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The dynamics of activated surface diffusion

Salvador Miret-Artés[1] **and Eli Pollak**[2]

[1] Instituto de Matemáticas y Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006 Madrid, Spain
[2] Chemical Physics Department, Weizmann Institute of Science, 76100 Rehovot, Israel

E-mail: s.miret@imaff.cfmac.csic.es and Eli.Pollak@weizmann.ac.il

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Abstract

An elementary process occurring on surfaces is diffusion. The dynamics is simplest when the concentration of adsorbates is sufficiently small that interaction between adsorbates can be ignored. But even for this tracer diffusion process, much remains to be uncovered. Here, we present the interplay between experimental measurement of tracer diffusion and its theoretical interpretation, which leads to good estimates of the interaction of the adparticle with the surface. We show how the results from three different experimental techniques—field ion microscopy, scanning tunnelling microscopy and quasielastic helium atom scattering—can be interpreted. Using the generalized Langevin equation as a model for the diffusion dynamics, we show how the turnover theory for activated diffusion may be used to describe the measured time evolution of the adparticle distribution on the surface. The different activation energy measured for hopping over single or double lattice lengths is shown to come from the added energy loss to the surface, as the particle moves over the longer path. We discuss some of the issues which are not yet clear; these include quantum effects, such as the quantum suppression of diffusion, vibrationally assisted diffusion, multidimensional effects and diffusion in the presence of external fields.

1. Introduction

The diffusion of adsorbates on surfaces is perhaps the most elementary dynamical process occurring on surfaces. It is a preliminary step to more complex surface phenomena such as crystal growth, associative desorption, heterogeneous catalysis and chemical reactions. The experimental development of methods which allow for an intimate probing of diffusion has also led to new results in the theory for the diffusion (tracer and collective or chemical) coefficients and friction constants. The detailed characterization of diffusion mechanisms and adsorbate–substrate, adsorbate–adsorbate interactions, has stimulated considerable progress in theoretical methods. Different experimental and theoretical techniques and methods have been reviewed during the past 15 years by Gomer [1], Lombardo and Bell [2], Hofmann and Toennies [3], Barth [4] and Ala-Nissila, Ferrando and Ying [5].

In most cases, one is considering an adatom or admolecule, which is trapped on a site on the surface. The adparticle can escape from the site only if it overcomes a barrier (whose height is denoted as $V^{\ddagger}$) which separates it from the adjacent site. The energy needed for this activation is supplied by the thermal energy of the surface, hence the terminology 'activated surface diffusion'. Elementary theory then implies that the diffusion coefficient obeys an Arrhenius law, and so it may be written down as

$$D(T) = D_0(T)\exp\left(-\frac{V^{\ddagger}}{k_{\mathrm{B}}T}\right). \tag{1.1}$$

Much theoretical work is geared towards understanding the structure of the surface and the adparticle sitting on it. *Ab initio* theoretical chemistry and semiempirical methods are used to determine the adiabatic potential felt by the particle [5]. The dynamics however is in the prefactor $D_0(T)$, which is the central object of this review. The theory presented sheds light on the mean free path of the particle, the probability for jumps over multiple sites, quantum effects such as tunnelling and above barrier reflection, the frictional forces exerted by the surface on the adparticle, intramolecular vibrational effects and more. We restrict this review to low surface coverage; that is, interactions between adparticles are neglected.

Diffusion times and thus diffusion coefficients may vary by orders of magnitude, depending on the temperature of the surface. Present day experimental methodology enables the accurate determination of diffusion coefficients which span more than ten orders of magnitude. However, different experimental methods are used for different diffusion times. Scanning tunnelling microscopy (STM) and field ion microscopy (FIM) are especially useful for slow diffusion, such that the time between jumps of the adatom is of the order of seconds. These measurements provide a direct observation of the diffusion process. Quasielastic helium atom scattering (QHAS) has been used to determine diffusion processes in which the time between jumps is of the order of microseconds. In section 2 we give a very brief review of these experimental methods. As contrasted with STM and FIM, QHAS provides information on the diffusion dynamics only indirectly. We therefore also provide in section 3 a review of the theory underlying the QHAS method and discuss some of the difficulties involved in interpreting the results. Special attention is given to the intertwining of vibrational adparticle motion with diffusion.

A very useful model for the diffusion dynamics is the Langevin equation or its generalization to include memory effects in the form of time dependent friction [6]. In a typical theoretical analysis, one obtains information over the potential of mean force governing the motion of the adparticle from a combination of *ab initio* chemistry computations and experimental data. The interaction of the adparticle with the surface is then typically represented in terms of a frictional force and a random force related to each other by the fluctuation–dissipation relation. One then carries out numerical molecular dynamics simulations, which are sufficient for determining the classical mechanics of the diffusion process. Classical mechanics is usually sufficient except for very light particles such as hydrogen. One of the successes of recent theory is in providing simple analytic expressions for the prefactor and the time dependent hopping distribution of the adparticles. These may then be used to directly interpret the experimental results, shedding light on the interaction of the adparticle with the surface. In section 4 we review the Langevin theory of diffusion, paying special attention to the analytical results.

Then in section 5 we discuss some of the remaining outstanding challenges facing theory. These include the theory of multidimensional diffusion, vibrational mediation of diffusion, quantum mechanical aspects and more.

2. Experimental methods

As mentioned in the introduction, we will be dealing exclusively with tracer diffusion, that is diffusion of a single adparticle that interacts with the surrounding surface, but is not influenced by other adparticles on the surface. An excellent review of the experimental methods available until the year 1990 may be found in the review by Gomer [1]. A more recent but also more concise review is given in [4]. Here we concentrate on three experimental methods, the field ion microscopy method, which was a forerunner of the scanning tunnelling microscopy method, and the quasielastic helium atom scattering method. Results from these three methods have been analysed and interpreted in terms of Langevin equations and so they are the mainstay of this review.

2.1. Field ion microscopy measurements

Field ion microscopy (FIM) [7] provided the first direct measurement of adatom diffusion. The method, which evolved from the field emission microscopy (FEM) technique [1], was the first to give a direct observation of the diffusion dynamics. A metal tip serves as the substrate for the adsorbed atoms. At a sufficiently low temperature, the adatom diffusion is so slow that it can be ignored. An inert imaging gas is ionized with a strong electric field and the emitted ions are detected on a screen. The ionization depends sensitively on the local surroundings and thus one can observe directly the location of adatoms on the surface. Since one is measuring the heavy ions, the method has a resolution of 1–2 Å and so provides a detailed picture of the location of adatoms on the surface.

After the first measurement the tip is rapidly heated, and kept at the 'hot' temperature for a fixed amount of time which is much longer than the time it took to heat the tip. Then the tip is rapidly cooled and the FIM measurement repeated. Any jump of adsorbed atoms will now reflect itself directly in the new field emission spectrum. Implicitly, one is assuming that no diffusion occurs during the heating and cooling periods. The heating and cooling must thus be short as compared to the time at which the system is kept at 'high temperature'. In order to obtain information on individual hops of the adparticles, the 'high temperature' period must be short enough so that a given adparticle will not jump more than a 'few' jumps during this period. For if it jumps many times, then the hopping distribution will be Gaussian with a width which gives the global diffusion coefficient, but does not provide information on individual hopping rates.

To be more precise, one assumes that the adparticle distribution on the surface is governed by a master equation [8]. To simplify, we assume that the adparticle can jump independently along two perpendicular lattice directions but with different hopping rates, denoted as Γ_j^1 and Γ_j^2, $j = 0, \pm 1, \ldots$. The location of the particle on the lattice is denoted by two indices l, m. At the initial time ($t = 0$) the particle is by definition at the site $l = m = 0$, that is $w_{l,m}(t = 0) = \delta_{l,0} \cdot \delta_{m,0}$. The probability distribution $w_{l,m}(t)$ for the particle to be at the l, m site at time t is then governed by the master equations:

$$\frac{\mathrm{d}}{\mathrm{d}t} w_{l,m}(t) = \sum_{j=-\infty}^{\infty} \Gamma_j^1 w_{l-j,m} + \sum_{j=-\infty}^{\infty} \Gamma_j^2 w_{l,m-j}. \tag{2.1}$$

By definition, the rates Γ_0^1 and Γ_0^2 are negative, allowing for escape from the l, m site, the rates $\Gamma_j^{1,2}$ are the rates of jumping directly over j sites.

The master equation is solved by Fourier transforms using the translational invariance of the surface. Denoting $\hat{w}(\mathbf{k}, t) = \sum_{l,m} w_{l,m}(t)\mathrm{e}^{\mathrm{i}(k_1 l+k_2 m)}$ and $\hat{\Gamma}^{1,2}(k) = \sum_l \Gamma_l^{1,2}\mathrm{e}^{\mathrm{i}kl}$ one readily finds the explicit result:

$$\hat{w}(\mathbf{k}, t) = \mathrm{e}^{-(\hat{\Gamma}^1(k_1)+\hat{\Gamma}^2(k_2))t}. \tag{2.2}$$

This then implies that $w_{l,m}(t) = w_l^1(t)w_m^2(t)$, with

$$w_l^{1,2}(t) = \frac{1}{2\pi}\int_0^{2\pi} \mathrm{d}k\, \mathrm{e}^{-\hat{\Gamma}^{1,2}(k)t}\mathrm{e}^{-\mathrm{i}kl}. \tag{2.3}$$

Since the distribution $w_l^{1,2}(t)$ is measured directly in the experiment, it can then be fitted by adjusting the hopping rate parameters $\Gamma_j^{1,2}$ as if they were independent fitting parameters [9, 10]. Typically, one finds that at most $j = 2, 3$ suffices for fitting the experimentally measured time dependent distribution. It should be stressed that it is the deviation of the time dependent distribution $w_l^{1,2}(t)$ from a Gaussian which allows accurate inversion to the individual hopping rates.

This then means that both FIM and STM (see below) are limited to slow diffusion, such that the mean time between jumps of the adparticle is of the order of 10^{-2} s and longer. For faster diffusion, one must resort to more indirect methods, of which the QHAS is an important one to be discussed below.

2.2. *The STM method*

The central difference between STM and FIM is in the means of observing the adparticle. In FIM, this is effected through the ionization of the inert gas. In STM, it comes from the change in the tunnelling current of the STM tip. Thus one scans a portion of the surface, covering typically an area of a few hundred Å^2 at the low temperature, then the surface is rapidly heated, allowing for diffusion to occur, and then cooled down again for the next STM measurement [11]. As in FIM, this limits the experiment to diffusion times which are of the order of seconds.

The spectacular achievement of STM has culminated in video recordings of atomic diffusion, which are available in the form of movies[3]. These show in detail the 'drunken walker' mechanism of diffusion, in which an adparticle jumps back and forth along a trough of a well characterized surface. These measurements have also shown that adatoms can, in a single jump, hop over lengths which are a few multiples of the lattice length of the surface.

Perhaps the most worrisome aspect of the STM method is that the strong field emanating from the tip can in principle change the local electronic surroundings of the adparticle and thus affect the natural diffusion process [12–14]. Various experiments have been carried out to determine the extent of the influence of the tip [15]. The central finding is that the field does not affect the activation energy 'too much'. However, a change of a few per cent in an activation barrier can lead to significant uncertainty in the prefactor $D_0(T)$ where all the dynamics is hidden, so that the effect of the STM field on the hopping characteristics has not yet been resolved.

Finally, we do note that in both FIM and STM one may alter the surface temperature at which the diffusion occurs to obtain directly an Arrhenius plot for the individual hopping rates. One of the interesting results is that the activation energy for double hops is somewhat higher

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[3] These can be found at the website of the Department of Physics and Astronomy of the University of Aarhus—http://www.phys.au.dk/camp/hot0017.shtm

than the activation energy for single hops [11]. We shall see below that this observation has been interpreted successfully in terms of the Langevin equation modelling of the diffusion.

2.3. The QHAS method

The QHAS method [3] can be considered as the surface science analogue of quasielastic neutron scattering, which has been widely and successfully applied to analyse diffusion in the bulk. The experimental layout incorporates a supersonic He atomic beam source, a very low pressure target chamber and a time-of-flight arm at a fixed angle of usually 95.8° to the incident beam direction. The resulting time-of-flight spectra are converted to an energy transfer scale and the parallel wavevector transfer is varied by changing the incident angle of the beam with respect to the surface normal. The coverage of adparticles is monitored via the He atom specular reflectivity, assuming a constant sticking coefficient. Van Hove [16] was the first to discuss the velocity requirement of probe particles needed to extract information about unaffected diffusion coefficients, spatial and time pair correlation functions, jump distributions, etc. The scattering particles should stay on the surface a time which is at least of the order of the relaxation time of the relevant correlation functions. In particular, He atoms emanating from a room temperature source fulfil this requirement, since their velocities are less than 3×10^3 m s^{-1}. Obviously, electrons and light scattering cannot be used as a similar probe.

Due to the relatively slow velocity of the He atom beam, the atoms probe only the outer surface dynamics. Especially in contrast with STM and FIM, the QHAS technique is nondestructive. It also provides information on the entire dispersion curves; in particular, to very low energy regions. Typically, He beams have the following properties: high angular resolution (around 0.3°), high velocity resolution ($\Delta v/v \sim 1\%$), a large dynamical range in intensity (several orders of magnitude) and a spectral range between 0.2 and 50 meV. With all these properties, the incident beam is highly monochromatic and well collimated and it will be coherent in both time and space over about 10^{-11} s and 100 Å, respectively. The method is sufficiently sensitive to probe very low surface coverages, down to $\sim$0.005. During the interaction time on the surface, the beam probes the spatial distribution of the adsorbate via the Doppler effect with large cross sections for the adparticles. This leads to a small energetic broadening of the He atoms scattered elastically from the diffusing particles, hence the name ‘quasielastic atom scattering’. The corresponding peak in the time-of-flight spectrum converted to an energy transfer scale is known as the quasielastic or Q peak. At present, QHAS is limited to systems with fast diffusion with coefficients $D > 10^{-6}$ cm^2 s^{-1}. As already mentioned, FIM and STM are restricted to slow diffusion with $D < 10^{-14}$ cm^2 s^{-1}.

In principle, adparticle diffusion is much slower than even the lowest frequency adsorbate vibrational modes and so the two are well separated in time. In particular, one of the lowest frequency adsorbate vibrational modes corresponds to the so-called frustrated translational mode or T-mode, leading to the T-mode peak in the He beam time-of-flight spectrum. However, for example, by increasing the surface temperature, the diffusion time may be reduced exponentially, the two motions become coupled, diffusion will be assisted by the low frequency vibrations which will contribute to the quasielastic peak. In the limit that the temperature is higher than the diffusion barrier, no detectable trace of pure vibrations is expected and only a broad quasielastic peak will be observed. A method for overcoming this mixing through adequate manipulation of the initial conditions of the atomic beam [17], taking advantage of the so-called inelastic focusing singularity from atom-surface scattering [18], has been recently proposed.

The major experimental challenge facing this technique is to extract the inherent widths of different line shapes (in particular, Q- and T-peaks) by deconvolution of the results from apparatus smearing. As also discussed below, the widths provide information on the relevant physical quantities such as the diffusion coefficient, the interaction of the adparticle with the surface (friction parameter), etc. Typically, the instrument response function of the apparatus is assumed to be Gaussian while the physically interesting response function of the scattering process is assumed to be Lorentzian. In fact, the corresponding line shapes are governed by the so-called motional narrowing effect [19, 17], first observed in the stochastic nuclear magnetic resonance lineshapes [20].

In summary, while the QHAS technique is nondestructive, its theoretical interpretation is substantially more difficult than that of FIM or STM. In the next section, we review briefly the theory underlying the QHAS technique, which then enables the interpretation of the scattering in terms of generalized Langevin equations.

3. Theoretical interpretation of QHAS measurements

3.1. General considerations

In QHAS measurements, the observed spectrum is the differential reflection probability, that is, the probability for an atom to be scattered into a certain solid angle Ω with an energy interchange $\hbar\omega$. In this section we shall show how these measurements are related to the detailed dynamics of the diffusion of the adparticle.

The QHAS signal is proportional to the dynamic structure factor, $S(\mathbf{K}, \omega)$, defined as the double Fourier transform of the G van Hove correlation function [21]

$$\frac{\mathrm{d}^2 R(\mathbf{K}, \omega)}{\mathrm{d}\Omega\, \mathrm{d}\omega} = N f^2 S(\mathbf{K}, \omega) = N f^2 \int\!\!\int G(\mathbf{R}, t) \mathrm{e}^{\mathrm{i}(\mathbf{K}\cdot\mathbf{R} - \omega t)}\, \mathrm{d}\mathbf{R}\, \mathrm{d}t \qquad (3.1)$$

where $\mathbf{K}$ is the wavevector transfer parallel to the surface,

$$\mathbf{K} = \mathbf{k}_f \sin\theta_f - \mathbf{k}_i \sin\theta_i \qquad (3.2)$$

and the energy interchange is

$$\hbar\omega = \mathbf{k}_f^2 - \mathbf{k}_i^2 \qquad (3.3)$$

where we have assumed that $\hbar^2/2m = 1$ and the standard notation has been followed: capital letters for vectors parallel to the surface and small letters for vectors in 3D.

In equation (3.1), f is the atomic form factor depending on the interaction potential between the projectile and the adparticles. The corresponding van Hove fluctuation density autocorrelation function [16] is written as

$$G(|\mathbf{R} - \mathbf{R}'|, t) = \Sigma \langle \delta\rho(\mathbf{R}', 0) \delta\rho(\mathbf{R}, t) \rangle \qquad (3.4)$$

with

$$\rho(\mathbf{R}, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \delta(\mathbf{R} - \mathbf{R}_i(t)). \qquad (3.5)$$

The density of adparticles is given by $\rho = N/\Sigma$ where Σ is the surface area and the coverage is defined by $\theta = N/N_{\text{max}}$, with N_{max} being the maximum number of sites in the area Σ. When the coverage on the surface is very low, adparticles can be treated as independent and only the self-part of the van Hove correlation function, G, is important.

It is sometimes convenient to express the dynamic structure factor in terms of the intermediate scattering function, $I(\mathbf{K}, t)$, which can be considered as the characteristic function of the stochastic process $\mathbf{R}(t)$,

$$I(\mathbf{K}, t) = \frac{1}{2\pi} \int \mathrm{d}t\, S(\mathbf{K}, \omega) \mathrm{e}^{\mathrm{i}\omega t} = \langle \mathrm{e}^{-\mathrm{i}\mathbf{K}\cdot\mathbf{R}(t) - \mathbf{R}(0)} \rangle = \langle \mathrm{e}^{-\mathrm{i}\mathbf{K} \int_0^t v_l(t')\, \mathrm{d}t'} \rangle, \qquad (3.6)$$

where v_l is the velocity of the adparticle projected along the wavevector transfer $\mathbf{K}$. A cumulant expansion to second order yields the standard result [22]

$$I(\mathbf{K},t) \sim \mathrm{e}^{-\frac{\mathbf{K}^2}{2}\int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \langle v_l(t')v_l(t'')\rangle} = \mathrm{e}^{-\mathbf{K}^2 \int_0^t (t-t')\psi(t')\,\mathrm{d}t'} \tag{3.7}$$

where $\psi(t) \equiv \langle v_l(t)v_l(0)\rangle$ is the velocity autocorrelation function of the adparticle. The first approximation comes from the truncation of the cumulant series, and the second equality holds if the velocity process $v_l(t)$ is stationary. For Gaussian stochastic processes, as is the case if the thermal noise is Gaussian white noise and there is no interaction potential or it is quadratic, equation (3.7) is exact. Higher cumulants have been derived by Rahman and co-workers [23]. Knowledge of $\psi(t)$ is in general insufficient to completely determine I.

3.2. *Free particle diffusion*

To gain a feeling for the form of the dynamic structure factor we first consider it in the limit of a free particle; that is, the adiabatic potential governing its motion is constant. The adparticle does feel however a random Gaussian force $F(t)$ with zero mean, induced by its interaction with the surface. The force autocorrelation function is related to the friction function by the fluctuation dissipation relation $\langle F(t)F(\tau)\rangle = k_\mathrm{B}T\gamma(t-\tau)$. If furthermore the friction function is Ohmic ($\gamma(t) = 2\gamma\delta(t)$, with $\delta(t)$ the Dirac 'δ' function), then the velocity autocorrelation function $\psi(t)$ decays exponentially with time [24], $\psi(t) = \langle v_l^2\rangle \mathrm{e}^{-t/\tau}$, and the time constant $\tau = 1/\gamma$, with τ the (normalized) correlation time for the adparticle velocity.

The intermediate scattering function can then be expressed as [22]

$$I(\mathbf{K},t) = \exp\left[-\chi^2\left(\mathrm{e}^{-t/\tau} + \frac{t}{\tau} - 1\right)\right] \tag{3.8}$$

with

$$\chi = \tau\sqrt{\langle v_l^2\rangle}|\mathbf{K}| = \frac{D|\mathbf{K}|}{\sqrt{\langle v_l^2\rangle}} \equiv \bar{l}|\mathbf{K}| \tag{3.9}$$

where $\bar{l}$ is the mean free path and

$$D = \tau\langle v_l^2\rangle = \tau k_\mathrm{B}T/m \tag{3.10}$$

is the diffusion coefficient. The shape of the dynamic structure factor is determined by the magnitude of the friction. For weak damping (long correlation time τ) the mean free path is large, a short time expansion of the exponent in equation (3.8) is in order and the dynamic structure factor is Gaussian:

$$S(\mathbf{K},\omega) \propto \frac{1}{|\mathbf{K}|v_l} \exp[-\omega^2/(2|\mathbf{K}|^2 v_l^2)]. \tag{3.11}$$

The corresponding full width at half maximum (FWHM) $\Delta S(\mathbf{K})$ with respect to the frequency is linearly dependent on the wavevector transfer and v_l, $\Delta S(\mathbf{K}) \propto v_l|\mathbf{K}|$. The corresponding van Hove function is also Gaussian

$$G(\mathbf{R},t) \propto \frac{1}{(v_l t)^2} \exp[-\mathbf{R}^2/(t^2 v_l^2)]. \tag{3.12}$$

This behaviour has been found in QHAS experiments of Xe adsorbates on a Pt(111) surface [25], providing evidence for a fully mobile two-dimensional gas of Xe atoms.

In the opposite case, when the damping is strong, we have the long time approximation ($t \gg \tau$ in equation (3.8)), $I(\mathbf{K},t) \propto \mathrm{e}^{-\mathbf{K}^2 Dt}$ and the spectrum has a Lorentzian line shape,

$$S(\mathbf{K},\omega) \propto \frac{|\mathbf{K}|^2 D}{\omega^2 + |\mathbf{K}|^4 D^2}. \tag{3.13}$$

The FWHM with respect to the frequency ω is now $\Delta S(\mathbf{K}) = D\mathbf{K}^2$.

We have thus seen that the shape of the dynamic structure factor can change from a Gaussian shape when χ (cf equation (3.9)) is large to a motionally narrowed Lorentzian when χ is small. The exact Fourier transform of equation (3.8) can be expressed in terms of the complete and incomplete Gamma functions as [26, 17]

$$S(\mathbf{K},\omega) = \frac{\mathrm{e}^{\chi^2}\tau}{\pi}\chi^{-2\chi^2}\,\mathrm{Re}\,\chi^{-\mathrm{i}2\omega\tau}\left[\Gamma(\chi^2+\mathrm{i}\omega\tau)-\Gamma\left(\chi^2+\mathrm{i}\frac{\omega\tau}{\chi^2}\right)\right]$$
$$= \frac{\mathrm{e}^{\chi^2}}{2\pi}\sum_{n=0}^{\infty}\frac{(-1)^n\chi^{2n}}{n!}\frac{2[(\chi^2+n)/\tau]}{\omega^2+[(\chi^2+n)/\tau]^2} \tag{3.14}$$

and one notes that the transition from a Gaussian form to a Lorentzian form is a function of the parameter χ defined in equation (3.9).

3.3. *QHAS for activated surface diffusion*

In activated diffusion the time between jumps is long so that jumps between different sites may be considered as instantaneous. This allows one to describe the jump dynamics in terms of the master equation given in equation (2.1) with the identification that $\hat{w}(\mathbf{k},t) = I(\mathbf{K},t)$. The master equation underlies the analysis of Chudley and Elliot [27] for the dynamic structure factor.

Appropriate Fourier transformation of the solution of the master equation will directly give the dynamic structure factor. In other words, the information content of the dynamic structure factor is precisely the hopping rates Γ_j^i which define the master equation. In the following section we shall describe the analytic Langevin theory which provides expressions for the hopping rates Γ_j^i which depend on a few physically meaningful parameters, such as the barrier height of the adiabatic potential, the damping constant which describes the interaction of the adparticle with the surface, the harmonic frequency of motion of the adparticle on the surface and the surface temperature.

The experimental results are usually described in terms of a plot of the dependence of the FWHM of the dynamic structure factor ($\Delta S(\mathbf{K})$) as a function of the energy transfer frequency ω at a fixed value of the momentum transfer $\mathbf{K}$. From the master equation (2.1) (in which we assumed that hopping may occur only in either the x or the y direction separately) and its formal solution (equation (2.3)), one readily finds that

$$\Delta S(\mathbf{K}) = 2\Gamma\sum_{j=0}^{\infty}\left[P_j^1(1-\cos(jl_xK_x)) + P_j^2(1-\cos(jl_yK_y))\right] \tag{3.15}$$

where l_x and l_y are the lattice lengths in the x and y directions respectively; Γ is the total unidirectional rate out of the initial well ($\Gamma = \sum_{j=1}^{\infty}(\Gamma_j^1+\Gamma_j^2)$) and $P_j^i = \Gamma_j^i/\Gamma$, $i = 1, 2$. The input then needed to obtain the FWHM function is the detailed jump rates Γ_j^i.

The major complication in the interpretation of the QHAS measurements is the possibility that inelastic processes interfere with the quasielastic peak. When this happens, one can no longer consider that the FWHM of the quasielastic peak is determined solely by the hopping rates. This type of phenomenon will be discussed further in section 5, below.

4. Analytic theory

4.1. *The equations of motion*

The centre of mass of a diffusing adatom or molecule (with mass m) moves in a three-dimensional configuration space—x and y are the coordinates along the plane of the surface and z is the coordinate perpendicular to the surface. The particle thus moves in a mean field of force whose potential $V_s(x, y, z, \underline{\boldsymbol{r}})$ is a function of the three coordinates and any additional internal degrees of freedom of the molecule, described by the vector $\underline{\boldsymbol{r}}$. In addition, the adsorbed particle may interact with the motion of the atoms on and below the surface. This interaction might typically be in the form of optical or acoustic phonons of the surface. In the former case one is considering a high frequency localized motion on the surface; in the latter case one has a continuum of low frequency modes. As long as the temperature is not too high, these interactions are well approximated in the form of a bilinear coupling of the adatom or molecule with a bath of harmonic oscillators. Thus a central model describing diffusion is that of a Hamiltonian whose form is

$$\begin{aligned} H = \frac{\hat{p}^2}{2m} + V(x, y, z) + \frac{1}{2}\sum_{j=1}^{N}\left[p_{x_j}^2 + \omega_{x_j}^2\left(x_j - \frac{c_{x_j}}{\omega_{x_j}^2}x\right)\right] \\ + \frac{1}{2}\sum_{j=1}^{N}\left[p_{y_j}^2 + \omega_{y_j}^2\left(y_j - \frac{c_{y_j}}{\omega_{y_j}^2}y\right)\right]. \qquad (4.1) \end{aligned}$$

The harmonic frequencies of the bath modes and the coupling coefficients are expressed in terms of spectral densities [28] defined as

$$J_i(\omega) = \frac{\pi}{2}\sum_{j=1}^{N}\frac{c_{i_j}}{m\omega_{i_j}^2}\left[\delta(\omega - \omega_{i_j}) - \delta(\omega + \omega_{i_j})\right], \qquad i = x, y. \qquad (4.2)$$

The associated friction functions are defined through the cos Fourier transforms of the spectral densities:

$$\gamma_i(t) = \frac{2}{\pi}\int_0^\infty \mathrm{d}t\, \frac{J_i(\omega)}{\omega}\cos(\omega t) \qquad i = x, y. \qquad (4.3)$$

This nomenclature has its origin [29] in the fact that the classical equation of motions obeyed by the Hamiltonian of equation (4.1) is the coupled set of generalized Langevin equations (for brevity, we omit here the internal degrees of freedom of the molecule)

$$m\ddot{z} + \frac{\partial V(x, y, z)}{\partial z} = 0 \qquad (4.4)$$

$$m\ddot{x} + \frac{\partial V(x, y, z)}{\partial x} + m\int^t \mathrm{d}t'\, \gamma_x(t - t')\dot{x}(t') = F_x(t) \qquad (4.5)$$

$$m\ddot{y} + \frac{\partial V(x, y, z)}{\partial y} + m\int^t \mathrm{d}t'\, \gamma_y(t - t')\dot{y}(t') = F_y(t) \qquad (4.6)$$

where $F_x(t)$ and $F_y(t)$ are independent Gaussian random forces, with zero mean, obeying the fluctuation dissipation relations $\langle F_i(t)F_i(t')\rangle = mk_\mathrm{B}T\gamma_i(t - t'), i = x, y$ where T is the temperature of the bath and the brackets denote the appropriate Gaussian averaging.

In many cases classical mechanics suffices for a description of the diffusion process, since the mass of the adatom or molecule is usually rather large. In some cases, depending on the geometry of the surface, one may approximate the diffusion along the surface to be one dimensional. This is typically the case when the diffusion occurs on a (100) or (110) surface. A further simplification occurs when the frequency of motion in the vertical z direction is much larger than the frequency of motion along the surface. One may then adiabatically eliminate the vertical motion and one is left with a purely one-dimensional generalized Langevin equation (GLE) model of surface diffusion:

$$m\ddot{x} + \frac{\mathrm{d}V(x)}{\mathrm{d}x} + m\int^t \mathrm{d}t'\, \gamma(t - t')\dot{x}(t') = F(t). \qquad (4.7)$$

This one-dimensional model serves as the basis for understanding the effect of friction on the diffusion process. We further assume that the potential $V(x)$ is a periodic potential (although on any given surface impurities will always limit the range over which the potential really is periodic) with lattice length l_0 and wells separated by barriers, whose height $V^{\ddagger}$ relative to the bottom of the wells is much larger than k_BT. This last assumption is crucial. If the reduced barrier height $\left(V^{\ddagger}/k_BT\right)$ is less than ∼3, then the theory breaks down. If the reduced barrier height is in the range ∼3–6 one must add finite barrier corrections to the theory [30–34]. Numerical solutions for the dynamics of the GLE abound, using various techniques, for a recent review see [5]. Here, we are interested in the analytic theory, described below.

4.2. Turnover theory of activated diffusion

The Langevin theory of diffusion answers the following questions:

(a) What is the rate of escape of the adatom trapped in the well?
(b) How is this rate affected by the frictional and random force?
(c) Once the particle escapes from a well, how many lattice lengths will it traverse before it is retrapped?
(d) Is there a difference between the dynamics of nearest neighbour hopping or hopping longer distances?
(e) What are the mean squared path length and the diffusion coefficient and how do they depend on the frictional and random force?

These questions have been addressed by various authors [35–38]; here we will provide a summary of the main results.

In the Langevin picture, one first considers a kinetic equation for the (reduced—$\epsilon \equiv E/k_BT$) energy distribution function of adatoms in the jth well. This density is affected by the rate of particles exiting the jth well and those arriving at the well from the $j-1$th and $j+1$th wells. The number of particles per unit energy and per unit time hitting the right (left) barrier of the jth well with positive (negative) velocity is denoted by f_j^+ (f_j^-). The reflection symmetry of the potential and the boundary conditions about the zeroth well implies that $f_j^{\pm}(\epsilon) = f_{-j}^{\mp}(\epsilon)$.

Initially, one assumes that the adatom was localized in the zeroth well and was at local equilibrium in that well. One then makes a steady state assumption for the population. This then gives the central steady state equation for the fluxes [36, 37]:

$$f_j^+(\epsilon) = \int_{-\infty}^{\infty} \mathrm{d}\epsilon'\, P(\epsilon|\epsilon')[R(\epsilon')f_j^-(\epsilon') + T(\epsilon')f_{j-1}^+(\epsilon')] \tag{4.8}$$

where $T(\epsilon)$ is the probability that the particle crosses the barrier as it approaches it at the (reduced) energy ϵ and $R(\epsilon)$ is the probability of being reflected by the barrier. Of course $T(\epsilon) + R(\epsilon) = 1$.

A central quantity in the theory is the conditional probability kernel $P(\epsilon|\epsilon')$ that the particle changes its (reduced) energy from ϵ' to ϵ as it traverses from one barrier to the next. This in turn depends on another central quantity, which is the (reduced) average energy loss δ as the adatom traverses from one barrier to the next. In the limit of weak friction, one may readily show that the energy loss is given in terms of the friction function and the unperturbed orbit of the particle at the barrier energy [36, 37]:

$$\begin{aligned}\delta &= \frac{m}{2k_BT}\int_{-\infty}^{\infty}\mathrm{d}t\int_{-\infty}^{\infty}\mathrm{d}t'\,\dot{x}(t)\gamma(t-t')\dot{x}(t')\\ &= \frac{m}{4\pi k_BT}\int_{-\infty}^{+\infty}\mathrm{d}\omega\,|\tilde{\dot{x}}(\omega)|^2\tilde{\gamma}(\omega).\end{aligned} \tag{4.9}$$

The unperturbed orbit of the particle is the solution of the frictionless equation of motion $m\ddot{x} + \frac{\mathrm{d}V(x)}{\mathrm{d}x} = 0$ at the barrier energy such that at time $t = -\infty$ the adatom is initiated at the first barrier and it reaches the adjacent barrier at $t = \infty$. In the second equality the tilde notation stands for the Fourier transform of the corresponding value ($\tilde{x}(\omega) = \int \mathrm{d}t\, x(t) \exp(-\mathrm{i}\omega t)$).

In the typical case that the friction is Ohmic, that is $\gamma(t) = 2\gamma\delta(t)$ where here $\delta(t)$ denotes the Dirac 'δ' function (which should not be confused with the reduced energy loss δ) one finds that the energy loss is linearly proportional to a product of the damping factor and the action of the adatom as it traverses from one barrier to the next:

$$\delta = \frac{m\gamma}{2k_{\mathrm{B}}T} \int_{-\infty}^{\infty} \mathrm{d}t\, \dot{x}(t)^2. \tag{4.10}$$

This then also means that the energy loss is proportional to the product of the damping constant and the reduced barrier height. Since typically many experiments are carried out under conditions of large reduced barrier heights, the reduced energy loss can be unity or even larger, even though the damping constant is rather small [39].

The central quantity of interest is the number of particles per unit time which are trapped in the jth well (Γ_j). From here, we deleted the superscript as we are dealing with one-dimensional diffusion. It is this distribution which provides the answers to all the questions posed above. It is obtained by considering the difference between the incoming and outgoing fluxes at the jth well:

$$\Gamma_j = \int_{-\infty}^{\infty} \mathrm{d}\epsilon\, T(\epsilon)[f_{j-1}^{+}(\epsilon) + f_{j+1}^{-}(\epsilon) - f_j^{-}(\epsilon) - f_j^{+}(\epsilon)] \tag{4.11}$$

obviating the necessity of obtaining the steady state fluxes. The probability of being trapped at the jth well ($j \neq 0$) is $P_j = \frac{\Gamma_j}{\Gamma}$ and the rate of escape from the zeroth well is $\Gamma = -\Gamma_0$. The mean squared path length is then by definition $\langle l^2 \rangle = l_0^2 \sum_{j=-\infty}^{\infty} j^2 P_j$ where l_0 is the lattice length. For one-dimensional diffusion, the diffusion coefficient is the product of the rate of escape and half the mean squared path length:

$$D = \tfrac{1}{2}\Gamma\langle l^2 \rangle = \tfrac{1}{2} l_0^2 \sum_{j=-\infty}^{\infty} j^2 \Gamma_j. \tag{4.12}$$

In the moderate to strong friction limit where the rate limiting step is spatial diffusion across the barrier, the rate of escape from the well is given by the Kramers–Grote–Hynes formula [40, 41] (the particle can escape from either side so that the rate is double the standard escape rate):

$$\Gamma_{\mathrm{sd}} = \frac{\omega_0}{\pi} \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \exp\left(-\frac{V^{\ddagger}}{k_{\mathrm{B}}T}\right) \tag{4.13}$$

where ω_0 is the harmonic frequency at the well, $V^{\ddagger}$ is the barrier height, $\omega^{\ddagger}$ is the parabolic barrier frequency, $\lambda^{\ddagger}$ is the positive root of the equation $s^2 + s\hat{\gamma}(s) = \omega^{\ddagger 2}$ where $\hat{\gamma}(s)$ is the Laplace transform of the time dependent friction $\gamma(t)$. In this spatial diffusion limit, one must only consider nearest neighbour hopping so that $\langle l^2 \rangle = l_0^2$ and

$$D_{\mathrm{sd}} = \tfrac{1}{2} l_0^2 \Gamma_{\mathrm{sd}}. \tag{4.14}$$

This result has been used extensively in the past. It ignores the possibility of multiple hops as well as the limitation set by the rate of energy diffusion when the friction is sufficiently weak.

To solve the integral equation one needs to specify the conditional probability kernel $P(\epsilon|\epsilon')$ as well as the energy dependent transmission and reflection coefficients. One may use different models for the conditional probability kernel, which would correspond to different dynamics. Here, we provide results specifically for the Langevin equation dynamics and the classical limit. The quantum form of the kernel has been derived and given in detail in [42]. The classical kernel is Gaussian and its Fourier transform has the simple form $\tilde{P}(is) = \exp[\delta(s^2 + s)]$. In the classical limit, the transmission and reflection probabilities are step functions—$T(\epsilon) = \theta(\epsilon)$, $R(\epsilon) = \theta(-\epsilon)$ where $\theta(x)$ is the unit step function.

The integral equation may now be solved by taking advantage of the periodicity of the problem and using Fourier transforms. The details are given in [43, 42, 36, 37]; here we give the results. For the partial rates one finds

$$\Gamma_j = -\Gamma_{\mathrm{sd}}\frac{1}{\pi}\int_0^{2\pi} \mathrm{d}k \sin^2\left(\frac{k}{2}\right)\cos(jk)\exp\left[\frac{1}{\pi}\int_0^{\infty}\mathrm{d}\tau\,\frac{\ln\left[\mathcal{G}\left(\tau - \frac{i}{2}, k\right)\right]}{\tau^2 + \frac{1}{4}}\right] \tag{4.15}$$

where the function $\mathcal{G}(is, k)$ is defined as

$$\mathcal{G}(is, k) \equiv \frac{1 - \tilde{P}^2(is)}{1 + \tilde{P}^2(is) - 2\tilde{P}(is)\cos(k)}. \tag{4.16}$$

The expression for the diffusion coefficient simplifies considerably because of the infinite summation over the partial rates (cf equations (4.12) and (4.15)):

$$D = D_{\mathrm{sd}}\exp\left[\frac{1}{\pi}\int_0^{\infty}\mathrm{d}\tau\,\frac{1}{\tau^2 + \frac{1}{4}}\ln\left(\frac{1 + \tilde{P}\left(\tau - \frac{i}{2}\right)}{1 - \tilde{P}\left(\tau - \frac{i}{2}\right)}\right)\right]. \tag{4.17}$$

These results provide uniform expressions for the partial rates, the decay rate and the diffusion coefficient in terms of the reduced energy loss δ and the rate expression in the spatial diffusion limit. They are valid for all values of the friction; the only real limitation is that the reduced barrier height is large enough, as already discussed above.

4.3. The exponential hopping limit

Although explicit expressions have been presented in the previous section for the hopping distributions, their form is rather complicated and it would be very useful to approximate them by some simpler result. Typically, the central source of friction of an adatom is phonon friction, which is Ohmic in nature [39] with a rather weak friction coefficient. But especially in STM and FIM experiments, which occur on timescales of seconds, the reduced barrier heights are typically greater than 10 so that the reduced energy loss is greater than unity. In this limit of weak damping but moderate to large energy loss, the expressions for the hopping distribution simplify considerably. In the classical limit they are exponential in the energy loss δ [44, 45]

$$P_{j+1} = P_{-(j+1)} \simeq \frac{j^{-3/2}}{\sqrt{\pi\delta}}\mathrm{e}^{-j\delta/4}, \qquad j \geqslant 1. \tag{4.18}$$

If the reduced energy loss is much larger than unity, only nearest neighbour hopping is important; the diffusion coefficient reduces then to the spatial diffusion limited diffusion coefficient given in equation (4.14). However, in the experimentally relevant cases where the reduced energy loss is of the order of unity, multiple hopping cannot be ignored, even though the hopping distribution is exponential.

The exponential hopping limit has a relatively simple physical interpretation. In this limit, the energy loss is sufficiently large so that the distribution of escaping particles may be assumed to be thermal. Assuming that the energy transfer probability kernel is Gaussian implies that the fraction of particles that start at a barrier top and make it to the adjacent barrier top is given by (the barrier energy is zero)

$$F_{2,1} \sim \int_0^{\infty}\mathrm{d}\epsilon\int_0^{\infty}\mathrm{d}\epsilon'\,P(\epsilon|\epsilon')\,\mathrm{e}^{-\epsilon'} = \mathrm{erfc}\left(\frac{\sqrt{\delta}}{2}\right) \sim \frac{2}{\sqrt{\pi\delta}}\mathrm{e}^{-\delta/4}, \qquad \delta \gg 1. \tag{4.19}$$

This result is then readily generalized to longer hops.

In this exponential hopping limit, the activation energy for a hop length of $(j+1)l_0$ is thus larger by $k_BT\delta/4$ than the activation energy for a hop whose length is jl_0. This result is in good agreement with experimental observation for the diffusion of Pt on the Pt(110)-(1×2) missing row reconstructed surface [11]. For this system, the reduced energy loss varies from 5.8 to 7.4 over the temperature range studied experimentally (300–380 K). The absolute magnitude of the energy loss is estimated to be 0.19 eV, leading to an added activation energy of $\sim$0.05eV for double jumps as compared to single jumps [46]. A somewhat different interpretation of the added activation energy has been suggested in [47].

4.4. Experimental application

The experimentally measurable quantity in STM or FIM experiments is the time dependent population of sites on the surface. At the initial time, one notes the position of an adatom and then one probes its position at later times. This experiment is then repeated many times, giving the time dependent probability distribution of the diffusing adatom. At long times the evolution is universal, controlled by the diffusion equation, and the shape of the distribution is Gaussian. At the early stage however, the shape of the distribution depends on the particle jump length between successive trappings. Having a solution for the hopping rates, one may also readily derive an expression for the time dependent probability distribution.

The formal solution of the master equation (2.1) for the time dependent population distribution was presented in equaton (2.3). All that was needed to complete the solution were explicit expressions for the hopping rates, and these were presented in the previous subsection. Specifically, from equation (4.15) one now has that

$$\hat{\Gamma}(k) = 2\sin^2\left(\frac{k}{2}\right)\Gamma_{\mathrm{sd}}\exp\left[\frac{1}{\pi}\int_0^\infty \mathrm{d}s\, \frac{\ln\left[\frac{1+\exp(-\delta(s^2+\frac{1}{4}))}{1-\exp(-\delta(s^2+\frac{1}{4}))}\right]}{s^2+\frac{1}{4}}\right] \tag{4.20}$$

thus providing an explicit solution for the time evolution of the probability distribution $w_{l,m}$.

In contrast to the parameter fitting employed by the experimentalists, in which each of the separate rates Γ_j was considered as an independent parameter, the Langevin theory provides a complete description of the probability distribution in terms of two parameters, the 'spatial diffusion rate' parameter Γ_{sd} and the energy loss parameter δ. As an example, which is readily applicable, we consider a periodic potential which has the form $V(x) = \frac{V^{\ddagger}}{2}(1-\cos(\frac{2\pi x}{l_0}))$ with Ohmic friction. The reduced energy loss parameter is then $\delta = \frac{2V^{\ddagger}\gamma}{k_BT\omega_0}$, where the frequency at the bottom of the well $\omega_0 = \pi\sqrt{\frac{V^{\ddagger}}{ml_0^2}}$ with m being the mass of the adparticle [34]. From the experimental data one has obtained the energy loss parameter δ and the barrier height $V^{\ddagger}$. One can thus immediately obtain the value of the friction parameter γ. Moreover, these three parameters can now *predict* the spatial diffusion rate Γ_{sd}, leaving us with a one-parameter fit of the data only. This scheme may be a bit too restrictive, since it implies that the barrier and well frequency of the periodic potential are the same. One can construct a periodic potential allowing for different frequencies, and then one has a two-parameter fit of the data. The truly important result to come out of the experimental measurement is the magnitude of the friction coefficient, which describes the interaction of the adparticle with the surface.

This theory has been successful in interpreting and fitting experimentally measured data. As already mentioned above, the diffusion of Pt on the Pt(110)-(1×2) missing row reconstructed surface measured by STM [11] was analysed in [46]. The diffusion of W and Pt on the W(211) surface, measured by FIM [48] was analysed in [49]. The diffusion of Na atoms on a Cu(001) surface, measured by QHAS [50] was analysed in [51, 52, 34].

5. The future

5.1. Quantum effects

Quantum effects can manifest themselves in a variety of ways. Tunnelling can lead to an enhancement of the diffusion constant, above barrier reflection to its reduction; at low temperatures even if the spectral density is Ohmic the quantization of the levels of the bath leads to memory effects in the random force autocorrelation function. A semiclassical generalization of the classical Kramers turnover theory discussed in the previous section has been derived in [37]. Perhaps the most interesting result was the discovery that the quantum diffusion coefficient can be *lower* than the classical. When considered as a function of the energy loss parameter δ, the quantum mean squared path length is always lower than the classical. The quantum rate of escape is always *greater* than the classical. The diffusion coefficient is a product of the two. When $\delta < 1$, the reduction of the mean squared path length is greater than the rate enhancement and the quantum diffusion coefficient is smaller than the classical. While the classical diffusion coefficient diverges as $1/\delta$ in the underdamped limit, the quantum diffusion coefficient diverges as $\delta^{\frac{1}{\alpha}-1}$ with $\alpha = \frac{2\pi}{\hbar\beta\lambda^{\ddagger}} > 1$. When $\delta > 1$ the opposite occurs and the quantum diffusion coefficient is greater than the classical. This novel quantum effect, which implies for example that in the relevant parameter range the diffusion of deuterium atoms can be faster than that of hydrogen atoms, has yet to be measured experimentally.

The quantum exponential hopping limit has been analysed in [45]. A central result is that

$$\frac{P_{j\geqslant 2}}{P_1} \simeq (\hbar\beta\lambda^{\ddagger}/4)\cot(\hbar\beta\lambda^{\ddagger}/4)\frac{P^{\mathrm{cl}}_{j\geqslant 2}}{P^{\mathrm{cl}}_1} \tag{5.1}$$

where the cl superscript denotes the classical hopping probabilities. This implies that in the exponential hopping limit quantum tunnelling and above barrier reflection reduce all the multiple hopping probabilities relative to the classical by the same amount. Tunnelling affects only the first and last of the $j \geqslant 2$ jumps. All intermediate jumps are described by transitions at energies close to the top of the barrier, which are only weakly influenced by tunnelling.

Experimentally, quantum effects have shown up whenever the diffusing atom is hydrogen or deuterium. Gomer and co-workers, using the field emission method, reported quantum tunnelling effects for the diffusion of H atoms on a W surface [53, 54]. They found that the diffusion coefficient becomes temperature independent at very low temperatures. More recent results were reported by Cao *et al* [55], who used laser induced desorption and optical diffraction techniques to study the diffusion of H and D atoms on a Ni(111) surface. They found a weaker tunnelling effect; however, the curvature of an Arrhenius plot of the diffusion coefficient is very obvious and the D diffusion coefficient was found to be substantially smaller than the H atom diffusion coefficient. To date though, these experimental findings have not been analysed using Langevin dynamics. Primarily the reason for this is that these experiments shed light only on the diffusion coefficient, but nothing is known about the hopping distribution. In addition the results of [55] disagree with those of Lin and Gomer [56]. Given the experimental uncertainties, and the lack of accurate knowledge of the energetics, it is not easy to provide a conclusive theoretical analysis. The diffusion of H and D on surfaces remains an area of active study; the experimentalists should analyse their results using the Langevin based theory instead of ad hoc expressions as in [55].

5.2. *Vibrational assisted diffusion*

In the STM and FIM experiments, one is not sensitive to the vibrational motion of the adatom on the surface. This is not the case in QHAS, where vibrational motion may interfere with the quasielastic peak, making it much more difficult to interpret the experimental measurement. As far as we know, the first attempt to consider the two kinds of motion on an equal footing was due to Chen and Ying [57]. A good way to illustrate and understand better some features of the vibration–diffusion coupling is to model the velocity autocorrelation function as [17]

$$\psi(t) = \langle v_l^2 \rangle \cos(\omega_{\mathrm{T}} t + \delta) \mathrm{e}^{-t/\tau_{\mathrm{T}}} \tag{5.2}$$

where ω_{T} is the frequency of motion of the adparticle parallel to the surface (the T-mode), τ_{T} is an overall correlation time and δ is a phase parameter which improves the fit of equation (5.2) to the actual velocity autocorrelation function. At high temperatures, diffusion is predominant and τ_{T} is approximately the diffusion coefficient divided by the scaled temperature $k_{\mathrm{B}}T$. At low temperature, jumps of the adparticle are rare events and one remains almost exclusively with the vibrational dynamics. In this limit the correlation time is inversely proportional to the friction coefficient $\tau_{\mathrm{T}}^{-1} \sim \gamma$.

With this phenomenological form for the velocity autocorrelation function one may carry out the time integration in the (Gaussian) expression for the intermediate scattering function (equation (3.7)). The explicit (somewhat lengthy) expression may be found in [17]. In contrast to simplified expressions used previously in the literature [50], the total line shape *is not* a simple sum of two contributions, one from the quasielastic peak and the other from the vibration. The two interfere with each other, displaying the motional narrowing effect, and in general cannot be separated.

Even with this simplified model, one already finds that deconvolution of the QHAS measurement is not trivial. One can improve it by doing away with the Gaussian approximation for the dynamic structure factor [17]. However, there is no guarantee that the functional form of equation (5.2) is an accurate representation of the 'true' velocity autocorrelation function. A 'good' theory which correctly describes vibrational assisted diffusion remains a challenge for the future. We also note that little is known about the effects of internal motion of the adparticle on the diffusion dynamics.

5.3. *Multidimensional theory*

The analytic theory presented in the previous section is a one-dimensional one; the underlying assumption is that the geometry of the surface is such that the adparticle is confined to diffuse along unidirectional channels. This is not the case when considering for example a (111) geometry of the surface. One must then consider at least the coupled motion of the adparticle in the plane, in addition to the dissipation. In the spatial diffusion limit, this does not pose any severe problem; the multidimensional generalization of the spatial diffusion escape rate has been considered by many authors [58, 59] and is well understood, even in the presence of strongly anisotropic friction [60]. In this limit, the particle is limited to hopping over single sites before being retrapped.

Difficulties occur when considering the underdamped to moderate damping regime of the diffusion. In the limit that the friction coefficient goes to zero, the diffusion constant no longer diverges; it goes to a constant [38]. The energy loss parameter now depends on the nonlinear dynamics of the motion along the plane of the surface [34]. This dynamics may be quasiperiodic, chaotic or mixed and influences the magnitude of the energy loss. If motion in the well is ergodic and the mixing occurs on a timescale that is short compared to the time it takes the adparticle to escape from the well, then one finds that the energy loss parameter is proportional to $\left(\frac{V^{\ddagger}}{k_{\mathrm{B}}t}\right)^{2}$ [61–64]. The strong coupling causes the rate to increase relative to the one-dimensional case, since the mixing enhances the energy transfer from the surface to the reactive mode. At the same time it reduces the mean hopping length, since it disallows multiple hops. Similar observations were found if one replaces the Langevin dynamics with a strong collision model [65].

If the two degrees of freedom are weakly coupled then the energy loss parameter behaves as in one dimension; it is linearly proportional to the reduced barrier height. This implies that multiple hops will in general be less important when the diffusion is truly multidimensional. Two-dimensional diffusion on a periodic interaction potential has been recently studied for Na atom diffusion on the Cu(001) surface [51, 52, 34]. The coupling between the two surface degrees of freedom was found to lead to an increase in the escape rate from the well and thus also an increase in the diffusion coefficient. Although anomalous diffusion may occur in the absence of friction, numerical observations lead to the conclusion that coupling to the phonon bath destroys the anomaly and the diffusion is normal [51, 66, 67].

The quantum dynamics of multidimensional diffusion has not been studied. We do not understand how the quantization of levels, multidimensional tunnelling and resonances affect the diffusion rate. The properties could be studied numerically by using reduced equations of motion, especially when the coupling is weak and Redfield type equations are valid. However, to date, to the best of our knowledge, this has not been done.

5.4. Manipulations with external fields

Activated diffusion in the presence of an external field is an important area of research. If the amplitude of the driving force is larger than the barrier height, then one loses the concept of activated diffusion. We are more interested in the effect of a field which does not alter the qualitative structure of the potential affecting the diffusion dynamics. Numerical investigations [68–70] led to the conclusion that in this limit the phenomenon of stochastic resonance is not observable in the diffusion coefficient. Varying the noise strength in the presence of an external field does not lead to a maximum in the diffusion coefficient [71]. Further investigations of stochastic resonance in multidimensional systems led to similar conclusions [72].

Two-dimensional diffusion in the presence of symmetric and asymmetric external ac electric fields has been studied in [73]. Diffusion on an asymmetric ratchet like two-dimensional potential in the presence of external fields was studied in [74]. Current reversals were found and could be controlled through the properties of the external field.

An external dc field can influence the hopping dynamics. As already mentioned in section 2, this is especially important when considering STM measurements. The field can change the mean potential [15], as well as the interaction of the adparticle with its surroundings. Theoretical studies may be found in [75–77]. It would seem that the field strength applied by an STM tip is strong enough to modify the hopping distribution.

Instead of considering the STM field as a perturbation on the diffusion, various researchers have suggested that one may be able to use the field to measure the diffusion of adparticles. Sumetskii and Kornyshev [78] suggested that one should analyse the transmitted current and associated noise and their dependence on the tip sample distance, temperature and other properties. Prostnev *et al* [79] suggested to use the scanning speed to extract both the diffusion coefficient and the mean jump length.

Activated diffusion has also been modelled in the presence of aperidoic [80] and stochastic potentials [81, 66, 67]. The dynamics becomes more complicated when considering motion in the presence of a space dependent friction (the friction felt by the adparticle at a barrier could be quite different from the friction at the well) and external forces which may also be stochastic [82]. Most recently, Lacasta *et al* [83], showed that for diffusion in two dimensions external forces can lead to sorting of adparticles.

All the studies mentioned above were based on classical mechanics. Quantum activated diffusion in the presence of an external field remains a topic for future studies.

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