varepsilon_a)^{1/2}} \sim k_B T/\varepsilon_a$, where we used $\varepsilon_a \sim m\omega_0^2 a^2$.

The results (2.129) are confirmed analytically (Melnikov, Hanggi) as well as numerically (e.g. BoCartling).

2.4 Kramers theory

For an approximate description of system dynamics, often the adiabatic approximation is used, when one assumes that the system moves along the so-called *adiabatic trajectory*, which connects the saddle points of the energy surface $\varphi(r)$ with the points corresponded to minima of the function $\varphi(r)$, along the curve of steeped descent.

give formula for 1 - saddle point, and 2 - saddle trajectory from my SS finite

When such a choice is not unique, then the saddle trajectory corresponds to that one which passes through the saddle point with smaller energy.

The atomic motion along the adiabatic trajectory is one-dimensional, and the system energy is periodic with the period a and the amplitude ε_a called the activation energy. Therefore, the diffusion coefficient is determined by (2.124).

Thus, in the case of strong friction, $\eta > \sim \omega_s$, the value of the diffusion coefficient is restricted by the diffusion in the coordinate space when the adatom overcomes the barrier, and $D_s \propto \eta^{-1}$. In the case of small friction, $\eta < \eta^*$, the escaping rate is restricted by diffusion in the energy space, the adatom should wait before it will get enough energy from the substrate to overcome the barrier, $R \propto \eta$. This effect is overcompensated by an increase of the free path length, $l \approx a(\eta^*/\eta)$ (Zhdanov). Thus, in this regime $D_s \propto \eta^{-1}$ as well. However, in real adsystems the existence of long jumps is problematic. First, there always exists the nonlinear coupling

between the motion along the adiabatic trajectory and others degrees of freedom, that decreases the mean free path l . Second, for the triangular or hexagonal substrate symmetry, the adiabatic trajectory is not a straight line in the coordinate space, thus overcoming the barrier, the adatom could go out the adiabatic trajectory and will swing in the new well, that also reduces l . Thus, in the low friction case one may expect the dependence $D_s \propto \eta$.

Finally, for the intermediate friction, $\eta^* \ll \eta \lesssim \omega_s$, the coefficient D_s does not depend on η , and the Kramers theory justifies the using of the ART theory (Eiring). Recall that in the framework of the ART, the probability of escaping of the adatom from the potential well is determined as the flux of atoms going into one direction crossing some surface which separates the nearest minima of the function $\varphi(r)$, and, main, it is assumed that the distribution function corresponds to the equilibrium state. Therefore, the ART neglects by two effects: first, by a deviation of the distribution function from the equilibrium form, and second, by the “back” flux of atoms, i.e. the ART does not include the trajectories where the adatom does not stop in a next well but is reflected and goes back to the same well it was escaped from.

The absolute rate theory (ART) states the following:

$$R = \frac{J}{\mathcal{N}}, \quad (2.130)$$

where the flux

$$J = \frac{1}{2\delta} \int_{-\delta}^{+\delta} dx \int_0^\infty dp \frac{p}{m} e^{-E/k_B T} \quad (2.131)$$

is determined by the integral near the saddle point, the normalization factor

$$\mathcal{N} = \int d\Gamma e^{-E/k_B T} \quad (2.132)$$

comes from the integral near the minimum, and

$$d\Gamma = \frac{dx dp}{2\pi\hbar} d\Gamma_T, \quad (2.133)$$

$d\Gamma_T$ corresponds to the thermostat (the substrate degrees of freedom) and to other degrees of freedom of the adatom. The total energy of the system is

$$E = \varphi(x) + \frac{p^2}{2m} + E_T. \quad (2.134)$$

Taking into account that

$$\frac{1}{\delta} \int_{-\delta/2}^{+\delta/2} dx e^{-\varphi(x)/k_B T} \approx e^{-\varepsilon_a/k_B T}, \quad (2.135)$$

$$\int_0^\infty \frac{dp}{2\pi\hbar} \frac{p}{m} e^{-p^2/2mk_B T} = \frac{k_B T}{2\pi\hbar}, \quad (2.136)$$

we obtain $R = R_0 e^{-\varepsilon_a/k_B T}$, where

$$R_0 = \frac{k_B T}{2\pi\hbar Z_A} A, \quad A = \frac{Z_T^*}{Z_T}, \quad (2.137)$$

$$Z_T = \int d\Gamma \exp(-E/k_B T) \quad (2.138)$$

is the statistical sum of the adatom at the minimum, and Z_T^* is that for the adatom in the saddle configuration. Recalling that the free energy $F = -k_B T \ln Z$, we obtain

$$A = \exp\left(-\frac{\Delta F_\perp}{k_B T}\right). \quad (2.139)$$

Next: $\Delta F_\perp = \Delta E_\perp - T \Delta S_\perp$, thus

$$A = \exp\left(\frac{\Delta S_\perp}{k_B}\right), \quad (2.140)$$

where ΔS_\perp is the difference of entropies in the saddle and minimum configurations. Putting $E = n\hbar\omega_0$, we get

$$Z_A = \left[1 - \exp\left(-\frac{\hbar\omega_0}{k_B T}\right)\right]^{-1}, \quad (2.141)$$

thus

$$R_0 = A \frac{k_B T}{2\pi\hbar} \left(1 - e^{-\hbar\omega_a/k_B T}\right), \quad A = \frac{\prod_i \left(1 - e^{-\hbar\omega_i/k_B T}\right)}{\prod_i \left(1 - e^{-\hbar\omega_i^*/k_B T}\right)}. \quad (2.142)$$

For classical mechanics, $k_B T \gg \hbar\omega_{a,i}$,

$$R_0 = A \frac{\omega_a}{2\pi}, \quad A = \frac{\prod_i \omega_i}{\prod_i \omega_i^*}. \quad (2.143)$$

Using ART for N -dimensional configuration space, let $i = 1$ corresponds to the saddle trajectory, and $i = 2, \dots, N$ are orthogonal to it. Then ART gives

$$R = R_{1D} A, \quad (2.144)$$

where A is called the entropy factor [Vineyard 1957], $A = F^*/F = \exp(k_B \Delta S)$, F and F^* are the statistical sums for all degrees of freedom except the adiabatic one, for the minimum and saddle configurations correspondingly, and ΔS is the difference in entropy of the minimum and saddle configurations. Assuming that for all degrees of freedom with $i \geq 2$ the motion is vibrational, we get

$$A = \prod_{i=2}^N \left(\frac{\omega_i}{\omega_i^*}\right) \quad (2.145)$$

for $k_B T \gg \hbar\omega_i$.

In the low-friction limit the multi-dimensional corrections were found in (M.Borkovec and B.J.Berne, J.Chem.Phys. 82(1985)794):

$$R_0 = \eta \left(\frac{\varepsilon_a}{k_B T}\right)^N \frac{1}{N!} \Omega. \quad (2.146)$$

Even for a single adatom we have $N = 3$, because the modes are coupled owing to the anharmonicity of the potential, and this coupling results in energy exchange between the modes with a rate η_{ex} ; the ART should operate as long as $\eta \gtrsim \eta_{\text{ex}}$ (?)

The ART result $D_0 = (\omega_0/2\pi) a^2$ follows also from the exact (?) solution of the FPK equation; also it is well confirmed by MD simulation [Doll 1985] for $m_a \gtrsim m_s$. The reason are the following: (i) $R < R_{\text{ART}}$ because of “back” jumps (the atom does not stop in new well after the jump but jumps back instead), and (ii) $l > a$ because long jumps always exist; these two factors approximately compensate one another.

2.5 Computer simulation: Molecular Dynamics

There are several papers (take refs from Zhdanov) where the dynamics of atomic motion was investigated with computer simulation. One class of works uses the MD method completely, i.e. the substrate is modeled by a cluster of finite number of atoms interacting with some law (e.g., with the Lennard-Jones potential), and then the Newton motion equations were solved and the average was done. Peculiarity of the full MD: the interaction potential should be realistic to provide stability of the crystal lattice.

Another class of works uses a “restricted” MD method for adatom and few nearest substrate atoms only, while the remainder of the substrate is treated within the harmonic approximation; this leads to a generalized Langevin equation (GLE) (e.g., see Adelman and Doll 1976, Tully 1980).

Important in MD: (i) it must be $T \ll T_{\text{melt}}$, (ii) it also should be $T \ll T_{\text{pair}}$ if defects (vacancy plus extra adatom) may be created, and (iii) T should be high enough to have an essential mobility of the atom and obtain a reliable statistics; all together results in a condition that reasonable temperatures should be of order $T \sim 0.5 T_{\text{melt}}$.

The calculations showed that the ART gives correct values for the diffusion coefficient D_s (e.g., Voter 1984a, 1984b). At high temperatures a probability of long jumps of the adatom ($l > a$) increases; this leads to $D_s > D_{\text{ART}}$ (Tully et al 1979, NoorBatcha 1985). For example, MD for Na–Na (DeLorenzi 1985) at $T \approx 0.4 T_{\text{melt}}$ showed long jumps on the (110) b.c.c. surface, and this effect was even more pronounced for the motion along furrows on the furrowed (112) b.c.c. surface; however, this may be an artifact because only the phonon friction was taken into account (so η was lower than the real could be). Besides, there exist also “back jumps”, when after escaping from a potential well the adatom reflects from the potential relief (?) and goes back to the same well, that decreases D_c comparing with D_{ART} . However, both effects approximately compensate one another, so finally $D_s \approx D_{\text{ART}}$ (Zhdanov [90?]).

In the discussion presented above, a role of the substrate was assumed to be passive: it produced the external periodic potential $\varphi(r)$, and also provides the “friction”, i.e. the energy exchange between the adatom and the substrate. However, the taking into account the motion of substrate atoms leads additionally to the following important effects:

(1) At $T > 0$ the substrate atoms vibrates with some amplitude δa , this results in that the average amplitude of the external potential produced by the substrate, should depend on T : $\varepsilon_a(T) \approx \varepsilon_a(0) \exp(-\dots \langle \delta a^2 \rangle)$. This is an analog of the Debye-Waller effect (see Metiu 1976).

(2) The substrate atoms near the adatom are displaced from their equilibrium positions to be adjusted to the adatom position (the so-called “polaronic effect”, see Metiu 1976). Clearly that the “adjusting” exists for the adatom at the potential minimum as well as for the adatom in the saddle configuration (for example, the substrate atoms may go away a little bit to allow the adatom to move, see MD of DeLorenzi 1985 for Na-Na(110)). Clearly also that a magnitude of the polaronic effect depends on the adatom velocity (and, therefore, on T), because at a high adatom velocity the substrate atoms will have no enough time to adjust themselves to the adatom position. Thus, in fact it moves not an isolated adatom, but a “quasi-adatom” (or “pseudo-molecule”), i.e. a dressed adatom, the adatom plus a cloud of virtual substrate phonons. This quasiparticle is characterized by its own m_{eff} and $\varphi_{\text{eff}}(r)$, all parameters being dependent on T .

Both effects described above, lead to an increase of D_s comparing with the value calculated for the fixed positions of substrate atoms. For example, for the H-Cu(100) adsystem D_s increases in few times at low T and in 1.3 times at $T = 1000$ K (Valone 1986, Lauderdale 1986).

(3) Finally, in some cases (for example, on furrowed substrates) the substrate atoms may

participate actively in the diffusion process, when the adatom “pushes” the substrate atom from its place in the lattice and occupies that place, while the “pushed” substrate atom moves further instead of the adatom. Such a diffusion mechanism, sometimes called the “exchange” mechanism, was observed in MD simulation of the Au- or Ir-Pt(110) adsystems (Garofalini 1981), and also for self-diffusion of an adatom on the (100) b.c.c. surface and for diffusion across the furrows on furrowed (112) b.c.c. surface (Na-Na, DeLorentzi 1985). Clearly that the latter mechanism leads to the increase of D across the furrows. However, the exchange mechanism belongs already to collective diffusion mechanisms considered in Chapter ??.

2.6 Lattice models

For chemically adsorbed atoms the amplitude of the external potential $\varphi(r)$ produced by the substrate, is typically not small, $\varepsilon_a \gtrsim k_B T$. In this case, even the use of the one-dimensional FKP equation leads to a partial differential equation for three variables, which is too complicated. The problem becomes even more complicated if (a) $\varphi(r)$ is 2D, and different symmetries should be studied, (b) the elementary cell is not simple (non Bravais), and (c) besides the absolute minima, the function $\varphi(r)$ has additional local minima.

In these cases for a qualitative study of diffusion one may use lattice-gas models, where it is assumed that the adatom can sit in fixed positions on the surface only, in the so-called adsorption centers, corresponded to minima of $\varphi(r)$. Then, we must assume that the atom can jump from one site to another one, and that jump’s time is much shorter than the mean residence time τ_r , this is valid if $k_B T \ll \varepsilon_a$. Let $P(i; t | i_0; t_0)$ denote the probability for the adatom to be at a given center i ; it is determined as the integral of the distribution function $f(x, p; t)$ over neighboring of the site i . The probability of a transition of the adatom from the center i to another center i' per one time unit is denoted by $R_{i'i} \equiv R(i' \leftarrow i)$; to know this parameter we have, of course, to solve the corresponding FPK equation; methods how to estimate it see in Sect. ?. Then, evolution of $P(t)$ is described by the kinetic equation

$$\frac{dR(i; t)}{dt} = \sum_{i' (i' \neq i)} [R_{i'i} P(i'; t) - R_{i'i} P(i; t)]. \quad (2.147)$$

The stationary solution of this equation must give the equilibrium state,

$$\dots \quad (2.148)$$

This *may be* satisfied automatically if the detailed balance condition is fulfilled

$$\dots \quad (2.149)$$

(Important comment: this is the simplest but not the only way of solution; besides, this condition overestimate ...). Then, to find a solution, we make the Laplace transform over t and the Fourier transform over the lattice i , and we come to a standard eigenvalue problem (the same as in band theory) with the Hermitian operator, thus eigenvalues are real, and spectrum is purely relaxation (overdamped; the vibrational modes are lost at all). [Dieterich p.530].

The simplest model: the jumps are allowed to nearest neighboring (NN) sites only, and the elementary cell is simple; in this case:

$$D = g a^2 R, \quad g = Z/2\nu. \quad (2.150)$$

Here g is called the geometrical factor, Z is the number of NN sites in the lattice, and ν is the system dimension ($\nu = 2$ for surface diffusion).

Complex unit cell ...
Several local minima ...
Long jumps ...

Chapter 3

Collective Diffusion

If the particles interact between themselves, the diffusion coefficient changes, in particular, due to collective, or concerned motion of atoms, for example by a relay-race mechanism. Often such effects may be described as different kinds of quasiparticles.

see Bokstein, refs to Manning

3.1 Mechanisms of interaction between adsorbed atoms

The mechanisms of interaction between the adatoms are the following:

(1) At short distances, the mechanism of interaction is the same as for atoms in a molecule – at very short distance the atoms experience a strong repulsion due to overlapping of atomic cores, while at less short distances, the overlapping of electronic shells leads to exponentially decaying attraction as in a usual chemical bond. This is the so-called “direct” interaction; because the electronic orbitals are only partially filled, the magnitude of attraction of chemisorbed atoms is smaller than that in a free molecule.

(2) The chemically adsorbed atoms experience the so-called “indirect” interaction due to exchange of electrons through the electron gas of the substrate. This interaction is long-ranged (it decays with distance according to a power law) and oscillating; its details depend on the electronic structure of the substrate, including a possible existence of surface electronic states.

(3) As is well known, the energy of interaction of two charges e separated by a distance r , being Coulomb in vacuum, undergoes screening owing to the substrate; in the bulk of a dielectric material the law changes as $e^2/r \rightarrow e^2/r\epsilon$, while in a metal, as $e^2/r \rightarrow e^2/r\epsilon(k\omega) \rightarrow (e^2/r)e^{-\kappa r}$; but for two charges near the surface this laws change to $2p^2/r^3$ or $e^2/r(\epsilon + 1)$ for the metal or dielectric substrate, respectively. Therefore, if the adatoms are charged, they experience the Coulomb repulsion for short distances on a metal surface and for any distance being adsorbed on a semiconductors or dielectric surface, while being adsorbed on the metal surface, at long distances the interaction always corresponds to the long-ranged dipole-dipole repulsion.

(4) In all systems, it exists the elastic interaction between the adatoms; it decays with the distance as r^{-3} .

The interatomic interaction leads to: (a) a change of the relief for motion of nearest atoms (Langmuir, saddle), (b) a concerned motion of adatoms, and (c) a mutual energy exchange \rightarrow additional friction mechanism.

3.2 Different diffusion coefficients

We assume that there is local equilibrium in the system.

3.2.1 Susceptibility

The susceptibility χ may be calculated by one of the following formulas:

$$\chi = \frac{\rho}{k_B T} \left(\frac{\partial \mu}{\partial \rho} \right)_{T, A}, \quad (3.1)$$

$$\chi = \frac{1}{k_B T \rho \kappa}, \quad \kappa = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial \Pi} \right)_{T, A}, \quad (3.2)$$

$$\chi = \frac{N}{\langle (\Delta N)^2 \rangle}. \quad (3.3)$$

Here μ is the chemical potential, $\rho = N/A$, A is the area, Π is the two-dimensional pressure.

Free 1D gas

Let $a_0 = L/N$. Then

$$F = -N k_B T \ln \left[\left(\frac{m k_B T}{2\pi \hbar^2} \right)^{1/2} a_0 \right] \quad (3.4)$$

$$S = N k_B \left\{ \frac{1}{2} + \ln \left[\left(\frac{m k_B T}{2\pi \hbar^2} \right)^{1/2} a_0 \right] \right\} \quad (3.5)$$

$$E = \frac{1}{2} N k_B T \quad (3.6)$$

$$\mu = -k_B T \ln \left[\left(\frac{m k_B T}{2\pi \hbar^2} \right)^{1/2} a_0 \right] \quad (3.7)$$

$$\langle (\Delta N)^2 \rangle = \langle N \rangle \quad (3.8)$$

$$\frac{\partial \mu}{\partial N} = \frac{k_B T}{N} \quad (3.9)$$

$$\chi = 1 \quad (3.10)$$

Free lattice gas

Let M be the number of sites, N be the number of atoms, and W be the number of undistinguished ways to put the atoms on the sites.

$$W(N, M) = \frac{M^N}{N!} \quad (3.11)$$

$$S = k_B \ln W = k_B N \ln M - k_B \ln N! \quad (3.12)$$

Stirling formula

$$S \approx k_B [N \ln M - N(\ln N - 1)] \quad (3.13)$$

$$F = \varepsilon N - TS = N(\varepsilon - k_B T \ln M) + k_B T N(\ln N - 1) \quad (3.14)$$

$$\mu = \frac{\partial F}{\partial N} = (\varepsilon - k_B T \ln M) + k_B T \left(\ln N - 1 + N \frac{1}{N} \right) \rightarrow k_B T \ln N \quad (3.15)$$

$$\frac{\partial \mu}{\partial N} = \frac{k_B T}{N} \quad (3.16)$$

$$\chi = \frac{N}{k_B T} \frac{\partial \mu}{\partial N} = 1 \quad (3.17)$$

Langmuir gas

$$W(N, M+1) = W(N, M) + W(N-1, M) \quad (3.18)$$

$$W(N, M) = \frac{M!}{N!(M-N)!} \quad (3.19)$$

Statistical sum

$$\mathcal{Z} = \sum_N \frac{M!}{N!(M-N)!} \quad (3.20)$$

$$S = k_B \ln W = -k_B [\ln N! + \ln(M-N)!] \quad (3.21)$$

$$\approx -k_B \{N(\ln N - 1) + (M-N)[\ln(M-N) - 1]\} \quad (3.22)$$

$$F = k_B T \{N(\ln N - 1) + (M-N)[\ln(M-N) - 1]\} \quad (3.23)$$

$$\mu = k_B T [(\ln N - 1) + 1 - \ln(M-N)] = k_B T \ln \frac{N}{M-N} \quad (3.24)$$

$$\frac{\partial \mu}{\partial N} = k_B T \left(\frac{1}{N} + \frac{1}{M-N} \right) = k_B T \frac{M}{N(M-N)} \quad (3.25)$$

$$\chi = \frac{M}{M-N} = \frac{1}{1-\theta} \quad (3.26)$$

1D gas of hard rods

$$\dots \quad (3.27)$$

3.2.2 Self-diffusion coefficient

The self-diffusion coefficient differs from D_μ in that it does not include correlations. It may be measured indirectly only, e.g., by inelastic scattering (?). In experiment, one of the atoms must be labelled; rigorously speaking, this will be already another particle. Solution: the “label” should not influence on the interaction of a given atom with other atoms, only the experimental setup should feel this label; e.g., use an isotope.

Notice that this is the example when in classical mechanics the particles are identical (undistinguished in principle).

Generalizing the definition (??) for a system of interacting atoms, i.e. considering the displacement of a given atom, we obtain

$$D_s = \lim_{t \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N [r_i(t) - r_i(0)]^2 / 2\nu t, \quad (3.28)$$

or

$$D_s = \lim_{\omega \rightarrow 0} \int_0^\infty dt e^{i\omega t} \frac{1}{N} \sum_{i=1}^N \frac{1}{\nu} \sum_{\alpha=1}^{\nu} \langle v_{i\alpha}(t) v_{i\alpha}(0) \rangle. \quad (3.29)$$

3.2.3 Mobility

The external force $\delta F(x, t)$ induces the total flux of atoms

$$J = \sum_{i=1}^N v_i, \quad \langle J \rangle = \langle j \rangle \rho, \quad j = \frac{1}{N} \sum_{i=1}^N v_i, \quad (3.30)$$

where N is the number of atoms per area unit. When the force is infinitesimal, we may write

$$\langle J(x, t) \rangle = \rho \int^t dt' B(t-t') \delta F(t'). \quad (3.31)$$

For the equilibrium state from the fluctuation-dissipation theorem it follows

$$B(t) = \frac{1}{\rho k_B T} \langle J(t) J(0) \rangle \Theta(t). \quad (3.32)$$

Fourier transform ...

Using formally the Einstein relation, we may define the collective diffusion coefficient as

$$D_\mu = k_B T B(\omega \rightarrow 0) = \frac{1}{\rho} \int_0^\infty dt \langle J(t) J(0) \rangle. \quad (3.33)$$

Thus,

$$D_\mu = D_s + \frac{1}{\rho} \sum_{i \neq j} \int_0^\infty dt \langle v_i(t) v_j(0) \rangle. \quad (3.34)$$

Here D_s accounts the interaction through the correlation of *positions* of nearest particles because of, e.g., changing of activation barriers, while the second term describes the interaction through the correlation of *motion* of nearest particles

3.2.4 Chemical diffusivity

A very important issue is the chemical diffusion coefficient D_c which couples the flux J with the gradient of density,

$$\langle J \rangle = -D_c \frac{\partial}{\partial x} \langle \rho \rangle, \quad (3.35)$$

when other parameters are kept constant. Let us couple D_c with D_μ .

Let us pick up an interval of length r_0 along the line perpendicular to the concentration gradient (r_0 is the mean distance between adatoms). Then the force acting on a given atom, is

$$\delta F = r_0 \Delta \Pi, \quad (3.36)$$

where $\Delta \Pi$ is the difference of the 2D pressure acting from the opposite sides on the given interval:

$$\Delta \Pi = \Pi(\text{left}) - \Pi(\text{right}) = r_0 \frac{\partial \Pi}{\partial x}. \quad (3.37)$$

The two-dimensional pressure (or surface tension) is defined as the derivative of the free energy F of the adlayer over the area A ,

$$\Pi = -\frac{\partial F(A)}{\partial A} = -\frac{1}{r_0^2} \frac{\partial F(N)}{\partial N} = -\frac{1}{r_0^2} \mu, \quad (3.38)$$

where we used $A = r_0^2 N$, and $\mu = \partial F / \partial N$ is the chemical potential. Substituting (3.37) and (3.38) into (3.36), we find the force acting on the particle,

$$\delta F = -\frac{\partial \mu}{\partial x}. \quad (3.39)$$

Using (3.36) and (??), we get

$$\rho \delta F = \frac{\partial \Pi}{\partial x} = \frac{\partial^2 F}{\partial x \partial A} = \frac{\partial}{\partial x} \frac{\partial F}{\partial N} \frac{\partial N}{\partial A} = \left(\frac{\partial}{\partial x} \mu \right) \rho. \quad (3.40)$$

Thus,

$$\langle J \rangle = \rho B \delta F = \rho \frac{1}{k_B T} D_\mu \delta F = \rho \frac{1}{k_B T} D_\mu \frac{\partial \mu}{\partial x}. \quad (3.41)$$

For *homogeneous one-phase system* we have $\mu = \mu(\rho)$ so that

$$\frac{\partial \mu}{\partial x} = \frac{\partial \mu}{\partial \rho} \frac{\partial}{\partial x} \langle \rho \rangle. \quad (3.42)$$

Substituting (??) into (??), we obtain

$$D_c = \chi D_\mu, \quad (3.43)$$

where

$$\chi = \frac{\rho}{k_B T} \left(\frac{\partial \mu}{\partial \rho} \right)_{T,V} \quad (3.44)$$

is known as thermodynamic factor.

Note:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{T,\Pi} = \left(\frac{\partial E}{\partial N} \right)_{S,V} = \left(\frac{\partial W}{\partial N} \right)_{S,\Pi} = -T \left(\frac{\partial S}{\partial N} \right)_{S,V}. \quad (3.45)$$

From

$$\langle J \rangle = -D_c \frac{\partial \rho}{\partial x} = -\chi D_\mu \frac{\partial \rho}{\partial x} = \frac{\rho}{k_B T} D_\mu \delta F \quad (3.46)$$

we have

$$\chi = -\frac{\rho \delta F}{k_B T (\partial \rho / \partial x)}. \quad (3.47)$$

The force acting on a unit of area, is

$$\rho \delta F = \frac{\partial \Pi}{\partial x} = \frac{\partial \Pi}{\partial \rho} \frac{\partial \rho}{\partial x}. \quad (3.48)$$

Thus,

$$\chi = -\frac{1}{k_B T} \frac{\partial \Pi}{\partial \rho} = -(\?) \frac{1}{k_B T \rho \kappa}, \quad (3.49)$$

where

$$\kappa = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial \Pi} \right)_{T,V} \quad (3.50)$$

is the isothermal compressibility.

Finally, because

$$\langle (\Delta N)^2 \rangle = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{T,A} = k_B T \rho \kappa_T N, \quad (3.51)$$

we have

$$\chi = \frac{N}{\langle (\Delta N)^2 \rangle}. \quad (3.52)$$

Experiment: smoothing of an initial step-like distribution ...

3.3 Ideology of quasiparticles

In order to describe collective effects, a standard approach in theoretical physics is to use the concept of quasiparticles. Diffusion is the process of mass transfer, therefore quasiparticles responsible for it, should correspond to localized topologically stable objects. An example – kinks – is given in the next Section.

Concentration might be nonconstant ...

If there are quasiparticles of two opposite signs such as, for example, the kinks and antikinks in the FK model, they may be thermally created (e.g., the $k\bar{k}$ pairs) – but this process will contribute to self-diffusion only (?).

Quasiparticles may be created at defects, boundaries ...

The main steps in this approach are the following:

- (1) to find parameters of the quasiparticles (which may depend on T),
- (2) to find their concentration, and
- (3) to couple D with the diffusion coefficient of the quasiparticles.

If the system allows the existence of different types of quasiparticles, an essential complication may emerge because of different types of diffusion coefficients, including D_{ij} (hetero-diffusion).

In comparing with experiments, one should be careful: what is measured in fact? Averaged D depends on all ...

3.4 One-dimensional chain (the Frenkel-Kontorova model)

The FK model ...

But the standard FK model is oversimplified. Generalizations:

- (1) A finite FK chain (mobility of clusters)
- (2) $V_{\text{int}} \neq$ harmonic:
 - anharmonic but convex, for example, exponential (= Toda) or power $\rightarrow D_c(\theta)$ takes the shape of the inverse Devil's staircase
 - nonconvex \rightarrow first-order phase transitions \rightarrow modulated (polymerized) GS
- (3) $V_{\text{sub}} \neq$ sinusoidal
 - the N- and I- PN barriers
 - shape modes
 - polikink systems
- (4) transverse degree of freedom \rightarrow zigzag kinks
- (5) deformable substrate
- (6) nonlocal friction
- (7) impurities

3.5 Gas model

...

3.6 Lattice models

The lattice models are indispensable in studies of the 2D system of interacting atoms. They may be applied, if and only if:

- (a) $\varepsilon_a \gg k_B T$,

(b) $\varepsilon_{\text{int}} \ll \varepsilon_a$,

(c) the atomic jumps are individual (in principle, one may generalize the model to include double *etc.* jumps, but this leads to a lot of new parameters \rightarrow unserious),

(d) the model is simple enough (otherwise there are too many poorly defined parameters).

Langmuir model \equiv hard-core model: not more than one atom in one elementary cell (the reason: core repulsion \rightarrow two atoms have no enough room to occupy the same potential well), and also $R(\theta) = R_0(1 - \theta)$ (blockade of a jump to the occupied site).

In the simplest case, when the NN interaction is ignored, the results are the following: $\mu = \mu_0 + k_B T \ln \theta / (1 - \theta)$, $\chi = 1 / (1 - \theta)$, $D_s(\theta) = D_s(0)(1 - \theta)$, and $D_c(\theta) = D_s(0)$. Thus, $D_c(\theta) \geq D_s(\theta)$. Physics: when $\nabla \theta \neq 0$, we have also a gradient of concentration of vacancies, $\nabla(1 - \theta) = -\nabla \theta \neq 0$, directed in the opposite direction, and the flux of vacancies increases the total flux. At $\theta \rightarrow 1$, $D_s \rightarrow 0$ because almost all sites are occupied, but $D_c \neq 0$ due to the flux of vacancies.

Generalization for a complex elementary cell:

(i) N equivalent sites in one cell \rightarrow spin- N model (see Dieterich p.547);

(ii) nonequivalent sites;

(iii) NNN interactions;

(iv) interaction in the saddle configuration (increases the number of parameters).

This model is equivalent to the Ising spin- $\frac{1}{2}$ model. When the interaction of NN is included, the following methods of solution may be used: SCF, Bethe-anzats, “chemical” approximation (Zhdanov book)

3.7 2D Frenkel-Kontorova model

system of coupled FK chains

vector 2D FK model

3.8 Phase transitions

The model must be 2D — in 1D system there are no phase transitions

3.8.1 First-order phase transition

When two phases I and II coexists in the system, then there are two self-diffusion coefficients $D_s^{(I)}$ and $D_s^{(II)}$, and an average coefficient is $D_s = \theta_I D_s^{(I)} + \theta_{II} D_s^{(II)}$. However, the chemical diffusion coefficient is zero, $D_c = 0$, because $\chi = 0$, $\nabla \theta \neq 0$ but $j = 0$. But:

A – defects \rightarrow dispersion of the boundary between two phases $\rightarrow D_c \neq 0$ (Lyuksyutov). Note: the boundary between the phases is (typically?) fractal.

B – close to T_c (but for $T > T_c$), where $G_i < 1$, there are fluctuating domains \rightarrow motion of domains and, depending on the domain size, its mobility may be larger or smaller than the background mobility; therefore, D may be lower or higher than ...; also it should be a compensation effect ...

3.8.2 Second-order phase transition

Cusp on $D(\theta)$ (Tarasenko: renormalization group, Zhdanov?)

Note: SCF incorrectly gives jumps in $D(\theta)$

3.9 Computer simulation

3.9.1 Monte Carlo simulation

Lattice model, Ising-type

Metropolis algorithm

it is relaxation dynamics, Markov dynamics

3.9.2 Molecular Dynamics simulation

...

Chapter 4

Defects

4.1 ...

...

Chapter 5

Experimental Methods

Refs to surveys (AGN-Vedula, Gomer, Ferrando, ?)

List of the main experimental methods

List of *reliable* experimental results

Experiment versus theory: what is already explained, what is still open/unclear

...

Chapter 6

Results

6.1 Quasi-one-dimensional systems

Furrow surfaces: (112) b.c.c., (110) f.c.c., (10 $\bar{1}$ 0) closely packed hexagonal

Exchange mechanism of surface diffusion:

first was observed for Pt/Pt(110) in 1978 [38?]

clearly was observed for W/Pt(110) with field-ion microscopy [95?]

MD DeLorentzi [37?]

...

6.2 ...

...

Chapter 7

Conclusion

...

Summary of methods to calculate D :

- (1) Calculate $v(t)$, then $D \propto \langle vv \rangle$ (MD Langevin)
- (2) Calculate $r(t)$, then $D \propto \langle r^2 \rangle / t$ (Langevin, LM)
- (3) Apply a small d.c. force, then $D \propto B = j/F$ (Smoluchowski, Risken)
- (4) Create a constant gradient then $D \propto j/\nabla n$ (FPK ?)

Formulate new problems

Reconstructions (which also might be induced by the adatoms as well) \rightarrow change of the system symmetry, change of activation barriers; but first one must have a description of the reconstruction itself ...