DIFFUSION OF AN ADSORBED PARTICLE: THEORY AND NUMERICAL RESULTS *

Göran WAHNSTRÖM

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

A theory for the motion of an atom adsorbed on a solid surface is developed, based on the Zwanzig–Mori approach and on nonlinear mode coupling ideas. It generalizes the Fokker–Planck equation by incorporating a general frequency, wavevector, as well as position dependent friction coefficient. The purpose of this paper is primarily to investigate the validity of the Fokker–Planck equation when applied to the motion of an adsorbed atom coupled to the phonon excitations of the substrate. This is the first in a series of papers dealing with this problem. The main conclusion drawn here is that for the situation when the adatom is identical with the substrate atoms the Fokker–Planck equation gives quite accurate results, provided one uses a proper position dependent friction coefficient. The position dependence found from the theory is such that it supports in this case the absolute rate theory for the diffusion constant.

1. Introduction

The study of surface self-diffusion of single atoms represents one fundamental step towards understanding many technologically significant surface processes [1], and it also gives information on the force laws governing the motion of the adsorbate–substrate system. In recent years detailed information on the migration of single atoms over crystal planes has become available, especially through the use of field ion microscopes [2]. Molecular dynamic calculations have also been done [3–9], where one can follow in detail the motion of individual atoms. These simulations can be used to compare with experiments and different empirically derived potentials can be tested. However, another important application is to test different theoretical models.

Due to the periodic arrangement of the substrate, the adsorbed particle experiences a static periodic potential along the surface. In many cases the activation energy, i.e. the difference between the maximum and the minimum of this potential, is large compared with the temperature. The diffusion process

---

becomes then thermally activated and the diffusion constant has the Arrhenius form

$$D = D_0 \exp(-E_0/k_B T),\tag{1}$$

which is fitted to the experimental data and the two parameters D_0 and E_0 are extracted. The activation energy E_0 gives information on the potential corrugation seen by the adparticle, and the prefactor D_0 contains information on the dynamics.

Different theoretical models have been used in explaining the Arrhenius curve (1) and in identifying the activation energy and the prefactor. The standard way is to use equilibrium statistical mechanics, known as the absolute rate theory [10], in spite of the nonequilibrium origin. However, this is seriously in error for both weak and strong coupling to the substrate, which was first pointed out by Kramers [11]. He based his analysis on a Brownian motion model for the dynamics of the adparticle. In that theory the dynamical interaction with the surrounding is approximated by a simple friction force and a purely stochastic force with a white noise spectrum. The appropriate transport equation is then the well-known Fokker–Planck equation [12] with a single parameter, the friction coefficient η, arising from the interaction with the substrate. Extensive calculations on the Fokker–Planck equation with a static potential have been performed in connection with diffusion in superionic conductors [13]. Several authors [14–18] have derived microscopic expressions for the parameter η, and with exception of Caroli et al. [16], they have taken into account only the interaction of the adparticle with the electronic degrees of freedom of the substrate. Since the electron mass is much smaller than the mass of any adparticle, the fluctuations in the surrounding are fast with respect to the adparticle motion, and the assumption behind the Fokker–Planck equation should be valid. However, the adparticle couples not only to the electronic excitations but also to the lattice vibrations. Using the Fokker–Planck equation in the latter case implies the assumption that the substrate atoms are fluctuating on a time-scale considerably smaller than that of the adsorbed atom. This is certainly a highly questionable assumption in real situations and Caroli et al. [16] as well as Suhl and Rezayi [19] also point this out.

The main purpose of this article is to relax the above restrictive assumption concerning the lattice motion and to present a more general theory for the motion of an adsorbed atom with particular reference to the effect of the phonon excitations. To do this, we first derive in section 2 a formally exact equation of motion for the adparticle, based on a projection operator formalism [20,21]. This procedure is nowadays well established [22,23] and therefore we concentrate here on the physics behind the equations and not on the more formal aspects. It leads to a generalized Fokker–Planck equation, where instead of a constant friction parameter enters a certain memory function which contains all the dynamics of the substrate excitations. Ap-

propriate approximations of this memory function can be made, based on mode coupling ideas, familiar from other fields of physics (see e.g. ref. [23] and references therein), and it leads to our Mode Coupling Approximation (MCA). In certain special cases further simplifying assumptions can be made. If the fluctuations in the substrate are fast or slow compared to the characteristic frequencies of the adatom we arrive at what we call the Initial Value Approximation (IVA) and the Equilibrium Density Approximation (EDA), respectively. The Fokker–Planck equation with a position dependent friction coefficient (FPA) is obtained if we make some further approximations in IVA and a microscopic expression for this friction coefficient is given. All this is presented in section 3. Extensive numerical calculations have been done for the situation with the adatom identical to the substrate atoms in order to find out more quantitatively when the different approximations apply, being aware of the fact that MCA gives the most detailed description of the physics involved. We are particularly concerned about the validity of the ordinary Fokker–Planck equation. This is discussed in sections 4 and 5 and our main conclusions are summarized in section 6.

2. General formulation

Consider one single adsorbed particle, with mass m, and a substrate in thermal equilibrium at the inverse temperature $\beta = 1/k_B T$. Assume that the adparticle interacts with the particles in the substrate through a pairwise additive potential $v(r)$ and denote the position and momentum of the adparticle by $R^a(t)$ and $P^a(t)$, respectively. The substrate consists of N particles ($N \to \infty$) with mass M, and positions $R_i(t)$, with the equilibrium sites forming a regular lattice. The motion of the adparticle is described by its microscopic phase-space density

$$f(1t) = \delta(r_1 - R^a(t)) \, \delta(p_1 - P^a(t)), \tag{2}$$

where 1 is a short hand notation for the phase-space point (r_1, p_1).

Analysis of the dynamics of interacting many particle systems is conventionally based on a discussion of correlation functions. Here we introduce the phase-space correlation function

$$C^s(11't) = \langle f(1') \rangle^{-1} \langle f(1t) f(1') \rangle, \tag{3}$$

which satisfies the initial condition

$$\delta(11') = \delta(r_1 - r_1') \, \delta(p_1 - p_1')$$

and where $\langle \cdots \rangle$ denotes the canonical ensemble average. By multiplying with different powers of momenta and integrating one can extract the more familiar density and current correlation functions. The latter will be used in determin-

ing the velocity correlation function and the diffusion constant, both defined in section 4. Using the projection operator technique, introduced by Zwanzig [20] and extended by Mori [21], the equation of motion for $C^s(11't)$ can be written as [24]

$$\left[\frac{\partial}{\partial t} + \frac{p_1}{m} \cdot \nabla_{r_1} + F^{\mathrm{ad}}(r_1) \cdot \nabla_{p_1} \right] C^s(11't)$$

$$= \int_0^t d\bar{t} \int d\bar{1} \, \nabla_{p_1} \cdot L(1\bar{1}t - \bar{t}) \cdot \left[\frac{\beta}{m} \bar{p}_1 + \nabla_{p_1} \right] C^s(\bar{1}1't). \tag{4}$$

The influence from the surrounding on the adparticle is here split into two parts, one static and one dynamic. The static part gives rise to a temperature dependent conservative force, $F^{\mathrm{ad}}(r) = -\nabla V^{\mathrm{ad}}(r)$, which we will call the adiabatic force. It is equal to the force acting on a fixed adparticle at position r when the surrounding is in thermal equilibrium around that particle and the corresponding potential, $V^{\mathrm{ad}}(r)$, is then equal to the free energy. The dynamic part, the last term in eq. (4), is a direct generalization of the Fokker–Planck term and it is responsible for fluctuation and dissipation of energy. The time dependent function $L(11't)$ is called the memory function.

3. Approximations

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, $\delta F = F - F^{\mathrm{ad}}$, of the force on the adparticle from its adiabatic value and it depends therefore on the simultaneous motion of this particle and the surrounding substrate atoms. Its initial value is given exactly by

$$L(11't = 0) = \delta(11') \langle \delta F(1) \, \delta F(1') \rangle_{r_1}, \tag{5}$$

where $\langle \cdots \rangle_r$ denotes an average over the degrees of freedom of the substrate in the presence of a fixed adparticle at r.

In deriving the ordinary Fokker–Planck equation one assumes that δF is a random stochastic force, uncorrelated at different times. This can never be completely true and the time extension of L depends on how the excitations in the substrate propagate and decay, as well as on the motion of the adparticle. These effects are incorporated in an approximative way in the so called mode coupling approximation, which takes explicitly into account the appropriate time-scale of the stochastic force through the inclusion of the dynamics of the surrounding substrate atoms. One then expresses the memory function in terms of products of the most relevant correlation functions. In the present case we shall write the time evolution of $L(11't)$ in terms of $C^s(11't)$ and $\langle \delta F(1t) \, \delta F(1') \rangle$ and the forces will be expressed in the microscopic density of

the surrounding medium. In the presence of a fixed adparticle the equilibrium positions of the substrate atoms are displaced and we will expand in the lattice displacements $u_l(t)$ from these perturbed equilibrium positions $R_l^0(R^a)$. This leads to the following mode coupling approximation (MCA)

$$L^{\beta\beta'}(11't) = C^s(11't) \sum_{ll'} \sum_{\alpha\alpha'} v_{\text{eff}}^{\alpha\beta}(r_1 - R_l^0) \langle u_l^\alpha(t) \, u_{l'}^{\alpha'} \rangle \, v_{\text{eff}}^{\alpha'\beta'}(r_1' - R_{l'}^0), \qquad (6)$$

with

$$v_{\text{eff}}^{\alpha\beta}(r - R_l^0) = \int d\bar{r} \, \nabla_r^\alpha \, \nabla_r^\beta \, v(r - R_l^0 - \bar{r}) \, w_l(\bar{r}), \qquad (7)$$

$$w_l(r) = \left(8\pi^3 U_l^{\|2} U_l^\perp\right)^{-1/2} \exp\left[-\frac{1}{2}\left(\frac{x^2 + y^2}{U_l^\|} + \frac{z^2}{U_l^\perp}\right)\right], \qquad (8)$$

and where $U_l^\|$ and $U_l^\perp$ are the mean square displacements parallel and perpendicular to the surface, respectively. We have assumed the harmonic approximation for the lattice motion and we have then a well-known expansion for the density correlation function in phonon terms (see e.g. ref. [25]). The zero-phonon term is exactly cancelled and second and higher order terms have been neglected. As long as the displacements $u_l(t)$ are small compared to the inverse of the wavevector q involved, these multiphonon processes can be neglected. The Debye–Waller factor (8) has been combined with the potential to an effective coupling term defined in (7).

The time dependence of the memory function $L^{\beta\beta'}(11't)$ is mainly controlled by the fastest decaying function. If the diffusion process is slow, two time-scales can be distinguished in the relaxation of the phase-space density correlation function $C^s(11't)$. It starts as a delta-function $\delta(11')$, and after a certain time the adparticle will be nearly thermalized inside the initial lattice cell. This determines the first time-scale and it depends on the vibrational frequency and the friction experienced by the adparticle. After that, the adparticle will slowly diffuse over the potential barrier to the other lattice cells, and it will finally reach its full equilibrium value. The appropriate parameter for this relaxation is the diffusion constant. The decay of C^s should be compared with the decay of the displacement correlation function for the substrate particles. The time-scale for the latter is given by the inverse of a typical phonon frequency. If the above time-scales are well separated from each other, further approximations of the memory function can be justified. Here we are going to discuss two such cases.

If the fluctuations in the substrate, determined by the displacement correlation function, have decayed before the adparticle has moved appreciably, we can replace C^s in (6) by its initial value $\delta(11')$. The memory function reduces then to

$$L^{\beta\beta'}(11't) = \delta(11') \sum_{ll'} \sum_{\alpha\alpha'} v_{\text{eff}}^{\alpha\beta}(r_1 - R_l^0) \langle u_l^\alpha(t) \, u_{l'}^{\alpha'} \rangle \, v_{\text{eff}}^{\alpha'\beta'}(r_1 - R_{l'}^0). \qquad (9)$$

The time dependence introduces a frequency dependent damping and (9) will be referred to as the initial value approximation (IVA).

Further, if one is interested in times longer than a typical relaxation time for $\langle u_l^\alpha(t) \, u_{l'}^{\alpha'} \rangle$, the equation of motion (4) reduced to the Markoffian equation [22]

$$\left[\frac{\partial}{\partial t} + \frac{p_1}{m} \cdot \nabla_{r_1} + F^{\mathrm{ad}}(r_1) \cdot \nabla_{p_1} \right] C^s(11't)$$

$$= \nabla_{p_1} \cdot \eta(r_1) \cdot \left[p_1 + \frac{m}{\beta} \nabla_{p_1} \right] C^s(11't), \tag{10}$$

with

$$\eta^{\beta\beta'}(r_1) = \frac{\beta}{m} \sum_{ll'} \sum_{\alpha\alpha'} v_{\mathrm{eff}}^{\alpha\beta}(r_1 - R_l^0) \int_0^\infty dt \, \langle u_l^\alpha(t) \, u_{l'}^{\alpha'} \rangle \, v_{\mathrm{eff}}^{\alpha'\beta'}(r_1 - R_{l'}^0). \tag{11}$$

This is the ordinary Fokker–Planck equation, but with a position dependent friction tensor, in contrast to what one in general assumes. In a homogeneous medium η is constant, but in our case the lattice breaks this symmetry. The variation of η along the diffusion path can be important and we will discuss that later. This approximation will be denoted by (FPA).

In the second case we consider the fluctuations in the substrate to decay slowly compared to the time it takes for the adparticle to get thermalized inside the initial lattice cell. We can then make the following approximation (EDA)

$$L^{\beta\beta'}(11't) = n^{\mathrm{ED}}(r_1) \, \Phi_{\mathrm{M}}(p_1) \sum_{ll'} \sum_{\alpha\alpha'} v_{\mathrm{eff}}^{\alpha\beta}(r_1 - R_l^0)$$

$$\times \langle u_l^\alpha(t) u_{l'}^{\alpha'} \rangle \, v_{\mathrm{eff}}^{\alpha'\beta'}(r_1' - R_{l'}^0). \tag{12}$$

Here C^s has been replaced by $n^{\mathrm{ED}}(r_1)\Phi_{\mathrm{M}}(p_1)$, where $n^{\mathrm{ED}}(r_1)$ is equal to the equilibrium density if r_1 belongs to the initial lattice cell and otherwise it is equal to zero and $\Phi_{\mathrm{M}}(p_1)$ is the Maxwell distribution function.

The equation of motion (4) together with the different approximations of the memory function, forms the basis of our treatment. Notice, that (6), (9), and (12) all can be regarded as Golden Rule type of expressions for transition probabilities. One essential difference between (6) and the other approximations is that (6) depends on the motion of the adparticle. This leads to a non-linear equation of motion, which must be solved self-consistently. We shall now turn to the problem of applying this formalism to a specific example.

4. One-dimensional motion

We will restrict ourselves to the motion of the adparticle in one dimension, say the x-direction. The limitation of this approximation will be discussed

later. However, the full three-dimensional motion of the substrate particles will be retained.

4.1. Transforms

Due to the lattice $C^s(11't)$ is not invariant under arbitrary translations. The spatial Fourier transform of C^s will contain two wavevectors, differing by a reciprocal lattice vector. For these wavevectors we are going to use the notation $q = \kappa + (2\pi/a)n$, where κ is restricted to the first Brillouin zone, a is the period of the lattice and n is an integer. If we further Laplace transform with respect to time, we can introduce

$$\hat{C}_{nn'}^s(\kappa z; \, pp') = \frac{1}{a} \int_{-a/2}^{a/2} dx' \int_{-\infty}^{\infty} dx \int_{0}^{\infty} d(t - t') \, e^{-z(t-t')}$$

$$\times e^{-i[\kappa + (2\pi/a)n]x} \, C^s(xpt; \, x'p't') \, e^{i[\kappa + (2\pi/a)n']x'}. \tag{13}$$

With this definition the ordinary temporal Fourier transform $C^s(\omega)$ is given by the real part of the Laplace transform on the axis of imaginary frequencies, i.e. $C^s(\omega) = 2\hat{C}^{s'}(\omega)$ with

$$\hat{C}^s(z = -i\omega + 0^+) = \hat{C}^{s'}(\omega) + i\hat{C}^{s''}(\omega).$$

Next, we expand the momentum dependence in a complete set of Hermite polynomials $H_\mu(p)$. The corresponding matrix elements are defined by

$$\hat{C}_{\mu\nu; nn'}^s(\kappa z) = \int dp \, dp' \, H_\mu(p) \, \hat{C}_{nn'}^s(\kappa z; \, pp') \, H_\nu(p') \, \Phi_M(p'), \tag{14}$$

where the polynomials are normalized according to

$$\int dp \, H_\mu(p) \, H_\nu(p) \, \Phi_M(p) = \delta_{\mu\nu}. \tag{15}$$

The first element C_{00}^s represents the density fluctuations, whereas C_{11}^s represents current fluctuations and so on. For the adiabatic potential we use similarly the Fourier series expansion, with

$$V_n^{ad} = \frac{1}{a} \int_{-a/2}^{a/2} dx \, e^{-i(2\pi/a)nx} \, V^{ad}(x), \tag{16}$$

and for the mean density

$$\langle n \rangle_n = \frac{1}{a} \int_{-a/2}^{a/2} dx \, e^{-i(2\pi/a)nx} \, L\langle n(x) \rangle. \tag{17}$$

The reason for introducing the linear dimension L of the substrate ($L \to \infty$) in (17) is that the equilibrium value $\langle n(x) \rangle$ is proportional to L^{-1}.

4.2. The memory function

To calculate the memory function we must have expressions for the motion of the substrate particles and for the interaction between the adparticle and a substrate particle. For convenience we introduce the following notation

$$P(xx't) = \sum_{ll'} \sum_{\alpha\alpha'} v_{\text{eff}}^{\alpha x}(r - R_l^0) \langle u_l^a(t) u_{l'}^{\alpha'} \rangle v_{\text{eff}}^{\alpha'x}(r' - R_{l'}^0), \tag{18}$$

and we shall discuss those approximations which in the preceding section were called the mode coupling approximation (MCA), the initial value approximation (IVA), the Fokker–Planck approximation (FPA) and the equilibrium density approximation (EDA).

Introducing the notation

$$\Gamma(xpx'p't) = -\frac{\partial}{\partial p} L^{xx}(xpx'p't) \left[\frac{\beta}{m} p' + \frac{\partial}{\partial p'} \right], \tag{19}$$

we have in our most general approximation (MCA) the following expression for the corresponding matrix elements

$$\Gamma_{\mu\nu}^{\text{MCA}}(xx't) = \frac{\beta}{m} \sqrt{\mu\nu} \, C_{\mu-1,\nu-1}^s(xx't) \, P(xx't). \tag{20}$$

We notice that in MCA we would have to calculate all the matrix elements $C_{\mu\nu}^s$ self-consistently. However, to simplify the calculations considerable we will only determine the Γ_{11} element self-consistently. This element will be denoted by $M(xx't) = \Gamma_{11}(xx't)$. For the other matrix elements $\Gamma_{\mu\nu}$, two different approximations will be used, namely

$$\Gamma_{\mu\nu}(xx't) = \mu\delta_{\mu\nu} M(xx't), \tag{21}$$

$$\Gamma_{\mu\nu}(xx't) = \delta_{\mu1}\delta_{\nu1} M(xx't). \tag{22}$$

Using (21), the initial values of all the matrix elements are reproduced correctly, but it implies also that all the elements decay in the same way. On physical ground one would expect the higher order elements ($\mu, \nu > 1$) to decay more rapidly than Γ_{11}. In (22) one makes the extreme assumption that all the higher order elements are zero from the beginning. In liquid dynamics one has been able to reproduce the experimental data in quite some detail by splitting the process into two parts, one representing rapid binary collisions and the other incorporating delayed feedback effects [26]. For the first part an approximation corresponding to (21) was used, whereas for the other part MCA was used with only Γ_{11} included. At the present level of experimental knowledge it is not motivated with such a detailed treatment for the problem faced here.

In IVA the initial value of $C^s(11't)$ is used and this leads to

$$\Gamma_{\mu\nu}^{\text{IVA}}(xx't) = \frac{\beta}{m}\mu\delta_{\mu\nu}\,\delta(x-x')\,P(xx't), \tag{23}$$

and in FPA the function $P(xx't)$ is replaced by its time integrated value. After Fourier transforming in time it means the zero frequency value of $\Gamma_{\mu\nu}^{\text{IVA}}(xx';\omega)$. Finally, in EDA the adparticle is assumed to have reached its thermal equilibrium value within the initial lattice cell. This implies that

$$\Gamma_{\mu\nu}^{\text{EDA}}(xx't) = \frac{\beta}{m}\delta_{\mu 1}\delta_{\nu 1}\,n^{\text{ED}}(x)\,P(xx't), \tag{24}$$

and only one matrix element Γ_{11} enters in our problem.

4.3. The equation of motion

The equation of motion (4) can be transformed into a corresponding matrix equation by using the above expansions, (13) and (14). Symbolically we may write

$$[z + \Omega^0 + \Omega^{\text{ad}} + \hat{\Gamma}]\,\hat{C}^s = 1, \tag{25}$$

where the static part is split into two parts, one containing the free streaming term Ω^0 and the other the adiabatic potential Ω^{ad}. Next, we introduce the solution C^0 to the equation of motion without the adiabatic potential and with only the diagonal part of our memory function Γ^0, with $\hat{\Gamma}^0_{\mu\nu;nn'}(\kappa z) = \mu\delta_{\mu\nu}\delta_{nn'}\hat{M}_{nn}(\kappa z)$. We write

$$[z + \Omega^0 + \hat{\Gamma}^0]\,\hat{C}^0 = 1, \tag{26}$$

and this solution is known [26–28]. If we use C^0, we can rewrite (25) in the following matrix form

$$\sum_{\lambda\bar{n}}\hat{A}_{\mu\lambda;n\bar{n}}(\kappa z)\,\hat{C}^s_{\lambda\nu;\bar{n}n'}(\kappa z) = \hat{C}^0_{\mu\nu;nn}(\kappa z)\,\delta_{nn'}, \tag{27}$$

with

$$\hat{A}_{\mu\lambda;nn}(\kappa z) = \delta_{\mu\lambda}\delta_{n\bar{n}} + \hat{C}^0_{\mu,\lambda+1;n\bar{n}}(\kappa z)\,i\frac{2\pi}{a}(n-\bar{n})\,V^{\text{ad}}_{n-\bar{n}}\sqrt{\frac{\beta}{m}}\,\sqrt{\lambda+1}$$

$$+ \sum_{\eta}\hat{C}^0_{\mu\eta,n\bar{n}}(\kappa z)\left[\hat{\Gamma}_{\eta\lambda,n\bar{n}}(\kappa z) - \lambda\delta_{\eta\lambda}\delta_{n\bar{n}}\,\hat{M}_{nn}(\kappa z)\right]. \tag{28}$$

By introducing C^0 we correctly reproduce the free particle behaviour in the appropriate limit and the treatment can be used for arbitrary temperatures. It also guarantees that $C^s(11't)$ is obtained correctly for short times, up to t^2, irrespective of what approximation one makes for the memory function. Kleppmann and Zeyher [29] have developed a theory, similar to ours, for diffusion in a deformable lattice. However, they do not use the complete

phase-space correlation function but only the first two Hermite components, density and current. Their approach is therefore only valid for temperatures substantially smaller than the barrier height, which they point out. Another advantage of introducing C^0 is that the numerical work can be reduced considerably. Typically, convergence is obtained by truncating the system of equations in (27) at $\lambda = 3\text{--}4$ and $|\bar{n}| = 3\text{--}5$.

4.4. Experimental quantities

By inverting the matrix A in (27) we can solve the equation of motion and obtain C^s, from which several quantities of particular interest can be extracted. Here, we are going to concentrate on the velocity correlation function $\phi(t)$ with its frequency spectrum given by

$$\phi(\omega) = \lim_{\kappa \to 0} \sum_{\bar{n}} \langle n \rangle_n \, C^s_{11;0n}(\kappa\omega). \tag{29}$$

$\phi(t)$ is normalized to unity at $t = 0$ and the self-diffusion constant D will be determined from the low frequency limit, according to

$$D = \frac{1}{2\beta m} \lim_{\omega \to 0} \phi(\omega). \tag{30}$$

5. Numerical results

We now turn to the presentation of numerical calculations on a specific and realistic system. We have restricted ourselves to a single-component system where the adparticle and all substrate particles have the same mass and the forces between every pair of particles are the same. For this interaction, entering in (18) as well as in determining the adiabatic potential, we have used a Lennard-Jones 6-12 potential,

$$v(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \tag{31}$$

It is convenient to introduce the following reduced time, distance, and energy variables: $t^* = t/\tau$, $r^* = r/\sigma$, and $T^* = k_B T/\epsilon$ with $\tau = (M\sigma^2/\epsilon)^{1/2}$.

The phonon spectrum is substantially altered at a surface of a solid, e.g. in a qualitative way through the appearance of surface modes. All these modes are needed when calculating the memory function and also in determining the thermal displacements in (8). Knowing the interaction, it is in principle possible to calculate the phonon modes, but a full lattice dynamical calculation would be very tedious. The elastic theory, while being less accurate, is simpler but would give all the essential features. We have therefore used the modes
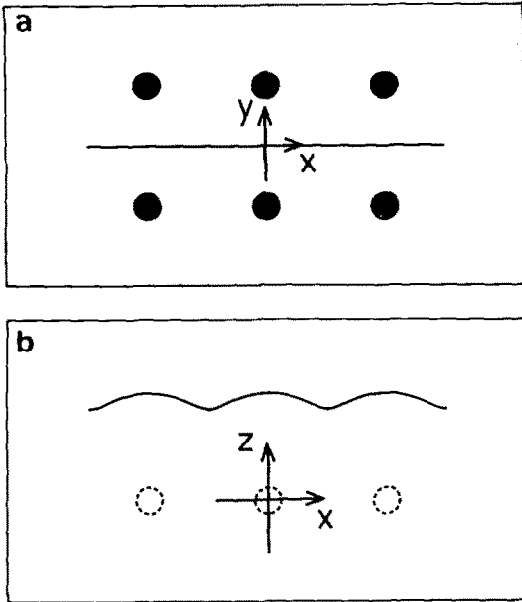
Fig. 1. (a) The trajectory of the adparticle seen from above. (b) Side-view of the trajectory.

appropriate for a semi-infinite continuous solid with a free surface [30–32]. This model contains both surface and bulk modes and is characterized by two parameters, the transverse and longitudinal sound velocities. For these we have used the numerical values $c_T^* = 5.41$ and $c_L^* = 9.70$, respectively, which have been determined from knowledge of the lattice structure and the pair interaction potential (31). Using the continuous model for the phonons in calculating the memory function should not bring in any significant errors.

The system we have been considering is one single atom adsorbed on a fcc (001) surface. This system has previously been studied using molecular dynamics techniques [3,7] and generalized Langevin dynamics [33]. Later, we will compare our results with these calculations. The melting temperature for a Lennard-Jones fcc lattice is about $T_m^* = 0.70$ and in all our calculations we have used the temperature $T^* = 0.30$. If one includes the thermal expansion of the crystal, the distance between nearest neighbours is 1.107 in reduced units at this temperature [3]. The (001) surface forms a quadratic lattice with the lattice distance a being equal to the nearest neighbour distance. Further, we assume that the adparticle moves between two rows of substrate particles (fig 1) and to simplify the calculations, we have restricted the summation over l and l' in (18) to these two rows. Due to the short range of the interaction potential, this approximation should be quite good.

5.1. The trajectory

To simplify the calculations we have restricted the motion of the adparticle to one dimension, or more precisely, the particle is restricted to move along a given trajectory. This is shown in figs. 1a and 1b. The trajectory is calculated under the assumption that the adparticle always moves in the minimum of the adiabatic potential in the y- and z-directions. As seen in the figure the distance to the surface is varying only slightly as function of x. The trajectory varies in such a way that the distance between the adparticle and the nearest substrate particles is nearly constant. At the centre position ($x = a/2$) it is $1.036a$ and at the bridge position ($x = 0$) it is $1.020a$.

In general, the results are sensitive to the treatment of the trajectory, mainly due to the strong repulsive part of the pair potential. For instance, a model with the adparticle moving at a constant distance from the surface introduces large deviations from the results presented here. If one includes the thermal fluctuations of the substrate atoms in the expression for the adiabatic potential, as we have done through the Debye–Waller factor, it is also important to include them in the effective coupling constants (7). The reason is that a cancellation occurs. If the temperature is raised, the z-distance will increase, due to the anharmonic character of the potential perpendicular to the surface. The magnitude of the second derivative in (7) then decreases, but due to the larger fluctuations entering through the Debye–Waller factor in (7) a large part of this decrease is cancelled.

The space derivatives, connected with the motion of the adparticle, should be taken along the trajectory and not in the x-direction. However, since the variation of the z-distance as function of x is small, this effect can be neglected.

5.2. The adiabatic potential

In this article we are not aiming at an accurate numerical description of the adiabatic potential. We have therefore not taken into account the relaxation of the lattice in the presence of the adparticle, but the mean thermal displacements have been incorporated in a proper way. We are planning to present a more detailed investigation later, but we believe that no essential physics has been left out at this level.

The potential along the surface is shown in fig. 2 as well as the mean density. This potential has been calculated along the trajectory, described above. The vibrational frequency for the adatom determined from the curvature at the bottom of the well is equal to 6.96 and the activation energy is 1.13, all in reduced units. It is this potential barrier that the adatom has to surmount in passing from one adsorption site to another. The corresponding frequency for vibrations perpendicular to the surface is 10.7 and the binding energy is
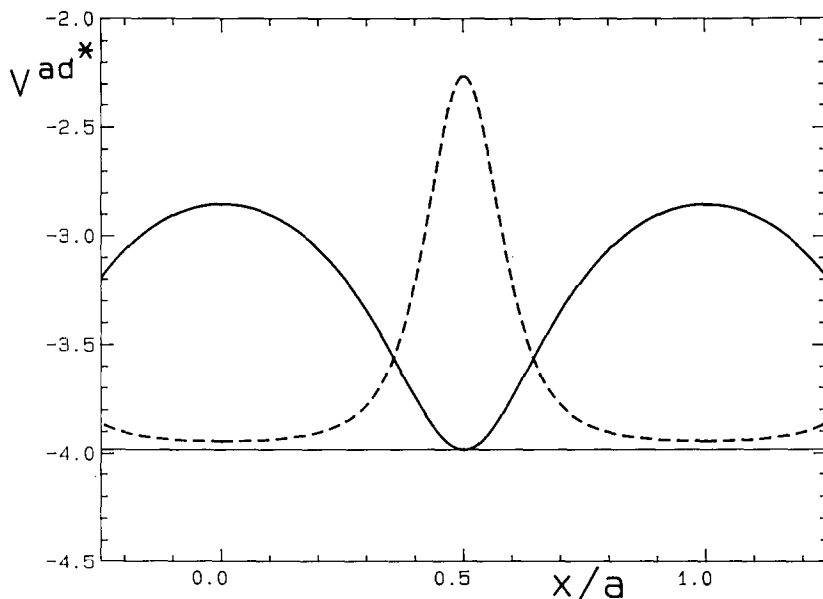
Fig. 2. The adiabatic potential (full curve) and the mean density (dashed curve) along the trajectory in fig. 1 in reduced units (introduced after eq. (31)).

3.98. In comparing the two barrier heights 3.98 and 1.13 to the reduced temperature 0.30, one would conclude that desorption from the surface can be neglected for our purpose.

5.3. The friction coefficient

The only component of the friction tensor, defined in (11), that enters in our one-dimensional equation of motion is the xx-component. Its position dependence along the chosen trajectory is shown in fig. 3 (full curve). This component is a measure of how strongly the motion in the x-direction is coupled to the vibrations of the atoms in the substrate. To understand the strong variation along the diffusion path we first notice that in FPA only the extreme low frequency phonons enter. This means that all substrate atoms in the vicinity of the adparticle are moving in phase. It is then clear from symmetry considera- tion that both at the centre position and at the bridge position one gets coupling only to the vibrations in the x-direction. Further, the strength of this coupling is determined by the following second derivative of the pair potential,

$$v^{xx}(r) = \left(\frac{x}{r}\right)^2 v''(r) + \left[1 - \left(\frac{x}{r}\right)^2\right]\frac{v'(r)}{r}. \tag{32}$$
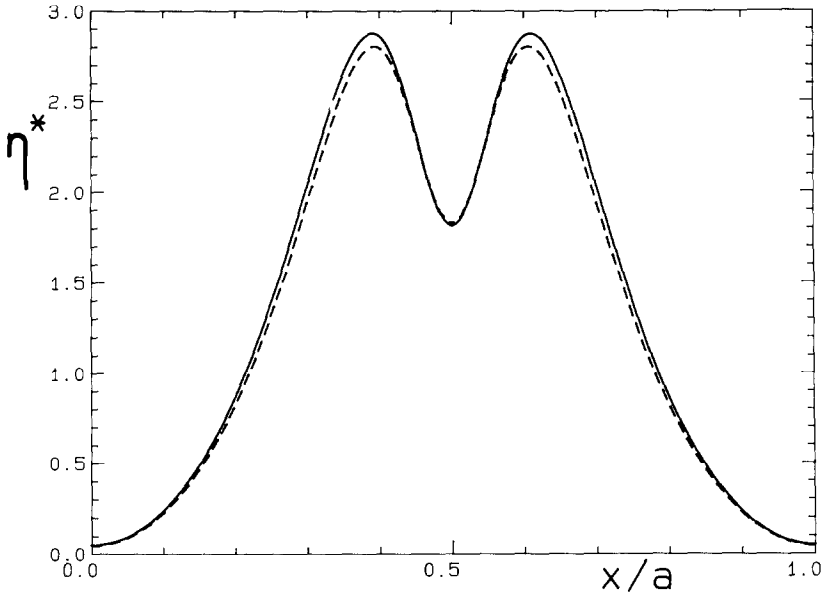
Fig. 3. The xx-component of the friction tensor along the chosen trajectory (full curve) in reduced units (introduced after eq. (31)). The dashed curve is calculated using (33) instead of (7).

The distance between the adparticle and the nearest substrate atoms is always very near the distance corresponding to the minimum of the pair potential. This implies that $v''(r)$ is considerably larger than $v'(r)/r$. However, at the bridge position ($x = 0$) only the second term on the right hand side of eq. (32) contributes and consequently $\eta^{xx}(0)$ is substantially smaller than $\eta^{xx}(a/2)$, as seen in fig. 3. For positions in between the adparticle couples also to the vibrations in the z-direction. This explains why $\eta^{xx}(x)$ has a maximum between $x = 0$ and $x = a/2$.

In a real situation the particle will not follow the chosen trajectory exactly, but depart from it both in the y- and z-directions. Especially, the motion in the z-direction could be essential, due to the fact that at a finite temperature the mean position will be slightly displaced from the position with minimum potential energy. To test our present approximation we have calculated the friction coefficient with a coupling $\bar{v}_{\text{eff}}^{\alpha\beta}$ that is weighted together with the mean density in the z-direction, i.e.

$$\bar{v}_{\text{eff}}^{\alpha\beta}(\mathbf{r}) = \int \mathrm{d}z \, \langle n(z) \rangle \, v_{\text{eff}}^{\alpha\beta}(\mathbf{r}). \tag{33}$$

The result is shown in fig. 3 (dashed curve) and we notice that the difference is surprisingly tiny. This is a strong argument for our restriction of the motion to the one-dimensional path in fig. 1.

5.4. The memory function

We have seen that the damping is frequency independent in the FPA. However, one expects that for very short times the adparticle does not collide and therefore moves undamped. This implies that the memory function should decay to zero for high frequencies. This decrease should appear at a typical Debye frequency, since the correlation time for the forces exerted by the lattice is of the order a period of the vibrations of the lattice ions. This is seen in fig. 4, where the four different approximations of $\hat{M}'_{00}(\kappa = 0, \omega)$ are shown. The cusp in the curves is caused by the Rayleigh mode.

One immediately sees that IVA is considerably better than EDA, and that the agreement between IVA and MCA is surprisingly good. This can be understood by comparing the important time-scales that are involved. To do this we define a force constant, by

$$k^{\alpha\beta}(r) = \left\langle \sum_l \nabla^\alpha \nabla^\beta v\left(r - R_l^0\right) \right\rangle = \sum_l v_{\text{eff}}^{\alpha\beta}\left(r - R_l^0\right). \tag{34}$$

The vibrational frequency is proportional to the square root of the force constant, $\omega = \sqrt{k/m}$, and from formula (11) we see that the friction coefficient
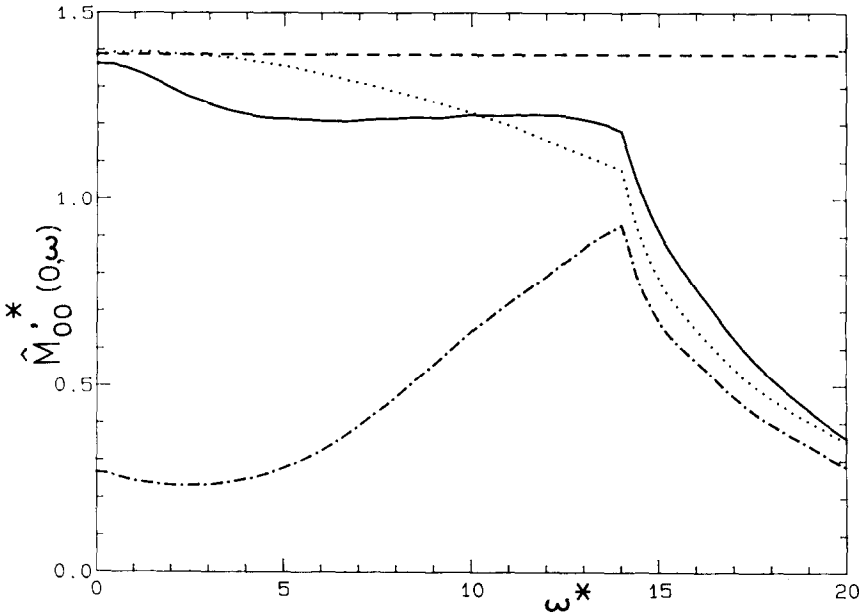

Fig. 4. The frequency dependence of the real part of the memory function for zero wavevector and $n_1 = n_2$, $\hat{M}'^*_{00}(0\,\omega)$, in reduced units (introduced after eq. (31)). The different curves correspond to the following approximations: MCA (full curve), IVA (dotted curve), FPA (dashed curve) and EDA (dash-dotted curve).
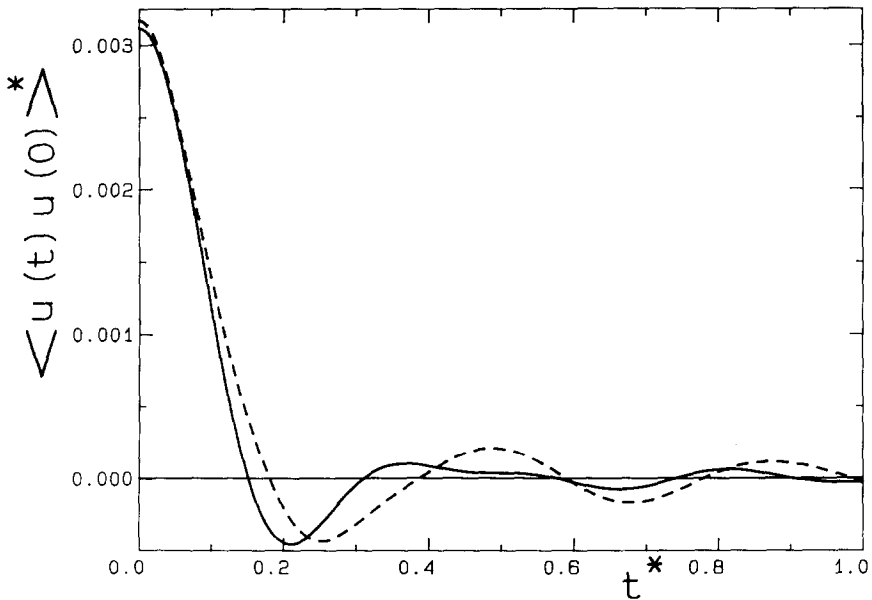
Fig. 5. The time dependence of the parallel (full curve) and perpendicular (dashed curve) components of the displacement correlation function for a substrate atom in the uppermost layer in reduced units.

is proportional to the square of k and is therefore very sensitive to the magnitude of v_{eff}. The ratio between the force constant for a substrate particle in the uppermost layer and for the adparticle, both located at their equilibrium sites, it found to be 6.0. The reasons for this rather large ratio are that the number of nearest neighbours differs and that the distance to the nearest neighbours is slightly larger for the adparticle than for a substrate particle. Consequently, the vibrational frequency for the adparticle is 2.4 times smaller than for a substrate atom, and this is the main reason why IVA is applicable. In other words, the adparticle is moving considerably slower than a substrate particle and it relaxes to equilibrium less rapidly.

Fig. 5 shows how the displacement correlation function $\langle u_l^\alpha(t) u_l^\alpha \rangle$ for a substrate atom in the uppermost layer varies with time. The full curve shows the parallel component ($\alpha = x$ or y) and the dashed curve shows the perpendicular component ($\alpha = z$). The mean square displacements $U^{\parallel}$ and $U^{\perp}$ are given by the initial values of $\langle u_l^\alpha(t) u_l^\alpha \rangle$ and a reasonable choice for the Debye frequency is $\omega_D^* = 20$.

We have found that within the characteristic relaxation time for the lattice displacements C_{00}^s has not changed significantly from its initial value. In considering the Γ_{22} element the current correlation function for the adparticle

enters. Even though this correlation function decays somewhat more rapidly than C_{00}^s, it is very likely that also the time dependence of Γ_{22} is dominated by the relaxation of the lattice displacements. Therefore, one should use approximation (21) in preference to (22) in the MCA.

5.5. The velocity correlation function

In the figs. 6–8 the frequency spectrum of the velocity correlation function $\phi(\omega)$ is shown. The details of the motion is rather well revealed in $\phi(\omega)$. At low temperatures, considered here, the particle is mainly localized around one of the potential minima and oscillates around it. This shows up in the pronounced oscillatory peak. The finite value at $\omega = 0$ gives the static diffusion constant, according to formula (30).

The different approximations (21) and (22) for the momentum dependence of the memory function in MCA have been compared and the result is shown in fig. 6. It is the term with the adiabatic force in eq. (4) that introduces coupling to the higher matrix elements through the p-derivative. This coupling is more pronounced at low temperatures.

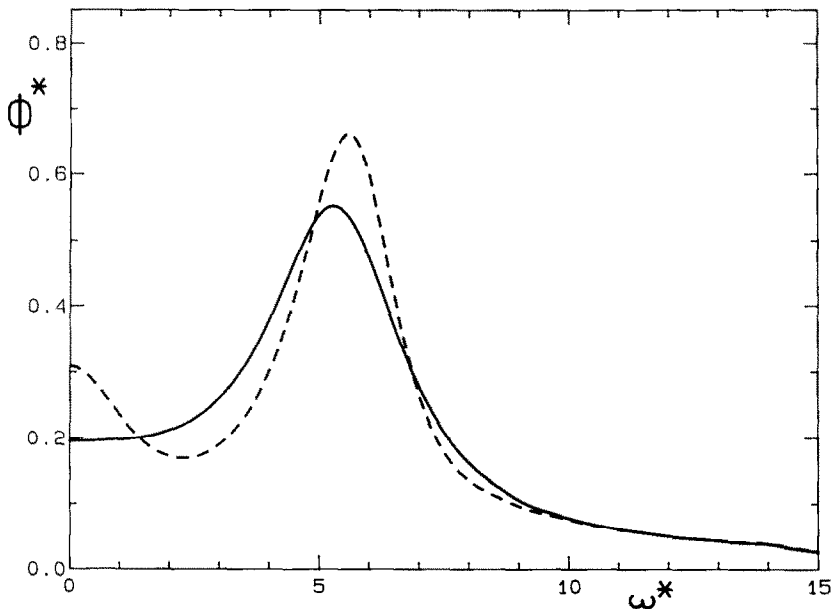In fig. 7 we compare the results from the MCA together with (21), IVA,

Fig. 6. The frequency spectrum of the velocity correlation function in reduced units (introduced after eq. (31)). The different curves correspond to the following approximations: MCA together with (21) (full curve) and MCA together with (22) (dashed curve).
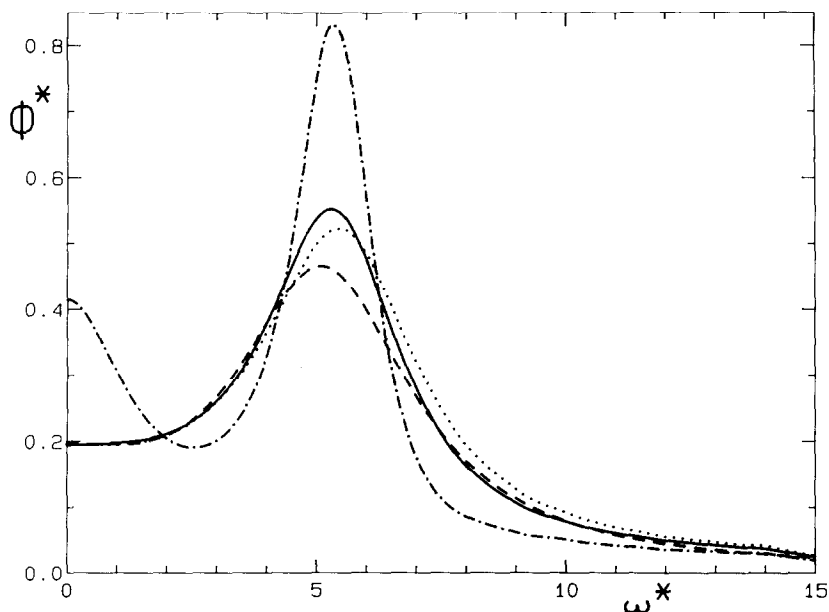
Fig. 7. The frequency spectrum of the velocity correlation function in reduced units. The different curves correspond to the following approximations: MCA together with (21) (full curve), IVA (dotted curve), FPA (dashed curve) and EDA (dash-dotted curve).

FPA, and EDA. The differences between the MCA, IVA, and FPA are small, which is seen already in fig. 4. As long as the resonance frequency is located well below the Debye frequency ω_D, all these three approximations are appropriate.

It should be noticed, however, that the position dependence in the friction coefficient is important. If one uses a constant friction coefficient, it is impossible to reproduce at the same time the correct height of the oscillatory peak and the correct value of the diffusion constant. This is seen in fig. 8, where the result from FPA (full curve) is compared with the corresponding curves determined with constant, i.e. position independent friction coefficients. To reproduce the height of the oscillatory peak one must use the value $\eta^* = 2.74$ (dotted curve), which is representative for the friction at the bottom of the well (cf. fig. 3). To get the proper value for the diffusion constant one needs the value $\eta^* = 0.95$ (dashed curve), which reflects the smaller friction at the top of the potential barrier.

The value of the calculated diffusion constant is $D^* = 0.029$. We can make a comparison with existing molecular dynamic calculations performed on exactly the same system, but for two-dimensional motion. Mruzik and Pound [3] and McDowell and Doll [7] have reported the values $D^* = 0.016$ and $D^* = 0.024$,
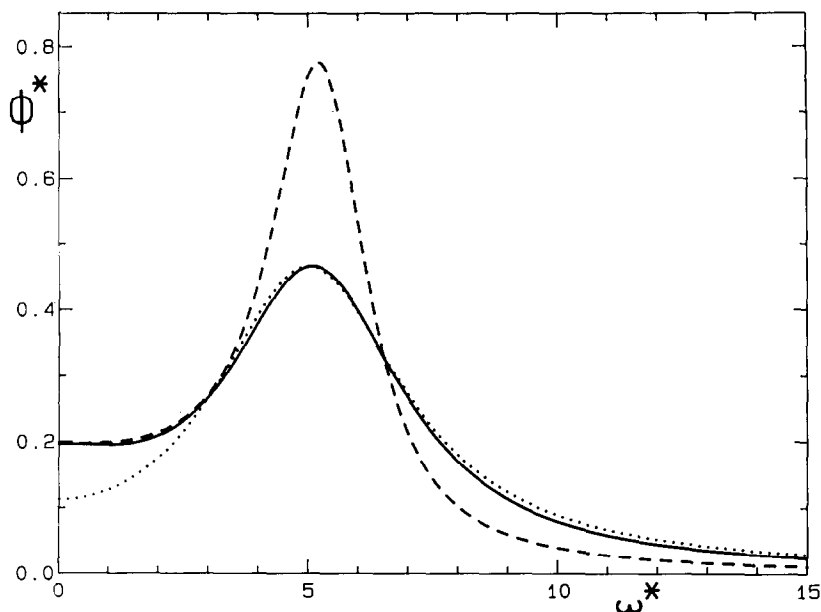
Fig. 8. The frequency spectrum of the velocity correlation function in reduced units. The different curves correspond to the following approximations: FPA (full curve) and the Fokker–Planck equation with constant friction, $\eta^* = 0.95$ (dashed curve) and $\eta^* = 2.74$ (dotted curve).

respectively. The results from these two simulations differ considerably and our calculated value is located well inside the error bars of these simulations. We have also compared the time dependence of the velocity correlation function with that in [3] and the agreement is good, implying that the magnitude of the friction we obtain agrees well with that from the computer simulations. Tully et al. [33] obtained the value $D^* = 0.027$ for the self-diffusion constant in our units.

The absolute rate theory (ART) [10] for the escape rate combined with the assumption of single uncorrelated jumps gives the value $D^* = 0.032$, if one uses appropriate values in this theory. This should be compared with our calculated value $D^* = 0.029$. For ART to be valid the interaction must be large enough so that the adparticle thermalizes rapidly inside the lattice cells, yet small enough so that it does not inhibit the crossing of the barriers. The position dependence of our friction coefficient (see fig. 3) is very well adapted for these assumptions. The close agreement found here between our calculated value of the diffusion constant and the corresponding ART result supports this conclusion.

The diffusion process is found to be quite well described through a jump diffusion model. However, certain quantitative differences from this model is observed, by looking at the width of the quasi-elastic peak in the dynamic

structure factor $S^s(q\omega)$. The latter consists of a quasi-elastic diffusive peak, whose width varies in a characteristic way with the wavevector, and an inelastic resonance peak, which increases in magnitude for larger wavevectors. This point will be more thoroughly discussed in a forthcoming paper.

6. Conclusions

We have developed a theory for the motion of a single adsorbed atom on a solid surface, which is free from the restrictive assumptions behind the ordinary Fokker–Planck equation. Further, it is demonstrated that an analysis, based on our mode coupling approximation (MCA), can be carried out with reasonable amount of numerical work.

The most important conclusion we can draw from our numerical comparisons is that, for the situation when the adatom is identical with the substrate atoms, the ordinary Fokker–Planck equation gives quite accurate results, provided one uses a proper position dependent friction coefficient. This may be somewhat surprising in light of what has been stated earlier and most recently by Suhl and Rezayi [19]. The fact that the adparticle has less nearest neighbours and that the nearest neighbour distance is slightly larger than for the substrate atoms makes that the adatom moves on a slightly slower time-scale than the substrate particles. We have found this to be enough to make the Fokker–Planck equation valid. However, the situation would be different for a lighter adatom, when its characteristic frequency is comparable to or larger than the corresponding one for the substrate atoms. Calculations have shown that the Fokker–Planck equation is seriously in error in this case and a report will be given in a separate paper [34].

The position dependence of the friction coefficient is found to be important. Any treatment based on a constant friction would spoil the agreement either for the diffusion constant or for the strength of the resonance peak in the frequency spectrum of the velocity correlation function $\phi(\omega)$. This position dependence, giving a considerably larger friction when the adparticle is at its potential minimum compared with the value at the top of the potential barrier, is well adapted for the assumptions behind the absolute rate theory for the escape rate. The agreement we find for the diffusion constant is in accordance with that.

The present calculations are done at the reduced temperature $T^* = 0.30$ and this corresponds to an activated diffusion with the activation energy $\Delta E = 3.8 k_B T$. In between the diffusion jumps the adparticle performs a dampled oscillatory motion which is clearly revealed in $\phi(\omega)$. This would be less pronounced if we increase the temperature or decrease the corrugation. Our present approach is equally well adapted for these cases and this will be discussed in more detail in a forthcoming paper.

We have here restricted ourselves to the phonon excitations in the substrate. For metals, plasmons and electron–hole pair excitations play an important role in surface kinetics. There is no difficulty to include this in our approach. The conduction electrons would renormalize the pair interaction potentials. Besides this, it seems obvious that they will give a position dependent, but frequency independent, contribution to the friction coefficient. Actually, considering a vibrating atom on a metal surface we recover quite directly the same result as obtained earlier by Hellsing and Persson [17], considering only the electronic excitations.

Acknowledgements

References

[1] G. Ehrlich and K. Stolt, Ann. Rev. Phys. Chem. 31 (1980) 603.
[2] G. Ehrlich, Surface Sci. 63 (1977) 422.
[3] M.R. Mruzik and G.M. Pound, J. Phys. F11 (1981) 1403.
[4] H.K. McDowell and J.D. Doll, Surface Sci. 121 (1982) L537.
[5] J.D. Doll and H.K. McDowell, Surface Sci. 123 (1982) 99.
[6] J.D. Doll and H.K. McDowell, J. Chem. Phys. 77 (1982) 479.
[7] H.K. McDowell and J.D. Doll, J. Chem. Phys. 78 (1983) 3219.
[8] S.H. Garofalini and T. Halicioglu, Surface Sci. 104 (1981) 199.
[9] G. de Lorenzi, G. Jacucci and V. Pontikis, Surface Sci. 116 (1982) 391.
[10] S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes (McGraw-Hill, New York, 1941).
[11] H.A. Kramers, Physica 7 (1940) 284.
[12] S. Chandrasekhar, Rev. Mod. Phys. 15 (1943) 1.
[13] T. Geisel, in: Topics in Current Physics, Vol. 15, Ed. M.B. Salamon (Springer, Berlin, 1979) pp. 201–246.
[14] W.L. Schaich, J. Chem. Phys. 60 (1974) 1087.
[15] A. Blandin, A. Nourtier and D.W. Hone, J. Physique 37 (1976) 369.
[16] C. Caroli, B. Roulet and D. Saint-James, Phys. Rev. B18 (1978) 545.
[17] B. Hellsing and M. Persson, Phys. Scripta 29 (1984) 360.
[18] P. Minnhagen, J. Phys. C15 (1982) 2293.
[19] H. Suhl and E.H. Rezayi, in: Many-Body Phenomena at Surfaces, Eds. D. Langreth and H. Suhl (Academic Press, New York, 1984) pp. 497–516.
[20] R. Zwanzig, in: Lectures in Theoretical Physics, Vol. 3, Eds. W.E. Brittin, B.W. Downs and J. Downs (Interscience, New York, 1961) pp. 106–141.
[21] H. Mori, Progr. Theoret. Phys. 33 (1965) 423.

[22] D. Forster, Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions (Benjamin, Reading, MA, 1975).
[23] J.P. Boon and S. Yip, Molecular Hydrodynamics (McGraw-Hill, New York, 1980).
[24] L. Sjögren and A. Sjölander, J. Phys. C12 (1979) 4369.
[25] N.W. Ashcroft and N.D. Mermin, Solid State Physics (Holt, Rinehart and Winston, New York, 1976).
[26] G. Wahnström and L. Sjögren, J. Phys. C15 (1982) 401.
[27] J.L. Lebowitz, J.K. Percus and J. Sykes, Phys. Rev. 188 (1969) 487.
[28] M.S. Jhon and D. Forster, Phys. Rev. A12 (1975) 254.
[29] W.G. Kleppmann and R. Zeyher, Phys. Rev. B22 (1980) 6044.
[30] H. Ezawa, Ann. Phys. (NY) 67 (1971) 438.
[31] A.A. Maradudin and D.L. Mills, Ann. Phys. (NY) 100 (1976) 262.
[32] G. Wahnström, Surface Sci., submitted.
[33] J.C. Tully, G.H. Gilmer and M. Shugard, J. Chem. Phys. 71 (1979) 1630.
[34] G. Wahnström, Surface Sci., submitted.