INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

SMR/291 - 17

SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

RATE EQUATIONS, RATE CONSTANTS AND SURFACE DIFFUSION

Göran WAHNSTRÖM
Institute of Theoretical Physics
Chalmers University of Technology
S-412 96 Göteborg
Sweden

Rate Equations, Rate Constants and Surface Diffusion

Göran Wahnström
Institute of Theoretical Physics, Chalmers University of Technology
S-412 96 GÖTEBORG, Sweden

CONTENTS

1. INTRODUCTION 1
2. JUMP DIFFUSION MODELS 2
  2.1. Non-interacting adatoms 2
    2.1.1. The self-diffusion constant 4
    2.1.2. Macroscopic approximation 6
    2.1.3. One-dimensional example 7
  2.2. Interacting adatoms 8
    2.2.1. Macroscopic description 9
    2.2.2. Hard core interaction 10
    2.2.3. General interaction 11
  2.3. Limitations 11
3. CONTINUOUS DIFFUSION MODELS 12
  3.1. Brownian motion theory 12
    3.1.1. Langevin's equation 12
    3.1.2. The fluctuation-dissipation theorem 13
    3.1.3. The self-diffusion constant 14
  3.2. Adatom dynamics 16
    3.2.1. Escape from a potential well 17
    3.2.2. Diffusion in a periodic potential 18
  3.3. Limitations with the Brownian motion model 20
    3.3.1. Three-dimensional motion 20
    3.3.2. Position dependent friction 20
    3.3.3. Memory effects 20
    3.3.4. Quantum effects 21
4. THERMAL RATE CONSTANTS 22
  4.1. The Born-Oppenheimer approximation 22
  4.2. Transition state theory 23
    4.2.1. One-dimensional example 23
    4.2.2. The multi-dimensional case 25
  4.3. Quantum transition state theory 28
  4.4. Dynamic correction factor 29
    4.4.1. Two-site system - heuristic derivation 30
    4.4.2. Two-site system - formal derivation 33
    4.4.3. Multi-site system 36
5. FRICTION COEFFICIENT AND MEMORY FUNCTION 38
  5.1. Formal exact equation of motion 38
  5.2. Fokker-Planck approximation 40
    5.2.1. Electron-hole pair excitations 41
    5.2.2. Phonons 42
  5.3. Mode coupling approximation 43

1. INTRODUCTION

One of the themes with the present "Spring College in Condensed Matter" is the way the basic interaction potential for adparticles physisorbed and chemisorbed on solid surfaces relates to the dynamics of adsorbed particles. In this set of lectures we will try to make this connection in some simple cases.

We will mainly treat the situation with a single atom adsorbed on the surface, but the extension to finite coverages will be discussed. Most of the theoretical models presented here can equally well be applied to the adsorption-desorption problem and they may also serve as a starting point to treat chemical reactions catalyst by a solid surface. The restriction to classical mechanics for the motion of adatoms are often natural, but in connection to diffusion of hydrogen we will comment on possible quantum effects. We will assume that the substrate form a perfect periodic lattice neglecting all defects, steps, polycrystalline effects etc. In order to obtain a detailed microscopic understanding of the dynamics simple and well defined models must be used.

The lectures are organized in the following way. In the first part we discuss two different phenomenological ways to treat surface diffusion. In Sec 2 jump diffusion models are presented and in Sec 3 models where the continuous motion of the adatom or adatoms are considered. The second part of the lectures are devoted to the microscopic basis for these two different kinds of models. In Sec 4 we derive and discuss the microscopic expressions for the rate constants introduced in connection to the jump diffusion models and in Sec 5 the microscopic basis for the models based on the continuous motion is presented. Both in Sec 4 and in Sec 5 we will discuss actual numerical calculations where the aim is to determine dynamical parameters from the basic interaction potentials.

2. JUMP DIFFUSION MODELS

Due to the periodic arrangement of the substrate particles, adsorbed atoms experiences a periodic potential along the surface. In many cases the activation energy for diffusion, i.e. the difference between the maximum and minimum of this potential energy along the surface, is large compared with the thermal energy. This implies that the adatoms are mainly localized at different surface lattice sites and the change of sites and in concequence the diffusion becomes thermally activated. The slow diffusive motion can be expressed in terms of the rate of change of the probabilities to be located at different sites. This is the basis for using jump diffusion models.[1]

2.1. Non-interacting adatoms

Consider first the simpliest case; a single adsorbed atom. The following description is also valid for an adsorbed layer of adatoms if the adatoms can be treated as completely non-interacting.

Introduce the notation $P^S(s_i,t)$ for the probability to find the single adatom at site i (i=1,...,N) at time t. The different sites are defined by the vectors s_i and N is the number of sites. We discuss in terms of probabilities and a statistical thermal average is assumed. By conservation of number of particles we have that

$$\sum_{i=1}^{N} P^S(s_i,t) = 1. \tag{2.1}$$

The probability to be located at a specific site i will decrease in time due to jumps from that site and increase in time due to jumps to the same site. $P^S(s_i,t)$ obeys the rate equation

$$\frac{\partial}{\partial t} P^S(s_i,t) = \sum_{j(\neq i)} [k_{j\to i} P^S(s_j,t) - k_{i\to j} P^S(s_i,t)] \tag{2.2}$$

where $k_{i\to j}$ is the rate by which the adatom is moving from site i to site j. The sites i and j need not to be adjacent in configuration space. We will call $k_{i\to j}$ the rate constants. Eq (2.2) is also valid in the quantum regime, provided the fluctuations in the surrounding is large enough to entirely eliminate coherent motion over two or more lattice spacings. This is general assumed to be the case for diffusion of hydrogen and other heavier particles at not too low temperatures.[2]

At equilibrium $P^s(s_i,t)$ is not changing in time, $P^s(s_i,t) = P^{s;eq}(s_i)$, and we have the detailed balance condition

$$\sum_{j(\neq i)} k_{j\to i}\, P^{s;eq}(s_j) = \sum_{(j\neq i)} k_{i\to j}\, P^{s;eq}(s_i)\,. \tag{2.3}$$

If all N sites are identical

$$P^{s;eq}(s_i) = \frac{1}{N} \tag{2.4}$$

and

$$k_{i\to j} = k_{j\to i}\,. \tag{2.5}$$

This assumption will be used henceforth. We introduce a matrix, the transfer matrix, according to

$$T(s_i,s_j) = \begin{cases} -k_{j\to i} & \text{if } i\neq j \\ \sum\limits_{m(\neq i)} k_{i\to m} & \text{if } i=j \end{cases} \tag{2.6}$$

and the rate equation can be written as

$$\frac{\partial}{\partial t} P^s(s_i,t) = -\sum_j T(s_i,s_j)\, P^s(s_j,t). \tag{2.7}$$

If the sites s_i form a Bravais lattice the transfer matrix can easily be diagonalized. By introducing the intermediate scattering function,

$$P^s(\mathbf{q},t) \equiv \sum_i \exp(-i\ \mathbf{q}\cdot s_i)\, P^s(s_i,t)\,, \tag{2.8}$$

the solution can be written as

$$P^s(\mathbf{q},t) = \exp(-t/\tau(\mathbf{q}))\, P^s(\mathbf{q},t=0)\,, \tag{2.9}$$

where the different relaxation times are defined by

$$\begin{aligned} \tau^{-1}(\mathbf{q}) \equiv T(\mathbf{q}) &\equiv \sum_i T(s_i,s_j)\ \exp(-i\ \mathbf{q}\cdot(\mathbf{s}_i - \mathbf{s}_j)) \\ &= 2 \sum_{j(\neq i)} k_{i\to j}\, \sin^2(\mathbf{q}\cdot(\mathbf{s}_j - \mathbf{s}_i)/2). \end{aligned} \tag{2.10}$$

$P^s(\mathbf{q},t=0)$ is the initial condition for the probability distribution and we have made use of the fact that the transfer matrix only depends on the relative distance, not on s_i and s_j separately. By transforming back to real space we can write the solution as

$$P^s(\mathbf{s}_i,t) = \frac{1}{N}\sum_{\mathbf{q}} \exp(i\ \mathbf{q}\cdot\mathbf{s}_i)\ \exp(-t/\tau(\mathbf{q}))\ P^s(\mathbf{q},t=0). \tag{2.11}$$

The sum over $\mathbf{q}$ is over all wave vectors in the first Brillouin zone of the reciprocal lattice.

2.1.1 The self-diffusion constant

The motion is conveniently characterized in terms of the self-diffusion constant, which is related to the mean square displacement of the adatom. Assume that initially the adatom is located at site k with $\mathbf{s}_k = \mathbf{0}$. The mean displacement of the adatom is zero,

$$< \mathbf{R}(t) > \equiv \sum_i \mathbf{s}_i\ P^s(\mathbf{s}_i,t) = \mathbf{0}, \tag{2.12}$$

but the mean square displacement,

$$< \mathbf{R}^2(t) > \equiv \sum_i \mathbf{s}_i^2\ P^s(\mathbf{s}_i,t), \tag{2.13}$$

is non zero. We can determine this quantity from Eq (2.11) but it is simpler to directly use the rate equation. Multiply both sides of Eq (2.2) with $\mathbf{s}_i^2$ and sum over i. By interchanging the summation indices for the first term on the right hand side we get

$$\frac{\partial}{\partial t} < \mathbf{R}^2(t) > = \sum_i \sum_{j(\neq i)} k_{i\to j}\, (\mathbf{s}_j^2 - \mathbf{s}_i^2)\ P^s(\mathbf{s}_i,t). \tag{2.14}$$

We introduce $\mathbf{s}_{i\to j} \equiv \mathbf{s}_j - \mathbf{s}_i$,

$$\frac{\partial}{\partial t} < \mathbf{R}^2(t) > = \sum_i \sum_{j(\neq i)} k_{i\to j} (s_{i\to j}^2 + 2\, \mathbf{s}_i \cdot \mathbf{s}_{i\to j}) P^s(\mathbf{s}_i,t) \qquad (2.15)$$

Both $k_{i\to j}$ and $s_{i\to j}$ depend only on the relative distance between site i and site j and if we use Eq (2.1) and Eq (2.12) we get

$$\frac{\partial}{\partial t} < \mathbf{R}^2(t) > = \sum_{j(\neq i)} k_{i\to j}\, s_{i\to j}^2 \qquad (2.16)$$

or

$$< \mathbf{R}^2(t) > = \sum_{j(\neq i)} k_{i\to j}\, s_{i\to j}^2\, t\,. \qquad (2.17)$$

We introduce the self-diffusion constant $\mathbf{D}^s$, which in the general case is a tensor, according to

$$\mathbf{D}^s = \frac{1}{2} \sum_{j(\neq i)} k_{i\to j}\, \mathbf{s}_{i\to j}\, \mathbf{s}_{i\to j}. \qquad (2.18)$$

For a lattice with cubic symmetry the diffusion is independent on the direction and we write

$$< \mathbf{R}^2(t) > = 2\, d\, D^s\, t \qquad (2.19)$$

with

$$D^s = \frac{1}{2d} \sum_{j(\neq i)} k_{i\to j}\, s_{i\to j}^2 \qquad (2.20)$$

Here D^s is the self-diffusion constant, d the dimensionality associated with the diffusion process (d=1 for linear motion, d=2 for motion in a plane, etc) and $s_{i\to j}$ the distance between site i and site j. Eq (2.19) gives the important connection between the mean square displacement for the adatom and the self-diffusion constant, and it can be viewed as a definition of D^s. In Sec 3 we will make this more precise. According to Eq (2.20) the self-diffusion constant D^s is simply related to the rate constants $k_{i\to j}$, and by calculating $k_{i\to j}$ the self-diffusion constant can be determined.

2.1.2. Macroscopic approximation

From Eq (2.11) it is evident that the solution consists of a sum a modes the relaxes with different relaxation times $\tau(\mathbf{q})$. At sufficiently long times only the modes that corresponds to the longest relaxation times will survive. Inspection of Eq (2.10) implies that in this limit only small wave vectors contribute and we can write

$$T(\mathbf{q}) = \frac{1}{2} \sum_{j(\neq i)} k_{i\to j} (\mathbf{q} \cdot (\mathbf{s}_j - \mathbf{s}_i))^2. \qquad (2.21)$$

In this limit the transfer matrix is related to the self-diffusion constant and for a system with cubic symmetry we can write

$$T(\mathbf{q}) = D^s\, q^2. \qquad (2.22)$$

If only small wave vectors are important , i.e. long wavelength, the lattice structure becomes unimportant and the difference equation (2.2) can be simplified to a differential equation. We call this the macroscopic approximation to indicate that the microscopic lattice structure is neglected. Expand $P^s(\mathbf{s}_j,t)$ around $\mathbf{s}_i$,

$$P^s(\mathbf{s}_j,t) = P^s(\mathbf{s}_i,t) + (\mathbf{s}_j - \mathbf{s}_i) \cdot \nabla P^s(\mathbf{s}_i,t) + \frac{1}{2} ((\mathbf{s}_j - \mathbf{s}_i) \cdot \nabla)^2 P^s(\mathbf{s}_i,t) + \dots \qquad (2.23)$$

and insert this expansion into the rate equation (2.2). The standard diffusion equation is then obtained,

$$\frac{\partial}{\partial t} P^s(\mathbf{r},t) = D^s\, \nabla^2 P^s(\mathbf{r},t). \qquad (2.24)$$

We have assumed cubic symmetry and $\mathbf{r}$ is a continuous variable with

$$P^s(\mathbf{s}_i,t) \equiv \int_{\Omega_i} d\mathbf{r}\, P^s(\mathbf{r},t) \qquad (2.25)$$

and where the volyme Ω_i defines the lattice site i.

The solution to Eq (2.24) with the initial condition $P^s(\mathbf{r},t=0) = \delta(\mathbf{r})$ is

$$P^s(r,t) = (4\pi D^s t)^{-d/2} \exp(-r^2/4D^s t), \tag{2.26}$$

which is easily obtained by Fourier transforming Eq (2.24). The probability distribution for the adatom is a Gaussian. Initially it is a delta-function and when time proceeds the distribution broadens and the rate of this broadening is determined by the self-diffusion constant.

2.1.3. One-dimensional example

Direct experimental observation of details of the motion of adatoms is obviously desirable. In the field ion microscopy (FIM) the diffusive motion of single metal atoms is directly observed.[3,4] The self-diffusion constant can be extracted from the mean square displacement of the adatom and also the actual probability distribution $P^s(s_j,t)$ can be obtained. The picture that has emerged is that the adatom motion over low-index surfaces is quite well described in terms of uncorrelated jumps between nearest-neighbour sites.[5,6]

On some crystal surfaces the adatom moves along channels and the diffusion becomes one-directional in nature. One such case which has been experimentally studied is W adatoms on the W(211)-surface.[7] If we assume that a single jump occurs only to two nearest-neighbour sites with the rate α and that successive jumps are independent on each other, the probability distribution can be expressed in terms of the modified Bessel function I_j of order j according to

$$P^s(s_j,t) = \exp(-2\alpha t)\ I_j(2\alpha t). \tag{2.27}$$

This result is obtained from Eq (2.11) with the initial condition $P^s(s_j,t=0)=\delta_{j,0}$. The self-diffusion constant is given by Eq (2.20), i.e.

$$D^s = \alpha a^2 , \tag{2.28}$$

where a is the lattice spacing. If we now allow for jumps to both nearest sites at a rate α and to second-nearest sites at a rate β, the probability distribution is given by

$$P^s(s_j,t) = \exp[-2(\alpha+\beta)t] \sum_{k=-\infty}^{\infty} I_{j-2k}(2\alpha t)\ I_k(2\beta t) \tag{2.29}$$

and the self-diffusion constant by

$$D^s = (\alpha+4\beta)\ a^2 . \tag{2.30}$$

We notice that the contribution to the self-diffusion constant scales as the square of the jump distance and it implies that even a small jump rate β gives a comparatively large contribution to the diffusion constant. Experimental observations of the probability distribution for W on the W(211)-surface have been compared with the predictions from the two above models.[7] In Fig 1 the results are shown at a time when the tungsten adatom has in average made half a jump. Points give results of the experiment, light bars indicate fit of experimental data to Eq (2.27) and dark bars to Eq (2.29). Best result is obtained on the assumption that β/α=0.1, i.e. their is a small tendency to correlated jumps.

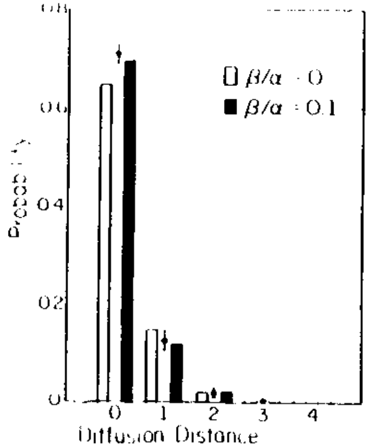

Fig 1. Probability distribution for a single tungsten atom diffusing on W(211). Points give results of experiment. Light bars indicate fit of experimental data to Eq (2.27) and dark bars to Eq (2.29) with β/α=0.1.

2.2. Interacting adatoms

So farl we have restricted ourselves to a single adsorbed atom or equally well the case with completely non-interacting adatoms. The situation is much more complicated if we have an adsorbed layer of interacting adatoms. To describe this situation we introduce the notation $P(s_i,t)$ for the probability to find one or maybe several adatoms at site i at time t. Conservation of number of particles implies that

$$\sum_{i=1}^{N} P(s_i,t) = N_p. \qquad (2.31)$$

where N_p is the number of adsorbed atoms. The concentration of adatoms is defined by

$$c = N_p / N. \qquad (2.32)$$

2.2.1. Macroscopic description

The phenomenological description of diffusion is embodied in Fick's law, which is an empirical statement that relates the diffusive flow of matter to concentration gradients. On a macroscopic level we neglect the lattice structure (cf. Sec 2.1.2.) and we write for the probability distribution, or density of adatoms, $P(\mathbf{r},t)$, where $\mathbf{r}$ is a continuous variable. Fick's law states that the flux of diffusing adatoms is proportional to the concentration gradient,

$$\mathbf{J}(\mathbf{r},t) = - D \, \nabla P(\mathbf{r},t) \qquad (2.33)$$

where the proportionality factor D is the diffusion constant. If we add the continuity equation

$$\frac{\partial}{\partial t} P(\mathbf{r},t) = -\nabla \mathbf{J}(\mathbf{r},t) \qquad (2.34)$$

to Fick's law the standard diffusion equation is obtained;

$$\frac{\partial}{\partial t} P(\mathbf{r},t) = D \, \nabla^2 P(\mathbf{r},t). \qquad (2.35)$$

D is sometimes called the chemical or collective diffusion constant and it is important to realize that D is <u>not</u> identical to the self-diffusion constant D^S. In Sec 2.1. the motion of a single adatom was monitored. Also when considering an adsorbed layer of interacting adatoms it can be useful to follow the motion of a specific, tagged, particle. The self-diffusion constant for the system of interacting adatoms is then related to the mean square displacement of the tagged particle. We use a superscript s on $P^S(\mathbf{r},t)$ and on D^S to indicate that these quantities are related to the self-motion of the adatom, in contrast to D and $P(\mathbf{r},t)$ which are a measure of the collective behaviour. Only when the adatoms can be treated as completely non-interacting D and D^S are identical.[8]

2.2.2. Hard core interaction

If we restrict ourselves to the case where double occupancy is prohibited but no other interaction between adatoms are present some progress can be made. We call this type of interaction hard core interaction.

The rate equation takes the form

$$\frac{\partial}{\partial t} P(s_i,t) = \sum_{j(\neq i)} [k_{j\to i} P(s_j,t) \, (1-P(s_i,t)) - k_{i\to j} P(s_i,t) \, (1-P(s_j,t))] \qquad (2.36)$$

which directly simplifies to

$$\frac{\partial}{\partial t} P(s_i,t) = \sum_{j(\neq i)} [k_{j\to i} P(s_j,t) - k_{i\to j} P(s_i,t)]. \qquad (2.37)$$

This equation is identical to Eq (2.2) and all results in Sec 2.1 can be used. In the limit of small wave vectors a connection to the diffusion equation can be made and we have the relation

$$D = \frac{1}{2d} \sum_{j(\neq i)} k_{i\to j} \, s_{i\to j}^{2} \qquad (2.38)$$

Notice that the rate constants here are related to the chemical diffusion constant D and not to the self-diffusion constant D^S. Surprisingly, the chemical diffusion constant is independent on the concentration c if hard core interaction is assumed.

To get an expresssion for the self-diffusion constant we must solve for $P^S(s_i,t)$. This is more complicated and no simple rate equation can be obtained.[9] Generally we have that

$$\frac{\partial}{\partial t} P^S(s_i,t) = \sum_{j(\neq i)} [k_{j\to i} P^S(s_j,t) \, (1-P(s_i,t)) - k_{i\to j} P^S(s_i,t) \, (1-P(s_j,t))] \qquad (2.39)$$

We can get a closed equation for $P^s(s_i,t)$ by using a mean field approximation, i.e. we simply replace $P(s_i,t)$ by c, the average concentration. Within this approximation the self-diffusion constant is given by

$$D^s = (1-c)\frac{1}{2d}\sum_{j(\neq i)} k_{i\rightarrow j}\, s_{i\rightarrow j}^{2} = (1-c)\,D \qquad (2.40)$$

The factor (1-c) is called the blocking factor. D^s decreases with incresing concentration which is evident from the relation between D^s and the mean square displacement of the tagged adatom. Notice that D and D^s become identical at low concentrations when interaction between adatoms can be neglected.

2.2.3. General interaction

In presence of nontrivial interaction between adatoms the calculation of both static and dynamic properties becomes involved. This goes far beyond the scope of the present lectures. The jump diffusion models can also be extended to several species and chemical reactions between species can be included.

2.3. Limitations

The jump diffusion models automatically exclude a description of the oscillatory motion of the adatoms. In neutron scattering experiments both the vibrational motion and the diffusive motion are revealed and for a proper intepretation of those experiments the vibrational motion must be included into the jump diffusion models. If the diffusive jumps are assumed to be uncorrelated to the vibrational motion this can easily be done.[10]

When the thermal energy becomes comparable to the activation energy for diffusion along the surface the adatoms are no longer mainly localized at different lattice sites. The time between two consecutive jumps becomes comparable to the duration of a jump and the subdivision into individual jumps loses its meaning. A more precise description of the motion is then needed. In the next section models based on the continuous motion of the adatoms will be presented.

3. CONTINUOUS DIFFUSION MODELS

The surrounding substrate influences in a very complicated way the motion of the adatom. In the previous section this influence was taken care of phenomenologically in two separate steps. First we made use of the periodic arrangement of the surrounding substrate atoms and we assumed that the adatom most of the time was located around stable lattice sites. Secondly, we incoperated into the rate constants the effect that the adatom can gain and lose energy to the substrate and thereby change site. In this section we will do a similar decomposition of the influence from the surrounding. The difference is that here we will treat the continuous motion of the adatom. This treatment is more general and the corresponding rate equation is more complicated and cannot be solved analytically in the general case. We restrict ourselves to a single adsorbed atom but the formalism can be generalized to incoperate interactions among adatoms. No attempts will be made to include quantum effects into the motion of the adatom.

If we know the force on the adatom we can solve Newton's equation and obtain the motion of the adatom. In principal we could use the microscopic equation of motion for the total system and obtain the time dependence of this force. Here we will approach the problem quite differently and more phenomenologically. We will try to describe the influence from the surrounding in some simple terms.

3.1. Brownian motion theory

First we restrict ourselves to a homogeneous medium. We disregard for a moment the static part of the force acting on the adatom and arising from the electrons and nuclei of the substrate in their average positions. The purpose is to present a phenomenological way to introduce the effect that the adatom can gain and lose energy to the substrate. Or in other words, we want to introduce dissipation and fluctuation of the energy of the adatom.

3.1.1. Langevin's equation

We split the force on the adatom in a smooth friction term, which we assume to be proportional to the velocity of the adatom, and a rapidly fluctuating force, the stochastic force, arising from the collisions with the individual surrounding particles. We write Newton's equation as

$$m\frac{d}{dt}V(t) = -m\,\eta\,V(t) + F^{st}(t), \qquad (3.1)$$

where $\mathbf{V}(t)$ is the velocity of the adatom, m its mass, η is the friction coefficient and $\mathbf{F}^{st}(t)$ the stochastic force. Eq (3.1) is called the Langevin's equation. The stochastic force is assumed to have zero average value,

$$< \mathbf{F}^{st}(t) > = \mathbf{0}, \tag{3.2}$$

and it is assumed to be totally uncorrelated in time, i.e. $< \mathbf{F}^{st}(t)\, \mathbf{F}^{st}(t') > = \mathbf{0}$ for $t \neq t'$. However, the average value of $< \mathbf{F}^{st}(t)\, \mathbf{F}^{st}(t) >$ cannot be zero and we postulate that

$$<\mathbf{F}^{st}(t)\, \mathbf{F}^{st}(t') > = \sigma\, \mathbf{1}\, \delta(t-t'), \tag{3.3}$$

where $\mathbf{1}$ is the unit tensor and σ is a constant, which for the moment is unspecified. We treat the motion of the adatom in a probabilistic manner. $\mathbf{F}^{st}(t)$ is a stochastic variable and we will only be able to give statistical predictions for the position $\mathbf{R}(t)$ of the adatom and for its velocity $\mathbf{V}(t)$. The brackets in Eqs (3.2) and (3.3) denote a canonical ensemble average and $<\mathbf{R}(t)>$ and $<\mathbf{V}(t)>$ will be the average values over this ensemble, characterized by the temperature.

3.1.2. The fluctuation-dissipation theorem

Direct solution of Eq (3.1) leads to

$$\mathbf{V}(t) = \mathbf{V}(0) \exp(-\eta\, t) + \frac{1}{m}\int_0^t dt' \exp[-\eta\, (t-t')]\, \mathbf{F}^{st}(t'), \tag{3.4}$$

where the fixed initial velocity of the adatom is denoted by $\mathbf{V}(0)$. From Eq (3.2) follows directly that the average velocity is

$$<\mathbf{V}(t)> = \mathbf{V}(0) \exp(-\,\eta\, t) \tag{3.5}$$

and for times $t >> 1/\eta$ there is no information left on the initial velocity and the average velocity is zero. This does not imply that $<V^2(t)>$ is zero. In fact we know from the equipartition theorem of classical statistical mechanics[11] that for a system in thermal equilibrium at the temperature T,

$$<V^2> = d\, \frac{k_B T}{m}\,, \tag{3.6}$$

where d is the dimension of the system and k_B is Boltzmann's constant. Using the formal solution of the Langevin's equation we have

$$V^2(t) = V^2(0) \exp(-2\, \eta\, t) + \frac{2}{m} \exp(-\eta\, t) \int_0^t dt' \exp[-\eta\, (t-t')]\, \mathbf{F}^{st}(t')\cdot \mathbf{V}(0)$$
$$+ \frac{1}{m^2} \int_0^t dt' \int_0^t t'' \exp[-\eta\, (t-t')] \exp[-\eta\, (t-t'')]\, \mathbf{F}^{st}(t')\cdot \mathbf{F}^{st}(t''). \tag{3.7}$$

By averaging over the thermal ensemble and by using the two properties of the stochastic force, postulated in Eqs (3.2) and (3.3), we get

$$<V^2(t)> = V^2(0) \exp(-2\, \eta\, t) + d\, \frac{\sigma}{2\eta m^2} [1 - \exp(-2\, \eta\, t)]\,. \tag{3.8}$$

We notice again that the initial information fades away exponentially in time. At sufficiently long times the adatom is assumed to reach thermal equilibrium and its mean squared velocity approaches the value given in Eq (3.6). In order to fulfil this we have to require that

$$\sigma = 2\, m\, \eta\, k_B T\,. \tag{3.9}$$

The parameter σ refers to the magnitude of the fluctuations in the medium, whereas η refers to the magnitude of the collective friction force. They are evidently related to each other and that is by no means obvious. The above relation is a special case of a general one, called the fluctuation-dissipation theorem. Any system which shows dissipative effects, as friction above, will also show fluctuations and there exists a relation between the two. The constant σ in Eq (3.3) is now specified in terms of the friction coefficient.

3.1.3. The self-diffusion constant

In Eq (2.18) we introduced the self-diffusion constant D^s by connecting it to the mean square displacement of the adatom. In the jump diffusion model the mean square displacemnet was linear in time for all times. This is not true in a more microscopic treatment. At very short times the adatom is moving as a free particle and

$$< |\mathbf{R}(t) - \mathbf{R}(0)|^2 > = < V^2(0) > t^2 = d\, \frac{k_B T}{m} t^2\,,\ \ (t \to 0)\,. \tag{3.10}$$

Here we have made a thermal average over all possible initial velocities. Eq (3.10) is an exact result and a model that is supposed to correctly describe the short time behaviour must fulfil this relation. If the motion becomes diffusive the mean square displacement will approach at long times a linear dependence on time. We <u>define</u> the self-diffusion constant through

$$D^s \equiv \lim_{t\to\infty} \frac{1}{2dt} < [\mathbf{R}(t) - \mathbf{R}(0)]^2 > . \tag{3.11}$$

The relation

$$\mathbf{R}(t) - \mathbf{R}(0) = \int_0^t dt' \ \mathbf{V}(t') \tag{3.12}$$

can be used to relate the mean square displacement to the velocity correlation function for the adatom. We get

$$\begin{aligned} < [\mathbf{R}(t) - \mathbf{R}(0)]^2 > &= \int_0^t dt' \int_0^t dt'' < \mathbf{V}(t')\cdot\mathbf{V}(t'') > \\ &= 2\int_0^t d\tau \ (t-\tau) < \mathbf{V}(\tau)\cdot\mathbf{V}(0) > , \end{aligned} \tag{3.13}$$

where we have made use of the property $< \mathbf{V}(t')\cdot\mathbf{V}(t'') > = < \mathbf{V}(t'-t'')\cdot\mathbf{V}(0) >$. We can now relate D^S to the velocity correlation function and a second and equivalent definition of D^S is obtained,

$$D^S \equiv \frac{1}{d}\int_0^\infty d\tau < \mathbf{V}(\tau)\cdot\mathbf{V}(0) > . \tag{3.14}$$

Eqs (3.11) and (3.14) can also be used as definitions of the self-diffusion constant for an adsorbed layer of interacting adatoms. The variables $\mathbf{R}(t)$ in Eq (3.11) and $\mathbf{V}(t)$ in Eq (3.14) are then the position and the velocity for a single tagged adatom, respectively. The chemical diffusion constant D can be defined in terms of another velocity correlation function.[8] The correlation function then contains the velocities of all adatoms and not only the velocity of a tagged adatom as in Eq (3.14).

Langevin's equation can be used to derive a connection between the self-diffusion constant and the friction coefficient. From Eq (3.4) we directly obtain

$$< \mathbf{V}(t)\cdot\mathbf{V}(0) > = d\,\frac{k_BT}{m}\exp(-\eta t). \tag{3.15}$$

If we insert this into Eq (3.13) we get

$$< [\mathbf{R}(t) - \mathbf{R}(0)]^2 > = d\,\frac{2k_BT}{m\eta}\left[\, t - \frac{1}{\eta}(1-\exp(-\eta t))\,\right] \tag{3.16}$$

which is consistent with Eq (3.10) at short times and in the limit t→∞ the identification

$$D^s = \frac{k_BT}{m\eta} \tag{3.17}$$

can be made.

3.2. Adatom dynamics

The substrate breaks the symmetry of the system and an adatom experiences a static potential arising from the electrons and nuclei of the substrate in their average positions. This part of the interaction with the substrate is crucial for the character of the adatom motion. It gives rise to the periodic force along the surface and to the attractive and repulsive forces perpendicular to the surface of the substrate. In order to properly describe surface dynamical problems as diffusion, adsorption and desorption one must, besides the above conservative part of the forces, also include the dissipative part. It is the latter that is responsible for dissipation and fluctuation of the energy of the adatom and these effects must be included.

A starting point for treating adatom dynamics is the following generalized Langevin's equation;

$$m\frac{d}{dt}\mathbf{V}(t) = \mathbf{F}^{ad}(\mathbf{R}) - m\,\eta\,\mathbf{V}(t) + \mathbf{F}^{st}(t) \tag{3.18}$$

with

$$<\mathbf{F}^{st}(t)\,\mathbf{F}^{st}(t')> = 2\,m\,\eta\,k_BT\ 1\ \delta(t-t'). \tag{3.19}$$

The static force $\mathbf{F}^{ad}(\mathbf{R}) = -\nabla V^{ad}(\mathbf{R})$ depends on the postion $\mathbf{R}(t)$ of the adatom and we call it the adiabatic force. This is the conservative part of the interaction with the substrate. The dissipative part is represented by the friction coefficient and by the stochastic force, which are connected by the fluctuation-dissipation theorem in Eq (3.19).

Eq (3.18) is a stochastic equation and one often converts it into an equation for the probability distribution $f(\mathbf{r},\mathbf{p},t)$ to find the adatom at time t at point $\mathbf{r}$ with momentum $\mathbf{p}$. This is the Fokker-Planck equation with a static force and it reads[12]

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}} + \mathbf{F}^{ad}(\mathbf{r})\cdot\nabla_{\mathbf{p}}\right] f(\mathbf{r},\mathbf{p},t) = \eta\, \nabla_{\mathbf{p}}\cdot\left[\mathbf{p} + m\, k_B T\, \nabla_{\mathbf{p}}\right] f(\mathbf{r},\mathbf{p},t). \qquad (3.20)$$

Eq (3.20) replaces the rate equation (2.2) and it was first given by Klein.[13] In the absence of the static force it can be solved analytically.[12] The incoperation of the static force complicates the situation considerable. Most discussions based on Eq (3.20) and aiming at analytic results have been restricted to one-dimensional models and to situations where the friction coefficient is either small or large compared to some typical frequency. Here, we will discuss two such models; the escape from a one-dimensional potential well and diffusion in a one-dimensional periodic potential.

3.2.1. Escape from a potential well

Kramers based a discussion of the <u>steady state escape rate</u> from a one-dimensional potential well on Eq (3.20) in a seminal paper.[14] He was not able to solve the equation for an arbitary value of η. He could, however, analyze the solution for small and large values of η.

For large values of η, so large that the distance a thermally drifting particle traverses in the time η^{-1} is small on the scale of variation of $V^{ad}(x)$, Eq (3.20) reduces to a diffusion equation for the density $\rho(x,t) = \int dp\, f(x,p,t)$ alone, the so called Smoluchowski equation. Kramers solved it for the steady state escape rate and under the additional assumption $\Delta E >> k_B T$ he obtained the rate,

$$k = \frac{\omega_A \omega^{\#}}{2\pi\eta} \exp(-\Delta E/k_B T), \quad (\eta >> \omega^{\#}). \qquad (3.21)$$

The frequencies ω_A and $\omega^{\#}$ are the ones associated with the second derivative of the static potential at the bottom and at the top of the barrier, respectively, and ΔE is the barrier height.

In the opposite limit, η small, the energy of the particle will be slowly varying, not its position. Eq (3.20) can then be reduced, by using a canonical transformation, to a diffusion equation for the probability $P(E,t)$ to find the particle with a certain energy. Kramers solves this equation too and using the same assumption about the barrier height as above, i.e. $\Delta E >> k_B T$, he finds the rate

$$k = \eta \frac{\Delta E}{k_B T} \exp(-\Delta E/k_B T), \quad (\eta << \omega_A k_B T/\Delta E). \qquad (3.22)$$

Kramers treatment is an attempt to go beyond the transition state theory (TST) for the escape rate, which for the above situation leads to the expression

$$k = \frac{\omega_A}{2\pi} \exp(-\Delta E/k_B T). \qquad (3.23)$$

The TST will be discussed in Sec 4. Here we only stress that their is no explicit dependence on the dissipative part of the forces in the TST. Kramers shows that by including dissipation and fluctuation through the use of the Brownian motion theory large deviations from the TST-result is obtained for small and large values of η. He also argues that TST applies for intermediate values of η, large enough to ensure replenishment of the equilibrium distribution but not so large as to inhibit the motion of escaping particles. It is the former effect that is responsible for the depletion of the rate in the low friction limit and the latter effect gives rise to the reduction of the rate in the high friction limit. From this follows that TST is always overestimating the true steady state escape rate.

3.2.2. Diffusion in a periodic potential

We now consider the motion in a one-dimensional periodic potential, $V(x)$. The diffusion constant is not solely determined by the escape rate, but also the jump distance is needed. This distance depends on how efficiently the energy of the diffusing atom is dissipated away.

For small values of η the jump distance can become large. If the coupling to the substrate is weak, i.e. η small, adatoms with energies above the potential barrier, activated adatoms, will move rather freely and adatoms with energies less than the barrier energy will vibrate locally for a long time. To a first approximation in the low friction limit only adatoms with energies above the potential barrier contribute to the diffusion constant. Their contribution is given approximatively by Eq (3.17). A more careful treatment leads to the result[15]

$$D^s = \frac{k_B T}{m\eta}\sqrt{\frac{2}{m\pi k_B T}}\int_{\Delta E}^{\infty} dE\, \bar{v}(E)^{-1}\exp(-E/k_B T)\,\{\frac{1}{a}\int_0^a dx\, \exp(-V(x)/k_B T)\,\}^{-1} \quad (3.24)$$

where $\bar{v}$ is the average velocity

$$\bar{v}(E) = \frac{1}{a}\int_0^a dx\, |v(x,E)|\,. \quad (3.25)$$

This is essentially Eq (3.17) times the probability to find the adatom above the potential barrier. Notice that we consider a system in thermal equilibrium and we always have adatoms with energies above and below the potential barrier. In the low friction limit both activation and deactivation of adatoms becomes equally inefficient.

In the opposite limit, η large, the energy dissipation is efficient and the jump distance is equal to the lattice spacing a. The diffusion constant is then given by Kramers result in Eq (3.21) times a^2. Again, the analysis can be made more presice and by solving the Smoluckowski equation one obtains[16,17,18]

$$D^s = \frac{k_B T}{m\eta}\,[\,\frac{1}{a}\int_0^a dx\, \exp(-V(x)/k_B T)\;\; \frac{1}{a}\int_0^a dx\, \exp(V(x)/k_B T)\,]^{-1} \quad (3.26)$$

In the limit $\Delta E >> k_B T$ Eq (3.26) reduces to Kramers result times a^2. We notice that the diffusion constant is proportional to η^{-1} in both limits, in contrast to the steady state escape rate that depends linearly on η in the small friction limit.

3.3. Limitations with the Brownian motion model

We end this section by pointing out some limitations with the Brownian motion model and by making some comments on the applicability of the above analytic results.

3.3.1. Three-dimensional motion

The result for the escape rate in Sec 3.2.1 and for the diffusion constant in Sec 3.2.2. are all based on one-dimensional treatments of the adatom motion. The results for the escape rate will not be qualitatively different if the full three-dimensional motion of the adatom is included.[19] However, it has been shown that in order to describe correlated jumps one has to include the three-dimensional character of the adatom motion.[20] A diffusing adatom follows to no extent the minimum energy path and it moves rather erratically on the surface. This can not be simplified to a one-dimensional motion without loss of qualitative features. The result in Eq (3.24) is therefore of limited value in the case of surface diffusion. Their is no problems, expect numerical, to go beyond the one-dimensional treatment within the Brownian motion model. One has to solve the full three-dimensional Fokker-Planck equation in Eq (3.20).

3.3.2. Position dependent friction

We have only considered a constant η, but in many situations it would be more appropriate to use a friction coefficient which depends on the position of the adatom. Such a situation obviously occurs in thermal desorption, where $\eta(z)$ approaches zero with increasing distance z from the solid surface. But also in surface diffusion the friction coefficient can have a strong dependence on the position of the adatom as well as on the direction of the adatom motion.[21] At the bridge position on a fcc (001)-surface the coupling to the vibrations of the substrate atoms is weak in the direction of the minimum energy path but strong in the two other directions. These effects can be incoperated into the Brownian motion model if one allows for a position dependent friction, $\eta \rightarrow \eta(\mathbf{r})$, and if tensor nature of the friction coefficient is included, $\eta(\mathbf{r}) \rightarrow \eta(\mathbf{r})$.

3.3.3. Memory effects

A more serious limitation with the above approach is connected to the basic assumption behind the Brownian motion model. In writing the equation of motion on the simple Langevin's form, one has assumed that the fluctuations in the surrounding are fast with respect to the adatom motion. This is the case if the adatom is much heavier than the substrate particles but it is certainly not true in the general case. For the latter cases Kubo has suggested that one should modify Langevin's equation to

$$m\frac{d}{dt}\mathbf{V}(t) = \mathbf{F}^{ad}(\mathbf{R}) - m\int_0^t dt'\,\Gamma(t-t')\mathbf{V}(t') + \mathbf{F}^{st}(t) \qquad (3.27)$$

where the simple friction term is replaced by a term that depends on the whole past history of the adatom. The function $\Gamma(t)$ is usually called the memory function. In Sec 5 we will come back to Eq (3.27), the generalized Langevin's equation, which can be shown to be exact as it is merely a formal separation of the total force on the adatom into different components.

3.3.4. Quantum effects

The Brownian motion model is based on the assumption that the motion of the adatom can be treated classically. In recent years a lot of attempts have been made to generalize the model to the quantum regime. The quantum version of Kramers problem has been solved[22,23] and results on the influence of a dissipative environment on the dynamics of a quantum system has been reviewed.[24]

4. THERMAL RATE CONSTANTS

In Sec 2 we discussed the jump diffusion model. The important parameter in that model is the thermal rate constant $k_{i\rightarrow j}$. In this section we will relate $k_{i\rightarrow j}$ to the basic interaction potential between the constituents.

4.1. The Born-Oppenheimer approximation

The dynamics of an atom adsorbed on a surface is fundamentally a complex quantum mechanical problem. An important simplification is obtained by using the Born-Oppenheimer approximation[25] to separate the motion of the nucleis from the electronic degrees of freedom. The quantum mechanical interactions of the electrons and nucleis are reduced to an interatomic potential energy hypersurface,

$$V(\mathbf{R}_0,\mathbf{R}_1,\ldots,\mathbf{R}_N). \qquad (4.1)$$

Here $\mathbf{R}_0$ denote the position of the adatom (previously denoted by $\mathbf{R}$) and $\mathbf{R}_i$, $i=1,\ldots,N$, denotes the positions of the N substrate atoms. The assumption of classical mechanics is usually appropriate and the motion of the atoms are obtained by solving Newton's equation,

$$m_i\frac{d^2}{dt^2}\mathbf{R}_i, = -\nabla_{\mathbf{R}_i}V(\mathbf{R}_0,\mathbf{R}_1,\ldots,\mathbf{R}_N)\ , \quad i=0,\ldots,N, \qquad (4.2)$$

with appropriate initial conditions. At low temperatures and for small masses m_i quantum mechanical effects such as zero point motion, tunneling and inteference phenomena may be important. Newton's equation is then replaced by the Schrödinger equation.

There are cases when the Born-Oppenheimer approximation must be improved. In several surface dynamical problems as for instance in ion neutralization and ionization at surfaces and, general, in chemical reactions more than one potential energy hypersurface is involved. For such cases "surface-hopping" techniques has been developed.[26] Metal surfaces introduces new phenomena, compared with gas phase reactions, due to the presence of the conduction electrons. The moving adatom may excite electron-hole pairs which can effectively dissipate excess energy. Electron-hole pairs can be provided with infinitesimal energy and the single Born-Oppenheimer potential hypersurface should be replaced by a continuous band of very nearly parallel hypersurfaces corresponding to different combinations of electron-hole pair excitations. This effect will be discussed in the next section in terms of a friction coefficient.

4.2. Transition state theory

Diffusion is in essence a dynamical problem but in an important class of theories the explicit dependence on the dynamics is bypassed and the diffusion constant is obtained from an equilibrium consideration. These are based on the transition state theory (TST) for the escape rate,[27,28] which originates from the absolute rate theory of Eyring.[29,30] In applications to solids the theory was developed through the work of Zener and Wert[31] and Vineyard.[32]

If we assume that the diffusive motion consists of uncorrelated jumps between adjacent lattice sites the diffusion constant is obtained from the relation

$$D^S = \frac{1}{2d} k\, a^2 , \tag{4.3}$$

where k is the escape rate from a lattice site. A key observation is that the change of sites is a thermally activated process. In the realm of classical mechanics the adatom must pass over the energy barrier that separates regions of lower energies from each other, the surface lattice sites. Thus, a barrier region is a transition state, a state that must be visited during the passage from one site to another and it acts as a bottleneck for the reaction.

4.2.1. One-dimensional example

To introduce the method of transition state theory (TST), we consider a one dimensional example, as shown in Fig 2. We want to calculate the rate $k_{A \to B}$ by which the particle is moving from site A to site B. In moving from A to B the particle has to pass the point S, the saddle point or the transition state. During a short time interval, say Δt, the particle will escape if it has positive velocity, v>0, and if it is within the distance $v\Delta t$ of S, i.e. $x_0 - v\Delta t < x < x_0$. The time interval Δt is choosen small enough so that the potential energy can be assumed to be constant over the distance $v\Delta t$. We now assume that the system is in thermal equilibrium at the temperature T. The probability to find the particle within the distance Δx of S is given by

$$P(\Delta x) = \Delta x \frac{\exp[-\beta V(x_0)]}{\int_{-\infty}^{x_0} dx \exp[-\beta V(x)]} \tag{4.4}$$

and the probability for the particle to have the velocity v is

$$P(v) = \frac{\exp[-\beta \frac{mv^2}{2}]}{\int_{-\infty}^{\infty} dv \exp[-\beta \frac{mv^2}{2}]} = \sqrt{\frac{m\beta}{2\pi}}$$

where $\beta = 1/k_B T$. Notice that in the expression for $P(\Delta x)$ we have normalized by integrating from $-\infty$ to x_0. We need the probability for the particle to be located at the transition state, provided it is situated in site A ($x<x_0$). The escape rate is now obtained by taking into account all positive velocities v, i.e.

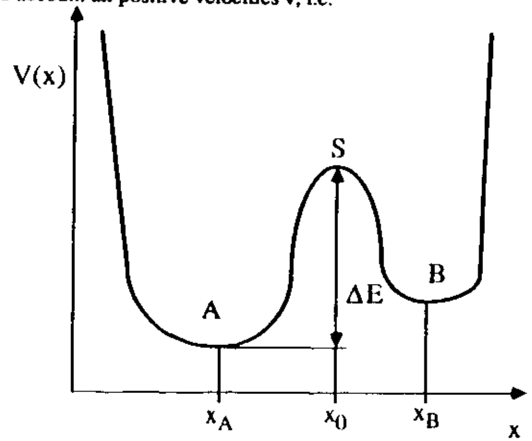

Fig 2. A one-dimensional potential V(x) for the reaction coordinate x. An energy barrier ΔE separates the two sites A ($x<x_0$) and B ($x>x_0$) from each other.

$$\Delta t\, k^{TST}_{A \to B} = \int_0^{\infty} dv\, P(v)\, P(\Delta x = v\Delta t) \tag{4.6}$$

or

$$k^{TST}_{A\to B} = \frac{\exp[-\beta V(x_0)]}{\sqrt{2\pi m\beta}\int_{-\infty}^{x_0} dx \exp[-\beta V(x)]} . \qquad (4.7)$$

Another way to write this is

$$k^{TST}_{A\to B} = < v\, \delta(x-x_0)\, \theta(v) >_A , \qquad (4.8)$$

where $\delta(x)$ is the Dirac delta function, $\theta(x)$ the Heaviside step function,

$$\theta(x) = \begin{cases} 1 & \text{if } x>0 \\ 0 & \text{if } x<0 \end{cases} , \qquad (4.9)$$

and where the subscript A in the bracket notation, $<...>_A$, indicates a ensemble average restricted to the configuration space of the site A only.

If the potential barrier is large compared to k_BT the integral in the denominator in Eq (4.7) is dominated by values around $x=x_A$. If we expand the potential,

$$V(x) = V(x_A) + \frac{1}{2} m\, \omega_A^2\, x^2 + ..., \qquad (4.10)$$

keep the quadratic term and extend the integration limit to infinite the well-known result

$$k^{TST}_{A\to B} = \frac{\omega_A}{2\pi} \exp(-\beta\, \Delta E) \qquad (4.11)$$

is obtained (cf. Eq (3.23). The prefactor $\omega_A/2\pi$, the so called attempt frequency, comes from proper normalization and has nothing to do with kinetics. The usual physical intepretation that $\nu_A=\omega_A/2\pi$ should be considered as the frequency with which the particle tries to escape is therefore somewhat misleading in this context.

4.2.2. The multi-dimensional case

The above one-dimensional expression for the TST escape rate can be extended to the multi-dimensional case. Fig 3 gives a two-dimensional picture of the motion in the (3N+3)-dimensional configuration space. It is useful to introduce new coordinates such that one coordinate, the reaction coordinate s, runs along the diffusion path between A and B. We denote the corresponding velocity by v_s. The value $s=s_0$ defines a (3N+2) dimensional surface, which we call the dividing surface or the TST surface. The TST value for the escape rate is now obtained by taking the probability to be located in the transition state region times the mean velocity in the reactive direction,

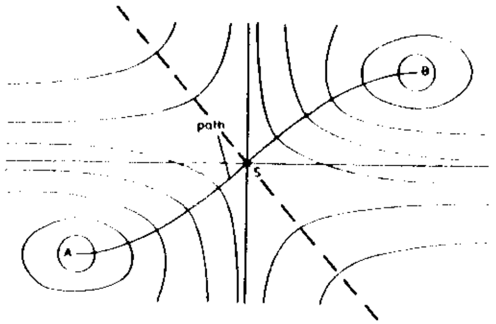

Fig 3. Two-dimensional picture of the (3N+3)-dimensional configuration space. A and B are the minima and S is the saddle point. The dividing surface is defined by $s=s_0$ and it is shown as a dashed line in the figure.

$$k^{TST}_{A\to B} = < v_s\, \delta(s-s_0)\, \theta(v_s) >_A , \qquad (4.12)$$

where the average is over all degrees of freedom of the system. The escape rate can also be written as

$$k^{TST}_{A\to B} = \frac{k_BT}{h} \frac{Q^{\#}_{cl}}{Q^{A}_{cl}} \qquad (4.13)$$

where Q^A_{cl} is the classical mechanical partition function for the system when the particle is located in the region A,

$$Q^A_{cl} = \int \prod_{i=1}^{3N+3} \left(\frac{dq_i\, dp_i}{h}\right) \exp(-\beta H) \qquad (4.14)$$

and $Q^{\#}_{cl}$ is the corresponding one when the particle is located in the transition state region,

$$Q_{cl}^{\#} = \int \prod_{i=1}^{3N+2} \left(\frac{dq_i\, dp_i}{h}\right) \exp(-\beta H^{\#}). \tag{4.15}$$

H is the total Hamiltonian for the system and $H^{\#}$ is defined in the transition state region, i.e. $s=s_0$ and v_s does not appear. Eqs (4.12) and (4.13) are two equivalent expressions for the escape rate within the transition state theory. It is worth noting that the integrals in Eqs (4.14) and (4.15) are equilibrium averages and can be evaluated exactly by means of numerical Monte Carlo methods.[33] The starting point is then an assumed form for a Born-Oppenheimer potential energy hypersurface. For computational reasons one often uses a model with pair-wise additive interaction potentials. This gives a connection between the escape rate within the transition state theory and the microscopic force laws.

In the same way as in the one-dimensional example we can expand the potential energy and get an expression valid in the harmonic approximation. We write for the potential energy around the stable point A

$$V(\ldots) = V_A + \frac{1}{2} \sum_{i=1}^{3N+3} m_i\, \omega_i^2\, q_i^2 + \ldots \tag{4.16}$$

and around the saddle point

$$V^{\#}(\ldots) = V^{\#} + \frac{1}{2} \sum_{i=1}^{3N+2} m_i\, (\omega_i^{\#})^2\, q_i^2 + \ldots \tag{4.17}$$

where ω_i and $\omega_i^{\#}$ are normal mode frequencies and q_i normal mode coordinates (not neccesernly the same in the two expressions). The phase-space integrals in Eqs (4.14) and (4.15) can now be performed and using the notation $\Delta E=V^{\#}-V_A$ we arrive at the frequency-product formula of Vineyard,[32]

$$k_{A\,,}^{TST} = \frac{1}{2\pi} \frac{\prod_{i=1}^{3N+3} \omega_i}{\prod_{i=1}^{3N+2} \omega_i^{\#}} \exp(-\beta \Delta E). \tag{4.18}$$

4.3. Quantum transition state theory

Classical concepts have been used in an essential way to obtain the transition state theory result in Eq (4.13). Especially in cases when hydrogen atoms are involved one would like to incoperate quantum effects into the expression for the rate constant.

First we make the obvious modification that the classical mechanical partition functions are replaced by their quantum counterparts,

$$Q_{cl}^{A} \rightarrow Q_{qm}^{A} = \mathrm{Tr}_A\{\, \exp(-\beta H)\, \}\,, \tag{4.19}$$

and correspondingly for $Q_{cl}^{\#}$. This takes into account the discretness of the excitation energies and it is important if a typical vibrational energy is large compared to the thermal energy. For hydrogen this can be important even at room temperature.

Secondly we notice that the factor k_BT/h in Eq (4.13) comes from the evaluation of the rate by which the particle cross the dividing surface. The calculation is based on the assumption that velocity and position coordinates are independent which is not true quantum mechanically. We must correct for tunneling through the potential barrier at energies below the classical threshold, as well as the possibility of reflection at energies above the classical threshold. To do this we look at the classical calculation,[27]

$$\frac{k_BT}{h} = \frac{1}{h}\int_0^{\infty} dp\, \frac{p}{m} \exp\left(-\beta\frac{p^2}{2m}\right) = \frac{1}{h}\int_0^{\infty} dE\, \exp(-\beta E) = \frac{1}{h}\int_{-\infty}^{\infty} dE\, T_{cl}(E) \exp(-\beta E)\,, \tag{4.20}$$

where $T_{cl}(E)$ is the classical probability of crossing the potential barrier at an energy E measured with respect to the barrier maximum, $T_{cl}(E)=1$ if $E>0$ and zero otherwise. This suggests that we replace $T_{cl}(E)$ by the quantum probability of crossing a suitable choosen one dimensional potential barrier at energy E. We define the quantum correction $\kappa(T)$, which takes into account tunneling and non-classical reflexion, through

$$\kappa(T) = k_BT \int_{-\infty}^{\infty} dE\, T_{qm}(E) \exp(-\beta E), \tag{4.21}$$

where $T_{qm}(E)$ is the quantum mechanical transmission coefficient and where the zero of the energy E is located at the classical threshold. We can now write the rate constant within the quantum transition state theory (QTST) as

$$k_{A\to B}^{QTST} = \kappa(T)\,\frac{k_B T}{h}\,\frac{Q_{qm}^{\#}}{Q_{qm}^{A}}\,. \tag{4.22}$$

There are several weaknesses in this simplified QTST. One of the main approximations in Eq (4.23) is the assumption of separability between the reaction coordinate and all the other degrees of freedom. Several attempts have been made to go beyond the assumption of separability.[27] The quantum transition state theory is, however, not as well founded as its classical counterpart. For applications of QTST to hydrogen diffusion on solid surfaces see the work by Lauderdale and Truhlar,[34,35] Valone, Voter and Doll[36,37] and Raquet and Miller.[38]

If we again use the harmonic approximation the partition functions Q_{qm}^{A} and $Q_{qm}^{\#}$ can be evaluated analytically. We can also determine $\kappa(T)$ in the same level of approximation. At not too low temperatures the rate will be dominated by the shape of the potential barrier in the vicinity of the classical threshold. We can then use a parabolic approximation

$$V(s) = -\frac{1}{2} m_s (\omega^{\#})^2 s^2 \tag{4.23}$$

for which the transmission probability is known.[39] The rate constant can then be written on the symmetric form

$$k_{A\to B}^{QTST} = \frac{\displaystyle\prod_{i=1}^{3N+3} \frac{\sinh(\beta\hbar\omega_i/2)}{(\beta\hbar\omega_i/2)}}{\displaystyle\frac{\sin(\beta\hbar\omega^{\#}/2)}{(\beta\hbar\omega^{\#}/2)} \prod_{i=1}^{3N+2} \frac{\sinh(\beta\hbar\omega_i^{\#}/2)}{(\beta\hbar\omega_i^{\#}/2)}}\; k_{A\to B}^{TST} \tag{4.24}$$

4.4. Dynamic correction factor

The TST is approximative and it does not give the correct value for the escape rate. The basic assumption in TST is that each crossing of the dividing surface corresponds to a reactive site change event. This is not true. TST ignores dynamical effects such as recrossing effects. Another assumption that must be made in order to describe diffusion using TST is that a particular jump mechanism must be imposed. If one assumes single

uncorrelated jumps between adjacent lattice sites the diffusion constant is related to the escape rate through Eq (4.3). The dynamic correction formalism[40,41] is a method by which both these assumptions can be relaxed simultaneously and formally exact expressions for the different rate constants are obtained.[42,43] They are expressed in terms of different reactive flux correlation functions. A major advantage with this approach is that the correct quantum version can be derived.[44,45] We consider first a two site system and thereafter the multisite case, necessary in describing correlated multiple jumps on a surface.

Before we discuss the dynamic correction factor we comment on the use of the equilibrium configuration in the transition state region. The adatom is in constant contact with a nearly infinite "heat bath" and it is therefore perfectly appropriate to use the canonical ensemble to describe this system. This is the basic assumption we make and the corresponding rate constant is then the thermal rate constant. The use of the equilibrium distribution in the transition state region is a rigorous result that directly follows from the use of the canonical ensemble.[46] It does not depend on how easy or difficult the bottleneck, i.e. the transition state region, is to enter, or on how quickly the typical trajectory passes through. It is misleading to regard the relaxation of the surrounding substrate atoms when the adatom is approaching the transitions state solely caused by the approaching adatom. It can equally well be that a fluctuation of the substrate atoms, a relaxation, makes the adatom approach the transition state. The jump event is more properly treated as a fluctuation in a many-body sytem at thermal equilibrium; the presence of the adatom in the transition state region neither causes, nor results from, but is rather instantaneously correlated with a relaxation in the mean positions of the surrounding substrate atoms. Similar arguments imply that the velocity distribution of adatoms found in the transitions state region is Maxwellian. Although a jumping adatom will usually need more than average kinetic energy to approach the saddle point, all this excess kinetic energy have in average been converted into potential energy at the saddle point, only to be recovered as kinetic energy during the descent.

4.4.1. Two-site system - heuristic derivation

As shown in Fig 4, we consider a system with two stable configurations, A and B, separated by an energy barrier at $s=s_0$. The reaction coordinate $s(t)$ can for instance be the distance $z(t)$ between an adsorbed atom and the surface in the case of thermal desorption. The "site" B then extends to infinity. In isomerization $s(t)$ can be an angle $\alpha(t)$ characterizing two different stable configurations of the m[illegible]e. Five typical trajectories which all cross the dividing surface at $s=s_0$ one or several times are shown. Only two of these trajectories, (a) and (b), are true reactive events for the reaction $A\to B$

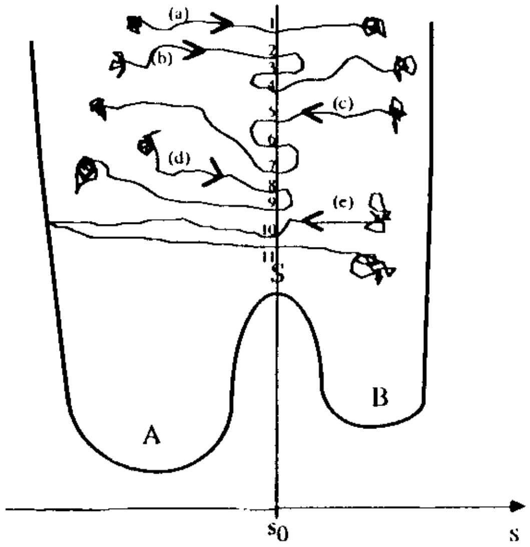

Fig 4. Five typical trajectories which all cross the dividing surface at $s=s_0$ one or several times. The arrows indicate the direction of the time. Only trajectory (a) and (b) correspond to true reactive events for the reaction $A\to B$.

and only these should contribute when calculating the rate constant $k_{A\to B}$. If we examine a canonical ensemble of systems at a given instant of time, we find that each of the eleven crossings shown in Fig 4 are present. If we now use the TST approximation, defined in Eq (4.12), we will find the following: Trajectory (a) will contribute. In trajectory (b) both crossing 2 and 4 will contribute, but not crossing 3 due to the negative sign of the velocity. The trajectory (b) is a single reactive event, but in TST it will contribute twice. The trajectories (c), (d) and (e) are all non reactive but in TST the crossings 6, 8 and 11 will contribute when calculating the rate constant. These "correlated dynamical events" cause the TST approximation to be an upper bound on the true rate constant, since each reactive event consists of at least one TST surface crossing.

To get the true rate constant one must ensure that a crossing corresponds to a reactive event and that no multiple counting of a single reactive event is performed. This is done by generalizing the TST expression in Eq (4.12) to[27,47]

$$k_{A\to B} = \langle\, \theta(s_0-s(-\Delta t))\; v_s\; \delta(s-s_0)\; \theta(s(\Delta t)-s_0)\,\rangle_A\,. \qquad (4.25)$$

For each crossing of the TST surface we must run the trajectory backward in time to ensure that it started in site A and forward in time to ensure that it ended in site B. This is taken care of by the two Heaviside step-functions. The time Δt is somewhat arbitary but in a system with well-defined reactive events the time Δt will also be well-defined.[48] More precisely, define τ_{corr} as the time-scale on which the correlated dynamical events occur and define τ_{rxn} as the average time between reactive events, i.e. the inverse of the true rate constant. Systems with well-defined reactive events will then be characterized by the time-scale separation $\tau_{corr} \ll \tau_{rxn}$ and the time Δt should be choosen longer than τ_{corr} but much shorter than τ_{rxn}. We now apply Eq (4.25) to the trajectories in Fig 4. The trajectory (a) still contributes to the rate. In trajectory (b) all three crossings contribute. However, crossing 3 gives a negative contribution ($v_s<0$) and in a perfect sampling of trajectories, crossings like 3 and 4 (or equally well 3 and 2) will exactly cancel each other. The net contribution form trajectory (b) will then be a single reactive event. The trajectories (c), (d) and (e) make no contribution to the rate due to one or both of the step-functions in Eq (4.25).

We can make a further simplification of the expression for the rate and write it as[48]

$$k_{A\to B} = \langle\, v_s\; \delta(s-s_0)\; \theta(s(\Delta t)-s_0)\,\rangle_A\,. \qquad (4.26)$$

This is seen by first using the identity $\theta(s_0-s(-\Delta t)) = 1 - \theta(s(-\Delta t)-s_0)$. From this it follows that the difference between Eqs (4.25) and (4.26) is the quantity $\langle\, \theta(s(-\Delta t)-s_0)\; v_s\; \delta(s-s_0)\; \theta(s(\Delta t)-s_0)\,\rangle_A$, which is the average flux across the surface $s=s_0$ given that $s(-\Delta t)>s_0$ and $s(\Delta t)>s_0$. According to Liouville's theorem, that averaged flux is zero.

Next we will derive Eq (4.26) in a more formal way and put it on a more rigid basis. Before doing this we notice that the TST result in Eq (4.12) is obtained by taking the limit $\Delta t\to 0$ in Eq (4.26). The TST is obtained by assuming that all trajectories passing the dividing surface in the reactive direction corresponds to a true reactive event.

4.4.2. Two-site system - formal derivation

Consider again the situation in Fig 4. We want to determine the rate by which the system is changing from A to B. To make the derivation more general we will do it fully quantum mechanically. We introduce the operator

$$A = \theta(s_0 - s) = \int_{-\infty}^{s_0} ds\, |s\rangle\langle s| \, , \qquad (4.27)$$

which is 1 if the sytem is in the configuration A and zero if it is in the configuration B. We also introduce the notation

$$B = 1 - A = \theta(s - s_0) = \int_{s_0}^{\infty} ds\, |s\rangle\langle s| \, . \qquad (4.28)$$

The variables s, A and B are now operators and we must keep track of the order. We assume the Hamiltonian to be on the standard form

$$H = \frac{p_s^2}{2m_s} + \sum_i \frac{p_i^2}{2m_i} + V(s, q_1, q_2, ..) \qquad (4.29)$$

and the time evolution of A is given by

$$A(t) = \exp(iHt/\hbar)\, A \exp(-iHt/\hbar) \, . \qquad (4.30)$$

The expectation value of A,

$$< A > = Z^{-1}\, \mathrm{Tr}\{\, A \exp(-\beta H) \,\} \qquad (4.31)$$

with

$$Z = \mathrm{Tr}\{\, \exp(-\beta H) \,\} \, , \qquad (4.32)$$

is the probability that the system is in configuration A.

We now perturb the system slightly from equilibrium by applying an external time-dependent field that couples to the dynamical variable A. We turn on the pertubation slowly and at t=0 it is suddenly turned off,

$$\delta a^{ext}(t) = \begin{cases} \delta a \exp(\varepsilon t) & \text{if } t<0 \\ 0 & \text{if } t>0 \end{cases} , \qquad (4.33)$$

with δa and ε small and positive. The unperturbed Hamiltonian H is modified to

$$H'(t) = H - A\, \delta a^{ext}(t) \qquad (4.34)$$

and at t=0 the expectation value of A, $<A>_{ne}$, will be slightly larger the equilibrium value. The subscript "ne" denotes a non-equilibrium average. After t=0, when the pertubation is turned off, the system will spontaneously relax back to the equilibrium configuration. By calculating the linear response to the weak external field $\delta a^{ext}(t)$ this relaxation is given by[49,50]

$$\delta<A(t)>_{ne} = \beta\, C(t)\, \delta a \qquad (4.35)$$

where

$$\delta<A(t)>_{ne} = <A(t)>_{ne} - <A> \qquad (4.36)$$

is the fluctuation from the true equilibrium value and where C(t) is the relaxation function

$$C(t) = \frac{1}{\beta} \int_0^{\beta} d\lambda < \delta A(-i\hbar\lambda)\, \delta A(t) > \, . \qquad (4.37)$$

By taking the time-derivative of Eq (4.35), we obtain the following expression for the relaxation of the perturbed system;

$$\frac{d}{dt}\delta<A(t)>_{ne} = \frac{\dot{C}(t)}{C(t)}\, \delta<A(t)>_{ne} \, . \qquad (4.38)$$

We now assume that a simple linear rate equation describes the relaxation, i.e.

$$\frac{d}{dt}<A(t)>_{ne} = k_{B\to A}<B(t)>_{ne} - k_{A\to B}<A(t)>_{ne} \qquad (4.39)$$

or

$$\frac{d}{dt}\delta<A(t)>_{ne} = -\, k_{eff}\, \delta<A(t)>_{ne} \qquad (4.40)$$

with

$$k_{\mathrm{eff}} = \frac{k_{A\to B}}{\langle B\rangle} . \qquad (4.41)$$

We expect the rate equation to valid for times $t > \tau_{\mathrm{corr}}$, where τ_{corr} is a microscopic time-scale that characterizes the rapid transient relaxation. We can then make the identification

$$k_{\mathrm{eff}} = -\frac{\dot{C}(\Delta t)}{C(\Delta t)} \qquad (4.42)$$

where the time Δt satisfies the condition

$$\tau_{\mathrm{corr}} < \Delta t . \qquad (4.43)$$

By numerically calculate the time dependent function $k(t) \equiv \dot{C}(t)/C(t)$ we can establish if the proposed phenomenological rate equation (4.39) is valid. In that case $k(t)$ should reach a constant value for times $t > \tau_{\mathrm{corr}}$, the plateau value behaviour, and the value of the rate constant can be extracted. If the plateau value behaviour is not observed one must conceive of a different phenomenology. The correlation function $C(t)$ is changing on the time-scale $\tau_{\mathrm{rxn}} \sim 1/k_{\mathrm{eff}}$ and as long as we are considering times $\Delta t \ll \tau_{\mathrm{rxn}}$ we can replace $C(\Delta t)$ by $C(0)$ in the denominator in Eq (4.42). In the classical limit we have the identity

$$C(0) = \langle A\rangle \langle B\rangle . \qquad (4.44)$$

In the quantum case this is an excellent approximation if the system is "well localized" in site A or in site B.[20,51] We can then write the rate constant on the form

$$k_{A\to B} = \frac{1}{\langle A\rangle} C_{fs}(\Delta t) , \qquad \tau_{\mathrm{corr}} < \Delta t \ll \tau_{\mathrm{rxn}} , \qquad (4.45)$$

where

$$C_{fs}(t) = Z^{-1} \frac{1}{\beta} \int_0^{\beta} d\lambda \, \mathrm{Tr}\{ \exp(\lambda H) F_A \exp(-\lambda H) B(t) \exp(-\beta H) \} \qquad (4.46)$$

Here F_A denotes the flux operator

$$F_A = -\dot{A} = \frac{i}{\hbar}[A,H] = \frac{1}{2m_s}(p_s \delta(s-s_0) + \delta(s-s_0) p_s) . \qquad (4.47)$$

Eq (4.45) is the quantum version of the classical expression in Eq (4.26). One can show that the initial value of the correlation function is zero in the quantum case, $C_{fs}(t=0)=0$,[52] in contrast to the classical limit where $C_{fs}(t\to 0^+)$ is finite and equal to the TST value.[48] This makes the problem of defining a quantum version of the classical TST apparent.

By using the fact that $C_{fs}(t=0)=0$ we can also write the rate constant as

$$k_{A\to B} = \frac{1}{\langle A\rangle} \int_0^{\Delta t} dt \, C_{ff}(t) , \qquad \tau_{\mathrm{corr}} < \Delta t \ll \tau_{\mathrm{rxn}} , \qquad (4.48)$$

where

$$C_{ff}(t) = Z^{-1} \frac{1}{\beta} \int_0^{\beta} d\lambda \, \mathrm{Tr}\{ \exp(\lambda H) F_A \exp(-\lambda H) F_A(t) \exp(-\beta H) \} . \qquad (4.49)$$

The rate constant describes how the sytem evolves over macroscopic times. In eq (4.48) it is related to a time-integral over a flux-flux correlation function, which decays on a microscopic time-scale. This kind of relation between a transport coefficient, the rate constant, and an equilibrium correlation function[53] is often called a Green-Kubo formula. In connection to reaction rates it was first given by Yamamoto.[44]

4.4.3. Multi-site system

In the case of surface diffusion the adatom can be located in more than two sites, allowing for the possibility that an energized adatom will make a correlated multiple jump and thermalize in a nonadjacent lattice site. This kind of system can be treated in a fashion similar to the two site system, using the formalism developed by Voter and Doll.[54] They simple generalize the expression for rate constant in Eq (4.26) to

$$k_{i\to j} = \langle v_i \, \delta_i \, \theta_j(\Delta t) \rangle_i , \qquad \tau_{\mathrm{corr}} < \Delta t \ll \tau_{\mathrm{rxn}} , \qquad (4.50)$$

where v_i is the velocity normal to the dividing surface (defined as positive when the system is exiting from site i) and δ_i defines the location of the dividing surface. The function $\theta_j(t)$ is 1 if the adatom is located in site j at time t and otherwise it is zero. Eq (4.50) connects the phenomenological rate constant $k_{i \to j}$, introduced in Eq (2.2), to the microscopic force law.

Voter and Doll have applied the formalism to a model system that is supposed to mimic the diffusion of a Rh-atom on a Rh(001) surface.[54] The Born-Oppenheimer potential energy surface is represented as a sum of pair-potentials of the Lennard-Jones form. They combine a Monte Carlo approach for static properties with molecular dynamics to obtain the time dependence needed in Eq (4.50). For computational reasons it is then crucial that the trajectories need to be followed only for relatively short times. In their case Δt is of the order 1ps. For that particular system they conclude that at T=1000 K and below the dynamical corrections are negligible, indicating that the TST-value for the escape rate together with the assumption of single uncorrelated jumps is a very good approximation. They also claim that it is probably true that dynamical correction factors are quite minor in general for surface diffusion of adatoms, provided the TST surface is chosen properly.[43] That conclusion is supported by FIM experiments.[6]

The method with dynamic correction factors can be extended to include interactions among adsorbed adatoms.[55]

5. FRICTION COEFFICIENT AND MEMORY FUNCTION

The phenomenological treatment in Sec 3 is based on the Langevin's equation, where the force on the adatom is divided into a friction force and a stochastic force. This is an approximation. In Sec 3 we pointed out that in order to generalize the Langevin's equation one has to incoperate memory effects into the formalism.

5.1. Formal exact equation of motion

It is more convenient to base a discussion on the generalization of the Fokker-Planck equation than on the generalized Langevin's equation in Eq (3.27). We want to derive an equation of motion for the probability distribution $f(\mathbf{r},\mathbf{p},t)$ to find the adatom at time t at position **r** with momentum **p**. To do this we introduce the microscopic phase-space density

$$\rho(1t) = \delta(\mathbf{r}_1-\mathbf{R}_0(t))\,\delta(\mathbf{p}_1-\mathbf{P}_0(t)), \qquad (5.1)$$

where 1 is a short hand notation for the phase-space point $(\mathbf{r}_1,\mathbf{p}_1)$. The position and momentum of the adatom is as previously denoted by $\mathbf{R}_0(t)$ and $\mathbf{P}_0(t)$, respectively. In thermal equilibrium we have the probability distribution

$$<\rho(1)> = <n(\mathbf{r}_1)>\,(\beta/2\pi m)^{3/2}\,\exp(-\beta\frac{p_1^2}{2m}), \qquad (5.2)$$

where $<n(\mathbf{r})>$ is the mean density of the adatom. To discuss dynamic phenomena in an equilibrium system we form the phase-space correlation function

$$C^s(11't) = <\rho(1')>^{-1} <\rho(1t)\,\rho(1')>. \qquad (5.3)$$

As previously, the superscript s indicates that we are treating the self-motion. $C^s(11't)$ is a mathematically well-defined quantity and it satifies the initial condition

$$C^s(11't=0) = \delta(11') = \delta(\mathbf{r}_1-\mathbf{r}_1')\,\delta(\mathbf{p}_1-\mathbf{p}_1'). \qquad (5.4)$$

It is equal to the conditional probability, i.e. the probability to find the adatom at time t at position **r** with momentum **p** if it at time t=0 was located at **r**' and moved with momentum **p**'. By multiplying the phase-space correlation function with different powers of momenta and integrating one can extract the more familiar density and current correlation functions. The latter can be used in determining the velocity correlation function and from Eq (3.14) one can then obtain the self-diffusion constant.

It is nowadays well established how one can derive formally exact transport equations. One method is based on the projection operator technique[49,50,56] introduced by Zwanzig[57] and extended by Mori.[58] If we apply that formalism to the phase-space correlation function we can write[21]

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\nabla_{\mathbf{r}} + \mathbf{F}^{ad}(\mathbf{r}_1)\cdot\nabla_{\mathbf{p}}\right] C^s(11't)$$

$$= \int_0^t d\bar{t} \int d\bar{1}\, \nabla_{\mathbf{p}}\cdot \mathbb{L}(1\bar{1}t-\bar{t})\cdot\left[\frac{\beta}{m}\mathbf{p} + \nabla_{\mathbf{p}}\right] C^s(\bar{1}1'\bar{t}) \,. \qquad (5.5)$$

This is a correct formal generalization of the Fokker-Planck equation. The influence form the surrounding on the adatom is split into two parts, one static and one dynamic. The static part gives rise to the conservative force $\mathbf{F}^{ad}(\mathbf{r}) = -\nabla V^{ad}(\mathbf{r})$, which is temperature dependent. It is equal to the force acting on a fixed adatom at position **r** when the surrounding is in thermal equilibrium around that atom. We can define it through

$$\mathbf{F}^{ad}(\mathbf{r}) = <\mathbf{F}(\mathbf{r})>_{\mathbf{r}} \qquad (5.6)$$

where $\mathbf{F}(\mathbf{r})$ is the force on the adatom and $<\ldots>_{\mathbf{r}}$ denotes an average over all the degrees of freedom of the substrate in prescence of a fixed adatom at **r**. The corresponding potential $V^{ad}(\mathbf{r})$ is a free energy and the mean density can be written as

$$<n(\mathbf{r})> = Z^{-1} \exp[-\beta V^{ad}(\mathbf{r})] \qquad (5.7)$$

where Z is the configurational part of the partition function,

$$Z = \int d\mathbf{r} \exp[-\beta V^{ad}(\mathbf{r})] \,. \qquad (5.8)$$

In average the force on the adatom is given by $\mathbf{F}^{ad}(\mathbf{r})$ and in transition state theory (TST) only this part of the interaction is included and all fluctuations of the force around the static value is neglected. The dynamic part, represented by the memory function $\mathbb{L}(11't)$, is a direct generalization of the friction term and it is responsible for fluctuation and dissipation of the energy of the adatom. Obviously, one can not evaluate the memory function exactly for any real many-body system, but its formal expression can be the base for relevant approximations. It contains the fluctuations, $\delta\mathbf{F} = \mathbf{F} - \mathbf{F}^{ad}$, of the force on the adatom from its adiabatic value and it depends therefore on the simultaneous motion of this atom and the surrounding particles.

5.2. Fokker-Planck approximation

In cases where their is a clear time-scale separation between the motion of the adatom and the motion in the surrounding, one can justify approximations of the memory function. If the fluctuations in the substrate have decayed before the adatom has moved appreciably, the motion of the adatom can be replaced by its initial value and the memory function reduces to

$$\mathbb{L}(11't) = \delta(11') < \delta\mathbf{F}(0)\, \delta\mathbf{F}(t) >_{\mathbf{r}_1} \,. \qquad (5.9)$$

Here $\delta\mathbf{F}$ is the fluctuating part of the force on the adatom, $\delta\mathbf{F} = \mathbf{F} - \mathbf{F}^{ad}$, and the subscript $\mathbf{r}_1$ in the bracket notation indicates that the force-force correlation function should be evaluated in the presence of a fixed adatom at position $\mathbf{r}_1$. The delta-function represents the effect that the adatom has no time to move or to change momentum during the time the force-force correlation function decays to zero. If we are only interested in times longer than the typical relaxation time of $< \delta\mathbf{F}(0)\, \delta\mathbf{F}(t) >_{\mathbf{r}_1}$ the equation of motion (5.5) reduces to the Markoffian equation[49,59]

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\nabla_{\mathbf{r}} + \mathbf{F}^{ad}(\mathbf{r}_1)\cdot\nabla_{\mathbf{p}}\right] C^s(11't) = \nabla_{\mathbf{p}}\cdot\eta(\mathbf{r}_1)\cdot\left[\mathbf{p} + \frac{m}{\beta}\nabla_{\mathbf{p}}\right] C^s(11't) \,. \qquad (5.10)$$

with

$$\eta(\mathbf{r}_1) = \frac{\beta}{m}\int_0^\infty dt < \delta\mathbf{F}(0)\, \delta\mathbf{F}(t) >_{\mathbf{r}_1} \,. \qquad (5.11)$$

This is the Fokker-Planck equation but with a position dependent friction tensor, in contrast to what was assumed in Eq (3.20). Eq (5.11) gives the microscopic expression for the friction coefficient and it is basically a property of the surrounding. The only dependence on the adatom is that the force-force correlation function should be evaluated in the presence of a fixed adatom.

5.2.1. Electron-hole pair excitations

The obvious candidate to treat within the Fokker-Planck approximation is the coupling to the electronic degrees of freedom.[60,61] Since the electron mass is much smaller than the mass of any adatom, the fluctuations in the surrounding is fast with respect to the adatom motion, and the assumption behind the Fokker-Planck equation should be valid. If we assume that the adatom couples to the density of the surrounding electrons, the force on the adatom can be written as

$$\delta \mathbf{F} = -\int d\mathbf{r}\ \nabla_{\mathbf{R}} V(\mathbf{R},\mathbf{r})\ \delta n_e(\mathbf{r}) \tag{5.12}$$

where $\delta n_e(\mathbf{r}) = n_e(\mathbf{r}) - \langle n_e(\mathbf{r})\rangle_{\mathbf{R}}$ is the fluctuating part of the density operator for the electrons, $\mathbf{R}$ is the position of the adatom and $V(\mathbf{R},\mathbf{r})$ describes the interaction between the electrons and the adatom. The friction coefficient can now be expressed in terms of the density-density correlation function for the electronic motion according to

$$\eta(\mathbf{R}) = \frac{\beta}{m} \int d\mathbf{r} \int d\mathbf{r}'\ \nabla_{\mathbf{R}} V(\mathbf{R},\mathbf{r}) \int_0^\infty dt < \delta n_e(\mathbf{r},0)\ \delta n_e(\mathbf{r}',t) >_{\mathbf{R}} \nabla_{\mathbf{R}} V(\mathbf{R},\mathbf{r}')\ . \tag{5.13}$$

An estimate of the order of magnitude of this expression leads to[60]

$$\eta \sim \frac{m_e}{m} \frac{\varepsilon_F}{\hbar} \tag{5.14}$$

where m_e is the electron mass, m the mass of the adatom and ε_F is the Fermi energy.

In order to evaluate the friction coefficient one has to calculate the density-density correlation function for the electronic motion in the presence of a fixed adatom. For a chemisorbed adatom this is very difficult to do from first principle. The density functional theory provides a one-electron scheme for calculating ground state properties, which takes into account exchange and correlation effects.[62,63] The friction coefficient is, however, a dynamic property but due to the time-integral from zero to infinity only the low lying excitations ($\omega \to 0$) are needed. It is then plausible that the density functional scheme can be used.[64] Within a one-electron scheme Eq (5.13) reduces to[65]

$$\eta^{\beta\beta'}(\mathbf{R}) = \frac{2\pi\hbar}{m} \sum_{\substack{\mathbf{k}\mathbf{k}' \\ (\varepsilon_{\mathbf{k}}=\varepsilon_{\mathbf{k}'}=\varepsilon_F)}} \int d\mathbf{r}\psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}'}(\mathbf{r})^* \nabla^\beta V(\mathbf{R},\mathbf{r}) \int d\mathbf{r}'\psi_{\mathbf{k}}(\mathbf{r}')^*\psi_{\mathbf{k}'}(\mathbf{r}')\nabla^{\beta'} V(\mathbf{R},\mathbf{r}') \tag{5.15}$$

where $\psi_{\mathbf{k}}(\mathbf{r})$ is a one-electron wavefunction with wavevector $\mathbf{k}$ and energy $\varepsilon_{\mathbf{k}}$, and β denotes a cartesian coordinate. The factor 2 comes from spin degeneracy. Actual calculations based on the density functional scheme with the local density approximation for the exchange-correlation potential have been performed.[66] Typically one finds $\hbar\eta$ of the order 1 meV for hydrogen chemisorbed on a jellium surface.

The excitations of electron-hole pairs in metals provide an energy dissipation mechanism in addition to coupling to phonons. In the language of Born-Oppenheimer potential energy hypersurfaces the electron-hole pair excitations promote transitions among nearby hypersurfaces.[26] The strength of this non-adiabatic coupling can be obtained from the above ab initio calculations. They can also be the starting point for quantitative investigations of the relative importance of electron-hole pair excitations versus phonons in adatom dynamics.

5.2.2. Phonons

If we instead consider coupling to phonons we can simply replace the electronic density in Eq (5.13) by the density of the substrate atoms. It is then convenient to expand in the lattice displacements $\mathbf{u}_l$ and the following formula for the friction coefficient can be derived,[21]

$$\eta^{\beta\beta'}(\mathbf{R}) = \frac{\beta}{m} \sum_{ll'} \sum_{\alpha\alpha'} v_{\mathrm{eff}}^{\alpha\beta}(\mathbf{R}-\mathbf{R}_l) \int_0^\infty dt <u_l^\alpha(t)\, u_{l'}^{\alpha'}> v_{\mathrm{eff}}^{\alpha'\beta'}(\mathbf{R}-\mathbf{R}_{l'})\ . \tag{5.16}$$

In deriving Eq (5.16) it is assumed that the adatom interacts with the substrate atoms through a pairwise additive potential $v(\mathbf{r})$. The subscript eff indicates that a Debye-Waller factor has been combined with the potential to an effective coupling term and α and β denote cartesian coordinates. In the presence of a fixed adatom the equilibrium positions of the substrate atoms are displaced and $\mathbf{u}_l$ are the displacements from these perturbed equilibrium positions, which are denoted by $\mathbf{R}_l = \mathbf{R}_l(\mathbf{R})$. The harmonic approximation for the lattice motion is assumed and only the one-phonon term has been retained. An estimate of the order of magnitude of this expression valid when the adatom is located around its equilibrium position leads to[67]

$$\eta \sim \frac{m}{m_s} \left(\frac{\omega_A}{\omega_D}\right)^4 \omega_D \tag{5.17}$$

where m_s is the mass of the substrate atoms, ω_A is the vibrational frequency for the adatom and ω_D is the Debye frequency of the substrate phonons.

Using the Fokker-Planck equation in this case is certainly highly questionable. Only when the adatom is much heavier than the substrate atoms the friction description is supposed to provide an accurate description of the coupling to the phonons. However, actual calculations of the motion of an adsorbed atom show that the time-scale separation between the motion of the adatom and the substrate motion need not to be large. If the Debye-frequency is at least twice as large as the characteristic vibrational frequency for the adatom, the Fokker-Planck equation gives quite accurate results, provided one uses a proper position dependent friction coefficient.[67]

5.3. Mode coupling approximation

For light adsorbates one has to go beyond the Fokker-Planck approximation and treat the memory function in a more accurate way. The time extension of this function depends on how the excitations in the substrate propagate and decay, as well as on the motion of the adatom and the coupling in between. These effects are incoperated in an approximative way in the so called mode coupling approximations, which take explicitly into account the appropriate time-scale of the fluctuating force through the inclusion of the dynamics in the surrounding. In the simpliest approach one write the memory function as a product of $C^s(11't)$ and a part that contains that substrate motion. The resulting equation of motion becomes non-linear in $C^s(11't)$ and has to be solved self-consistently. The lack of translational symmetry makes the numerical work complicated and only studies where the adatom is restricted to move in one dimension have been performed.[21,68]

---

[1] C. P. Flynn, *Point Defects and Diffusion*, (Clarendon Press, Oxford, 1972).
[2] Y. Fukai and H. Sugimoto, Adv. Phys. **34**, 263 (1985).
[3] E. W. Müller and T. T. Tsong, *Field Ion Microscopy* (Elsevier, New York, 1968).
[4] G. Ehrlich, Phys. Today **6**, 44 (1981).
[5] G. Ehrlich and K. Stolt, Ann. Rev. Phys. Chem. **31**, 603 (1980).
[6] V. T. Bien, ed. *Surface Mobilities on Solid Materials* (Plenum Press, New York, 1983).
[7] G. Ehrlich, J. Vac. Sci. Technol. **17**, 9 (1980).
[8] G. Mazenko, J. R. Banavar and R. Gomer, Surf. Sci. **107**, 459 (1981).
[9] K. W. Kehr, R. Kutner and K. Binder, Phys. Rev. **B23**, 4931 (1981).
[10] K. Sköld, in *Hydrogen in Metals I, Basic Properties*, Eds G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978).
[11] F. Reif, *Fundamentals of Statistical and Thermal Physics*, (McGraw-Hill, Tokyo, 1965)
[12] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[13] O. Klein, Ark. Mat. Astron. och Fys. **16**, 1 (1922).
[14] H. A. Kramers, Physica **7**, 284 (1940).
[15] H. Risken and H.D. Vollmer, Phys. Lett. **69A**, 387 (1979).
[16] R. L. Stratonovich, *Topics in the Theory of Random Noise*, (Gordon & Breach, New York, 1967).
[17] V. Ambegaokar and B. I. Halperin, Phys. Rev. Lett. **22**, 1364 (1969).
[18] D. L. Weaver, Physica **98A**, 359 (1979).
[19] J. R. Banavar, M. H. Cohen and R. Gomer, Surf. Sci. **107**, 113 (1981).
[20] G. Wahnström, J. Chem. Phys. (in print).
[21] G. Wahnström, Surf. Sci. **159**, 311 (1985).
[22] P. G. Wolynes, Phys. Rev. Lett. **47**, 968 (1981).
[23] P. Hanggi, J. Stat. Phys. **42**, 105 (1986).
[24] A. J. Leggett et. al., Rev. Mod. Phys. **59**, 1 (1987).
[25] A. Messiah, *Quantum Mechanics Vol 2* (North-Holland Publishing Company, Amsterdam, 1961).
[26] J. C. Tully, Ann. Rev. Phys. Chem. **31**, 319 (1980).
[27] P. Pechukas, in *Dynamics of Molecular Collisions, Part B*, Ed. W. H. Miller (Plenum Press, New york, 1976).
[28] D. G. Truhlar, W. L. Hase and J. T. Hynes, J. Phys. Chem. **87**, 2664 (1983).
[29] H. Eyring, J.Chem. Phys. **3**, 107 (1935).
[30] S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).
[31] C. A. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).
[32] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).
[33] A. F. Voter, J. Chem. Phys. **82**, 1890 (1985).
[34] J. G. Lauderdale and D. G. Truhlar, Surf. Sci. **164**, 558 (1985).
[35] J. G. Lauderdale and D. G. Truhlar, J. Chem. Phys. **84**, 1843 (1986).
[36] S. M. Valone, A. F. Voter and J. D. Doll, Surf. Sci. **155**, 687 (1985).
[37] S. M. Valone, A. F. Voter and J. D. Doll, J. Chem. Phys. **85**, 7480 (1986).
[38] R. Jaquet and W. H. Miller, J. Phys. Chem. **89**, 2139 (1985).
[39] D. L. Hill and J. A. Wheeler, Phys. Rev. **89**, 1102 (1953).
[40] J. C. Keck, Adv. Chem. Phys. **13**, 85 (1967).
[41] C. H. Bennett, in *Diffusion in Solids: Recent Developments*, ed. A. S. Nowick and J. J. Burton (Academic Press, New York, 1975).
[42] D. Chandler, J. Stat. Phys. **42**, 49 (1986).
[43] J. D. Doll and A. F. Voter, Ann. Rev. Phys. Chem. **38**, 413 (1987).
[44] T. Yamamoto, J. Chem. Phys. **33**, 281 (1960).
[45] W. H. Miller, S. D. Schwartz and J. W. Tromp, J. Chem. Phys. **79**, 4889 (1983).
[46] C. H. Bennett, in *Algorithms for Chemical Computations*, ed. R. E. Christoffersen (American Chemical Society, Washington D. C., 1977).
[47] W. H. Miller, Acc. Chem. Res. **9**, 306 (1976).
[48] D. Chandler, J. Chem Phys., **68**, 2959 (1978).

---

[49] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions*, (W. A. Benjamin, Reading, Massachusetts, 1975).

[50] S. W. Lovesey, *Condensed Matter Physics: Dynamic Correlations*, (The Benjamin/Cummings Pub., Menlo Park, California, 1986).

[51] G. Wahnström and H. Metiu, J. Phys. Chem. (in print).

[52] J. Costley and P. Pechukas, Chem. Phys. Lett. **83**, 139 (1981).

[53] R. W. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965).

[54] A. F. Voter and J. D. Doll, J. Chem. Phys. **82**, 80 (1985).

[55] A. F. Voter, Phys. Rev. **B10**, 6819 (1986).

[56] B. J. Berne, in *Statistical Mechanics, Part B: Time-Dependent Processes*, ed. B. J. Berne (Plenum Press, New York, 1977).

[57] R. Zwanzig, in *Lectures in Theoretical Physics, Vol 3*, eds. W. E. Brittin, B. W. Downs and J. Downs (Interscience, New York, 1961).

[58] H. Mori, Progr. Theoret. Phys. **33**, 423 (1965).

[59] W. L. Schaich, J. Chem. Phys. **60**, 1087 (1974).

[60] E. G. d'Agliano, P. Kumar, W. Schaich and H. Suhl, Phys. Rev. **B11**, 2122 (1975).

[61] A. Blandin, A. Nourtier and D. W. Hone, J. Physique **37**, 369 (1976).

[62] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[63] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[64] B. Hellsing and M. Persson, Physica Scripta **29**, 360 (1984).

[65] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* , (McGraw-Hill, New York, 1971).

[66] M. Persson and B. Hellsing, Phys. Rev. Lett. **49**, 662 (1982).

[67] G.Wahnström, Surf. Sci. **164**, 449 (1985).

[68] W. G. Kleppmann and R. Zeyher, Phys. Rev. **B22**, 6044 (1980).