Diffusion of desorbing adsorbate: Study of a mesoscopic model

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Recent experimental data on surface diffusion for adsorbates that can desorb and diffuse at appreciable rates call for a better understanding of the phenomenon of combined diffusion and desorption. For denser adsorbate, models of hydrodynamic behavior for desorbing adsorbates have been discussed previously. In this paper we discuss a simple mesoscopic model for combined diffusion and desorption, which is based on the master equation approach. We study that model for realistic solid surface structures, i.e., graphite surface and fcc(111) or hcp(0001) metal surfaces. The differences in the coupling between diffusion and desorption caused by the presence of inequivalent adsorption sites and the related appearance of a new time scale is discussed. The analysis of available experimental data suggests that far-from-equilibrium measurements, for example scattering measurements of the dynamic adsorbate structure factor $S(q,\omega)$, combined with laser-induced thermal desorption, can access those time scales.

I. INTRODUCTION

The science of diffusion is one of the best developed areas of physics,1 yet there are several experimentally investigated new diffusionlike processes that so far had not been analyzed in great detail from a microscopic point of view. The specific problem we have in mind is the diffusion of an adsorbate on a surface of the solid when the adsorbate can also desorb at an appreciable rate. Those two phenomena, diffusion and desorption, contribute to the decay of the inhomogeneity in the local adsorbate density and, therefore, can jointly influence local density fluctuations measurements. One of the experiments in which such a coupling should show up is the laser-induced thermal desorption (LITD) and following it a refilling of the illuminated "hot spot."2

In this paper we intend to discuss a mesoscopic model which permits us to analyze the process of surface diffusion in the presence of desorption taking into account several peculiarities related to the complex structure of the solid surface on which both of those processes do happen. The necessity of developing microscopic or mesoscopic theories of surface diffusion for such a situation has been noted for some time. Earlier attempts were made to include substrate-adsorbate interaction and desorption into phenomenological, hydrodynamical-type theories.3,4 Those works were mostly interested in pointing out and discussing repercussions of such an effect on hydrodynamics itself, for example, the existence of a $d = 2$ hydrodynamics. Indeed, coupling to a substrate in a one-particle form, as discussed in Refs. 3 and 4, removes infrared divergences responsible for the nonexistence of the transport coefficients in exactly two-dimensional hydrodynamics. Recently, it was pointed out that some of the features of the adsorbate diffusion and desorption can be imitated by studying a properly tailored kinetic Ising model5 and, in the case of an adsorbate undergoing phase transformation,6,7 a similarly modified kinetic multistate Potts model.8 The general strategy of formulating the problem in terms of the master equation was outlined without, however, presenting specific applications.9 In this work we shall follow the master equation approach restricting, however, our analysis to the simplest possible situation of low-coverage density. That shall permit us to use the linear master equation.

The physical situation we envisage is as follows. Consider the surface of a real solid obtained by cutting a bulk crystal along a given crystallographic plane, for example a basal plane of graphite or (111) and (0001) planes of fcc and hcp crystals, respectively. Each of those surfaces is characterized by the presence of specifically located sites at which, when the surface will be exposed to the interaction with the ambient gas, the adsorbate atoms become physisorbed. The binding potential usually has several energy levels (from a few to several hundreds) and the dynamic interaction between the adatom and the solid surface can be viewed as a phonon-mediated reshuffling of the adatom over the ladder of those localized states. Occasionally phonons might induce the transition from one of the bound states to the continuum; the act of such a transition is called desorption.10 However, the dynamic interaction with the substrate might also induce the transitions between adatom levels at one adsorption site and the other, the process which we shall call jump. On a macroscopic scale this process is the surface diffusion of adsorbed species.

There are extensive studies of surface diffusion thought of as the motion of a single adatom over the corrugated surface described usually as the potential field developing several maxima and minima. Those theories range from detailed analyses based on modern liquid theories11 to purely mathematical works analyzing the possibility of localization understood as the lack of diffusion in specific kinds of corrugated potentials, for example in the periodic Lorentz model12 or in particular periodic potentials.13
Neither of those analyses offer the possibility of taking into account desorption and its coupling to the lateral motion of an adatom.

The meaningfulness of the master equation approach depends on the choice of the transition probabilities (or rates) which should satisfy certain general requirements, the detailed balance condition is of a predominant importance among them. In very few cases those rates can be calculated exactly from first principles, thus we usually have to postulate their form on the basis of a physical understanding of the problem. In an important paper the phonon-induced quantum tunneling of an atom from one interstitial position within the crystal to another was discussed in some detail. A particular form of the rates, which takes into account the possibility of a multilevel structure of each site, was derived there. We found it possible to carry out our analysis using a fairly general form of the transition probabilities. When we find it necessary to use an explicit form of the rates we will adopt those proposed in Ref. 15.

The model proposed in this paper should be applicable to several other problems, e.g., in solid-state optics where the intersite transitions are driven and/or coupled to intrasite ones and transitions to continuum. An example would be a fluorescence in the presence of traps in semiconducting materials.

II. THE MODEL

Consider a crystal surface obtained by cutting a bulk crystal along a given crystallographic plane. In general, there will be more than one adsorption site per each \( d = 2 \) (surface) unit cell. We shall label the cells by the position vector \( \mathbf{R}_i \), \( i = 1, \ldots, N \). The position of the adsorption site will be denoted then as \( \mathbf{X}_{i, \alpha} = \mathbf{R}_i + d_{i, \alpha} \) where \( d_{i, \alpha} \) labels the sites within the \( i \)th unit cell. An adatom at the site \( \mathbf{X}_{i, \alpha} \) may find itself in one of several possible localized states labeled by the index \( \alpha \). Note that the states \( \alpha \) are not necessarily quantum states corresponding to the adatom motion in the direction perpendicular to the solid surface. The detailed nature of these states is of secondary importance for our analysis. The fundamental dynamical variable is now the probability density, \( n_{\kappa, \alpha}^{\alpha}(\mathbf{R}_i, t) \), for an adatom to occupy one of the states \( \alpha \) at the site \( \kappa \) in the \( i \)th cell. The total number of atoms in both the gas and adsorbed phases is \( N_d \) and the total number of adatoms on the surface is given by \( N_s(t) = N_d \sum_{i, \kappa, \alpha} n_{\kappa, \alpha}^{\alpha}(\mathbf{R}_i, t) \). Similarly we may introduce the probability density \( n_{\kappa, \alpha}(t) \) for an atom in the gas phase to occupy a state, conventionally labeled by its momentum \( \kappa \). The conservation of particles is now expressed by

\[
\sum_{i, \kappa, \alpha} n_{\kappa, \alpha}^{\alpha}(\mathbf{R}_i, t) + \sum_{\kappa} n_{\kappa}(t) = 1 .
\]  

In equilibrium, the occupation probabilities \( n_{\kappa}^{\alpha} \) are given by the proper quantum distribution function

\[
n_{\kappa}^{\alpha}(\mathbf{R}_i) = \frac{1}{N_d \exp[\beta(E_k^{\alpha} - \mu)] + 1} ,
\]  

where the sign depends on the particle statistics. A similar formula holds in the gas phase with energies \( E_k^{\alpha} \) replaced by the free-atom kinetic energies \( E_k \). For low pressures of the gas and at not too low temperatures both distributions can be approximated by the Boltzmann distribution function with energies \( E_k^{\alpha} \), where in the gas phase \( \xi \) denotes momentum and in the adphase it stands for the set of labels \( (i, \alpha, \kappa) \). The chemical potential \( \mu \) is related to the ambient gas pressure \( P \) via the standard relation

\[
\exp(\beta \mu) = (2\pi \hbar)^3 P / (2\pi m / \beta)^{1/2} .
\]

Now, assume that the adatom, due to the interaction with the host solid, undergoes the transition to another state which might belong to the same or a different site. The transition probabilities for such a process should satisfy the detailed balance condition. We shall write them in a factorized form

\[
W_{\kappa, \kappa'}^{\alpha, \alpha'}(\mathbf{R}_i, \mathbf{R}_j) = M_{\alpha, \alpha'}^{\kappa, \kappa'} F_{\kappa, \kappa'}(\mathbf{R}_i - \mathbf{R}_j),
\]  

where \( M_{\alpha, \alpha'}^{\kappa, \kappa'} \) satisfy the detailed balance condition

\[
M_{\alpha, \alpha'}^{\kappa, \kappa'} \exp(-\beta E_k^{\alpha'}) = M_{\kappa', \kappa}^{\alpha, \alpha'} \exp(-\beta E_k^{\alpha}) .
\]

The function \( F_{\kappa, \kappa'}(\mathbf{R}_i - \mathbf{R}_j) \) describing the spatial dependence of the intersite jumps,

\[
F_{\kappa, \kappa'}(\mathbf{R}_i - \mathbf{R}_j, t) = f(|\mathbf{X}_{i, \alpha} - \mathbf{X}_{j, \alpha'}|)
\]  

satisfies an obvious symmetry condition \( F_{\kappa, \kappa'}(\mathbf{R}_i - \mathbf{R}_j) = F_{\kappa', \kappa}(\mathbf{R}_j - \mathbf{R}_i) \) which guarantees that \( W_{\kappa, \kappa'}^{\alpha, \alpha'}(\mathbf{R}_i - \mathbf{R}_j) \) satisfies the detailed balance. In the above, \( \beta = \frac{1}{kT} \) is the inverse temperature in energy units.

Before writing down our master equation we shall comment on the intrasite transition probabilities \( W_{\kappa, \kappa'}^{\alpha, \alpha'}(0) \), which are not necessarily given by \( F_{\kappa, \kappa'}(0)M_{\alpha, \alpha'}^{\kappa, \kappa'} \). Indeed, the only condition for this rate is the detailed balance. On physical grounds we will assume that intrasite transitions are fast enough to effectively equilibrate population probabilities in each of the sites before any macroscopic time evolution of desorption and/or diffusive character occurs. In the final stage of our analysis, when we will need to use an explicit form of the \( M_{\alpha, \alpha'}^{\kappa, \kappa'} \) matrices, we shall use the rates from Ref. 15,

\[
M_{\alpha, \alpha'}^{\kappa, \kappa'} = W_{\kappa, \kappa'} \exp\left(-\frac{\beta}{4\Delta}(E_k^{\alpha'} - E_k^{\alpha} - \Delta)^2\right) .
\]  

A similar form of the transition probabilities were used for intrasite transitions to study desorption and sticking on surfaces. The spatial part of the transition probabilities might be assumed in the form

\[
f(|\mathbf{R}|) = \frac{A_c}{2\pi\sigma^2} \exp\left(-\frac{|\mathbf{R}|^2}{2\sigma^2}\right) ,
\]

where \( A_c \) is the area of the unit cell. The length \( \sigma \) denotes the characteristic root-mean-square jump distance for the adatom and is taken to be of the order of the nearest-neighbor distance in the adsorption sites lattice.
We are now prepared to write down the master equation which will be the starting point of our analysis
\[
\frac{\partial n_{\alpha}^{\alpha}(R_j,t)}{\partial t} = \sum_{i',x',\alpha'} W_{\alpha\alpha'}^{\alpha'}(R_j-R_{i'}) n_{\alpha'}^{\alpha'}(R_{i'},t) \\
- \sum_{i',x',\alpha'} W_{\alpha\alpha'}^{\alpha}(R_{i'}-R_j) n_{\alpha'}^{\alpha}(R_j,t) \\
- Q_{\alpha}^{\alpha} n_{\alpha}^{\alpha}(R_j,t) .
\] (2.8)

The last term on the right-hand side (rhs) of Eq. (2.8) describes transitions from the adsorbed state into the gas continuum which are responsible for the desorption process. Desorption rates might be different at different non-equivalent adsorption sites in a unit cell and we will analyze how the overall result depends on that difference. For surfaces with one adsorption site per unit cell, like a graphite surface, it is relatively easy to parametrize the desorption rate \( Q \) by heat of desorption. For inequivalent sites such a parametrization is not as clear.

It is convenient to denote the matrix operator at the rhs of Eq. (2.8) as
\[
\hat{W}_{\alpha\alpha'}^{\alpha}(R_j-R_{i'}) = W_{\alpha\alpha'}^{\alpha}(R_j-R_{i'}) \\
- \delta^{\alpha\alpha'} \delta_{\alpha,\alpha'} \sum_{i',x',\alpha'} W_{\alpha\alpha'}^{\alpha}(R_{i'}-R_j) \\
- \delta^{\alpha\alpha'} \delta_{\alpha,\alpha'} Q_{\alpha}^{\alpha}
\] (2.9)

and perform a customary lattice Fourier transform by writing
\[
n_{\alpha}^{\alpha}(R_j,t) = \frac{1}{N} \sum_{q} e^{iq.R_j} n_{\alpha}^{\alpha}(q,t),
\] (2.10)

where \( N \) is the total number of surface unit cells. After straightforward algebra the master equation reads
\[
\partial_t n_{\alpha}^{\alpha}(q,t) = \sum_{\alpha'} \hat{W}_{\alpha\alpha'}^{\alpha}(q) n_{\alpha'}^{\alpha}(q,t),
\] (2.11)

where
\[
\hat{W}_{\alpha\alpha'}^{\alpha}(q) = W_{\alpha\alpha'}^{\alpha}(q) - \delta^{\alpha\alpha'} \delta_{\alpha,\alpha'} \sum_{\alpha''} W_{\alpha\alpha''}^{\alpha}(q=0) \\
- \delta^{\alpha\alpha'} \delta_{\alpha,\alpha'} Q_{\alpha}^{\alpha}.
\] (2.12)

Both matrices \( \hat{W}(q) \) and \( \hat{W}(q) \) can be unitarily transformed into Hermitian ones. \(^{10,14}\) Therefore, their spectra are real and can be shown to be negative. Recall that the spectrum of the master operator \( \hat{W}(q) \) consists of inverses of all time scales present in the system. The lowest eigenvalues of \( \hat{W}(q) \) and \( \hat{W}(q) \), denoted by corresponding diacriticals and taken with negative sign, differ in their long-wavelength limit
\[
\lim_{q \to 0} \hat{\chi}^{(0)}(q) = 0 ,
\] (2.13a)
\[
\lim_{q \to 0} \hat{\chi}^{(0)}(q) \neq 0 .
\] (2.13b)

Equation (2.13a) expresses the conservation of particles in the adsorbate in the absence of desorption, while (2.13b) reflects the loss of the particles from the surface due to desorption.

So far our analysis was very general. We shall make one of the most important simplifying approximations. We already have mentioned that the intrasite transitions are much faster than the remaining ones. It follows therefore that there exists a characteristic thermalization time, the short time scale in our problem, during which the quasistationary character of occupation probabilities is established.\(^{10,18}\) With a good approximation we can write
\[
n_{\alpha}^{\alpha}(R_j,t) = \exp(-\beta E_{\alpha}^{\alpha}) \phi_{\alpha}(R_j,t),
\] (2.14)

where \( \phi_{\alpha}(R_j,t) \) is a slowly varying function of time. For mathematical convenience we write
\[
n_{\alpha}^{\alpha}(R_j,t) = \frac{1}{Z_{\alpha}} \exp(-\beta E_{\alpha}^{\alpha}) \phi_{\alpha}(R_j,t),
\] (2.15)

where \( Z_{\alpha} \) is the kth site partition function defined, as usual, \( Z_{\alpha} = \sum_{\alpha'} \exp(-\beta E_{\alpha}^{\alpha}) \). Following this ansatz, the occupation of the kth site, \( n_{\alpha}(R_j,t) = \sum_{\alpha'} n_{\alpha}(R_j,t) \), can be conveniently parametrized as
\[
n_{\alpha}(R_j,t) = \sqrt{Z_{\alpha}} \phi_{\alpha}(R_j,t).
\] (2.16)

Upon inserting the above into Eq. (2.11) we obtain the matrix equation of motion for \( \phi_{\alpha} \) which, after taking the lattice Fourier transform, reads
\[
\partial_t \phi_{\alpha}(q,t) = \sum_{\alpha'} \hat{W}_{\alpha\alpha'}^{\alpha}(q) \phi_{\alpha'}(q),
\] (2.17)

where the matrix \( \hat{W}(q) \), which is Hermitian by virtue of the detailed balance condition for the rate matrix Eq. (2.3), has the form
\[
\hat{W}_{\alpha\alpha'}^{\alpha}(q) = \frac{1}{\sqrt{Z_{\alpha} Z_{\alpha'}}} \sum_{\alpha''} \hat{W}_{\alpha\alpha''}^{\alpha}(q) \exp(-\beta E_{\alpha''}^{\alpha'}) \\
= \frac{1}{\sqrt{Z_{\alpha} Z_{\alpha'}}} \sum_{\alpha''} \hat{W}_{\alpha\alpha''}^{\alpha}(q) \exp(-\beta E_{\alpha''}^{\alpha'}) - \delta_{\alpha\alpha'} \Lambda_{\alpha},
\] (2.18)

where
\[
\Lambda_{\alpha} = \frac{1}{Z_{\alpha}} \sum_{\alpha'} Q_{\alpha}^{\alpha} \exp(-\beta E_{\alpha}^{\alpha})
\] (2.19)
is the thermally averaged desorption rate from a kth adsorption site.

The eigenvalues of \( \hat{W} \) determine relevant slow time scales of processes in our system and we can easily write down the solution of the initial value problem for Eq. (2.16), which transformed back to the occupation probabilities of the kth site in the configuration space and has the form
\[
n_{\alpha}(R_j,t) = \sum_{i',x'} G_{\alpha\alpha'}(R_j-R_{i'},t) n_{\alpha'}(R_{i'},0) .
\] (2.19)

\( G \) is the lattice Green function for the combined diffusion and desorption problem which is expressed in terms of eigenvalues \( \hat{\chi}^{(0)}(q) \), and the corresponding set of orthogon-
nal and complete eigenvectors $A_{k}^{(v)}(q)$ of the matrix $\hat{\Pi}(q)$ as follows:

$$G_{\kappa\kappa}(R,t) = \frac{1}{N} \left| \frac{Z_{\kappa}}{Z_{\kappa'}} \right|^{1/2} \sum_{v} \sum_{q} A_{k}^{(v)}(q) A_{k'}^{(v)*}(q) \exp[iq \cdot R - t\lambda^{(v)}(q)].$$

(2.20)

For the sake of further analysis we rewrite Eq. (2.19) in $q$ space using the set of projection operators $P_{\kappa\kappa}(q)$

$$P_{\kappa\kappa}(q) = \left[ \frac{Z_{\kappa}}{Z_{\kappa'}} \right]^{1/2} A_{k}^{(v)}(q) A_{k'}^{(v)*}(q).$$

(2.21)

We have then

$$G_{\kappa\kappa}(q,t) = \sum_{(v)} P_{\kappa\kappa}(q) \exp[-t\lambda^{(v)}(q)].$$

(2.22)

It follows immediately from Eq. (2.19) that, in general, there is no simple macroscopic equation for decay of the adsorbate density $N_d(t) = N_v \sum_{i} n_{v}(\mathbf{R}_i,t)$. The decay of $N_d(t)$ is related to the whole vector $\{\eta_n(t=0)\}$. In order to access time scales with which the adsorbate density evolves we use a standard statistical-mechanics relation between the Green's function $G(q,t)$ and the autocorrelation function of the density fluctuations. The latter is in principle measurable in the scattering experiments. The dynamical structure factor $S(q,\omega)$ is related to the trace of the Laplace transform of the Green function $G(q,\omega)$

$$S(q,\omega) = 2\pi \sum_{\kappa} G_{\kappa\kappa}(q,\omega = \omega + i0^+),$$

(2.23)

and we are primarily interested in its long-wavelength limit. Using Eqs. (2.22) and (2.23) we obtain for $|q| \to 0$

$$S(q,\omega) = 2\pi \sum_{(v)} \sum_{\kappa} P_{\kappa\kappa}(v) \frac{\lambda^{(v)}(q)}{\omega^2 + [\lambda^{(v)}(q)]^2}.$$

(2.24)

Equation (2.24) is the starting point for the analysis of the combined diffusion-desorption processes. We will now evaluate the eigenvalues and eigenvectors for the symmetrized master operator $\hat{\Pi}(q)$ for several cases of experimental interest. We shall first analyze the basal graphite surface and then surfaces of fcc(111) and hcp(0001) solids. These examples differ not only in their crystalline symmetries but, even more important, in the number of adsorption sites per unit cell and offer a possibility of assessing differences stemming from nonequivalency of different adsorption sites.

**III. GRAPHITE SURFACE**

In Fig. 1 we have shown the atomic arrangement of the surface of graphite cut along its basal plane. The surface unit cell is spanned by standard bulk lattice vectors $a_1 = a(1,0,0)$ and $a_2 = a(0,1,0)$, where $a$ is the in-plane graphite lattice spacing. In each unit cell there is only one adsorption site per cell, denoted by a six-pointed star. Heavy points denote the host surface atoms. The adsorption sites form a hexagonal $d=2$ lattice. For this arrangement $\kappa=0$ and $d_0=0$. The matrix $\hat{\Pi}$ now becomes just a function of $q$

$$\hat{\Pi}_{00}(q) = -f(a)[3-S_d(q)]B_{00}-\Lambda_0.$$

(3.1)

In deriving Eq. (3.1) we assumed that the jumps are to the nearest neighbors only. That restricts the sums over the lattice vectors in Eq. (2.8) accordingly. Thus, $S_d(q)$, the hexagonal planar lattice structure factor, is given by

$$S_d(q) = \sum_{\mu} \cos(q_\mu a) + 2 \cos(q_\mu a/2) \cos(\sqrt{3}q_\mu a/2).$$

(3.2)

$f(a)$ is given by Eq. (2.5), $\Lambda_0$ is the thermally averaged desorption rate, viz., Eq. (2.18), and

$$B_{00} = \frac{1}{Z_0} \sum_{a,a'} M^{aa'}_{00} \exp(-\beta E^{aa'}_{00}).$$

(3.3)

The eigenvalue of $\hat{\Pi}$ is now just the negative value of its only matrix element, $\lambda(q) = -\hat{\Pi}_{00}(q)$. Thus, there is only one time scale in the problem determined by combined desorption and diffusion rates. In the long-wavelength limit $\lambda(q)$ becomes

$$\hat{\lambda}(q) = \lambda_d + Dq^2,$$

(3.4)

where $\lambda_d$ and $D = \frac{1}{2}f(a)B_{00}a^2$ is the diffusion constant. The explicit temperature dependence of $D$ is contained in $B_{00}$ and will be discussed later on. Note that, as expected, the dynamic structure factor (2.24) now has the form of a simple Lorentzian with the zero wave-vector width determined by the desorption rate $\lambda_d$. Therefore, the presence of desorption removes the infrared divergence in the adsorbate density autocorrelation function. That observation was made earlier on purely phenomenological, hydrodynamical grounds.
IV. CLOSE-PACKED CRYSTAL HEXAGONAL SURFACES

In Fig. 2 we have shown the surfaces of fcc(111) or hcp(0001) solids. The absorption sites are now arranged in the hexagonal planar lattice with two inequivalent sites per unit cell, denoted as six-pointed stars and octagons, respectively. The host surface atoms are denoted as heavy points. The lattice vectors are the same as in the graphite case with the lattice constant a now equal to the nearest-neighbor distance in these two close-packed crystals. There are now two \( \mathbf{d}_k \) vectors: \( \mathbf{d}_0 = 0 \) and \( \mathbf{d}_1 = (a_1 + a_2)/3 \), and the distance between the nearest inequivalent adsorption sites is \( |d_1| = a/\sqrt{3} \).

The matrix \( \tilde{H} \) is a two-by-two matrix (\( \kappa = 0,1 \)) which, after restricting the jumps to those between the nearest (inequivalent) adsorption sites, can be written as

\[
\tilde{H}(q) = \chi \begin{pmatrix}
-3 \left[ \frac{Z_1}{Z_0} \right]^{1/2} - l_0 & S_n(q) \\
S_n^*(q) & -3 \left[ \frac{Z_0}{Z_1} \right]^{1/2} - l_1
\end{pmatrix},
\]

(4.1)

where \( \chi = f(a/\sqrt{3})B_{10}, \ l_k = \Lambda_k/\chi \),

\[
B_{10} = B_{01} = \frac{1}{\sqrt{Z_1Z_0}} \sum M_{10}^{\alpha\beta} \exp(-\beta E_0^{\alpha\beta}),
\]

(4.2)

and the relevant structure factor is

\[
S_n(q) = 1 + \exp(-iq_xa) + \exp[-iq_x + \sqrt{3}q_ya]/2.
\]

(4.3)

The matrix \( \tilde{H} \) in Eq. (4.1) is obviously Hermitian and after some algebra we obtain the following expressions

\[
\mathbf{E}^{(1)}(q) = \begin{pmatrix}
\mathbf{P}(q) & \frac{1}{\gamma} \left[ \frac{Z_0}{Z_1} \right]^{1/2} S_n(q)[1 - 2P(q)] \\
\frac{1}{\gamma} \left[ \frac{Z_0}{Z_1} \right]^{1/2} S_n^*(q)[1 - 2P(q)] & 1 - P(q)
\end{pmatrix}^{1/2},
\]

(4.6)

where

\[
P(q) = \frac{4|S_n(q)|^2}{\gamma + [\gamma^2 + 4|S_n(q)|^2]/2 + 4|S_n(q)|^2}.
\]

(4.7)

Projection operators form a complete set, therefore \( \mathbf{P}^{(1)} = 1 - \mathbf{P}^{(0)} \).

The complicated structure of the eigenvalues, Eq. (4.4), reflects the difference in the thermal properties of inequivalent adsorption sites. Indeed, the site desorption rates \( \kappa \Lambda_k \) and site free energies \( \mathcal{F}_n = -\beta \ln(Z_n) \) are then different. We are now able to analyze the dynamic structure factor for this case. We shall first take the long-wavelength limit of the eigenvalues. We have

\[
\tilde{\lambda}^{(0)}(q) \approx \frac{X}{2} \left[ \gamma - (\gamma^2 + 36)^{1/2} + \frac{3}{(\gamma^2 + 36)^{1/2}} (qa)^2 \right] = \lambda + Dq^2,
\]

(4.8)

\[
\tilde{\lambda}^{(1)}(q) \approx \frac{X}{2} [\gamma + (\gamma^2 + 36)^{1/2}] \equiv \lambda.
\]
Note, that $\lambda$ — the $q$-independent term in $\hat{\lambda}^{(0)}$ — vanishes when desorption is neglected resulting in the usual infrared divergent term in the density fluctuation autocorrelation function.

The diffusion coefficient in Eq. (4.8) equals

$$D = \frac{3\gamma^2}{2(\gamma^2 + 36)^{3/2}}. \quad (4.9)$$

The above expression indicates the coupling between the intersite jumps and desorption. Indeed, $D$ depends on the difference of the desorption rates between inequivalent desorption sites $\Lambda_0 - \Lambda_1$ appearing in $\gamma$. The other contribution to the diffusion coefficient comes from the difference in thermal properties of the individual inequivalent sites contained in $\gamma$ via the individual sites partition functions. The eigenvector $\hat{\lambda}^{(1)}$ sets up the time scale for atomic jumps between the inequivalent adsorption sites within a single unit cell. This is a process occurring on short distances, thus it is not included in diffusion which, by definition, is a long-range effect of precisely the same intersite jumps. As seen from above, our model provides deeper microscopic insight into the process of single-particle surface migration than the usual theory of diffusion.

The dynamic structure factor in the long-wavelength limit reads

$$S(q, \omega) \approx 2 \left[ \frac{\lambda + Dq^2}{\omega^2 + (\lambda + Dq^2)^2} + \frac{\hat{\lambda}}{\omega^2 + \hat{\lambda}^2} \right], \quad (4.10)$$

explicitly exhibiting two time scale structures of the adsorbate density fluctuations. Note that $\lambda$ in Eq. (4.8) becomes the thermally averaged desorption rate $\Lambda$ in case of identical adsorption sites. Simultaneously, the diffusion coefficient becomes $D = f(a / \sqrt{3})B_{10}a^2/4$ (compare with the diffusion coefficient from Sec. III), but $\hat{\lambda}$ does not vanish, again showing the difference between the case of one and several equivalent adsorption sites per unit cell.

V. DISCUSSION AND CONCLUSIONS

In the preceding sections we have presented a fairly general analysis of the combined desorption diffusion process happening on the crystalline surface with one and/or several inequivalent adsorption sites per unit cell. In this analysis we have made assumptions, which can now be recapitulated as follows.

(i) The process is described by a linear master equation (2.8), which in the absence of desorption conserves the total number of particles. This equation is valid in case of low adsorbate coverage. In case of higher coverages the master equation should be modified to include blocking factors preventing double occupation of a given adsorption site. Such an analysis was outlined in Ref. 9. Another possibility would be to use the generalization of the Kawasaki transition probabilities known from the kinetic theory of conserved order-parameter phase transformations. Either of those generalizations will result in a nonlinear theory.

(ii) The transition probabilities used so far were very general. The only important property was the detailed balance and the fact that intersite jump rates depend on the distance between the sites $|X_{i}\rightarrow X_{j}|$, and only the nearest-neighbor jumps were taken into account. The latter restriction is of a technical nature, and can be removed resulting in more complicated expressions without bringing any new physical insight.

(iii) We have assumed that the intrasite transition rates are the fastest rates in the problem. Therefore, on-site fast thermalization ansatz, Eq. (2.14), is justified.

Any further development of theory requires a fully microscopic description, which would allow for an evaluation of the transition rates from first principles. Clearly this is a necessary step forward presenting considerable theoretical and technical challenges. Alternatively, one can postulate a specific form of those rates and try to get some deeper insight into the predictions of our model by correlating them with few existing experimental results. One such possible choice for the transition probabilities is from Ref. 15, given in Eqs. (2.3) through (2.7). Using these rates for the one adsorption site model as discussed in Sec. III, the diffusion coefficient from Eq. (3.4) can now be evaluated exactly giving

$$D = \frac{4}{\sqrt{3}f} \exp(-\beta\Delta/4) \frac{1}{Z_0} \times \sum_{o} \exp \left[ -\frac{\beta}{2} \left( \frac{E_{o}^a - E_{o}^b}{2\Delta} + (E_{o}^a + E_{o}^b) \right) \right]. \quad (5.1)$$

One expects that for low temperatures the dominant temperature dependence of $D$ is contained in the factor $\exp(-\beta\Delta/4)$. Indeed, for low $T$ the dominant contribution to the double sum in (5.1) and to $Z_0$ stems from the bottom level in the adsorption potential well. In this limit $D \approx 3f(a)\exp(-\beta\Delta/4)/4$, and $\Delta/4$ serves as the activation energy barrier for the diffusion process. Evaluation of $B_{10}$ using energy levels for the Morse surface potential for H on graphite as adsorbance on graphite confirms this argumentation. For H on graphite the desorption time can be parametrized as $\tau_{D} = \frac{5.6 \times 10^3}{T} \text{exp}(-149.3/T) \text{sec}^{-1}$. Conventional diffusion is written as $D = D_{0} \exp(-E_{\text{diff}}/T)$. Choosing a typical value for the prefactor $D_{0} = 10^{-4} \text{cm}^2/\text{sec}$ and less, and following the experimentally established rule that for this class of systems $E_{\text{diff}}$ is of the order of 10% to 30% of the heat of desorption, we find that diffusion and desorption contributions to the decay of the adsorbate density fluctuations are of comparable order for temperatures of the order of 20 to 30 K. One should keep it in mind that there is a considerable uncertainty as to the value of the prefactor $D_{0}$ which can vary from $10^{-6}$ to $10^{-4} \text{cm}^2/\text{sec}$ for hydrogen on some metal surfaces. This uncertainty affects our estimates considerably.

In order to check predictions of our model for several inequivalent adsorption sites we use experimentally available data for CO diffusion on the Rh[111] surface. According to Ref. 21 the Rh[111] surface contains two inequivalent sites on which CO (and also H2 or D2) can adsorb. The binding energies of CO on these two sites differ by few kcal/mole, and equal 31 and 26 kcal/mole, respec-
tively. Those values seem to be fairly typical: for CO on Pt(111) the corresponding numbers are 30 and 22 kcal/mole. Diffusion activation energy for both systems equals about 7.1 kcal/mole and is of the order of 25% to 30% of the desorption energy. As before, the values of $D_0$ are fairly uncertain. The upper bound seems to be $10^{-4}$ cm$^2$/sec, although for an otherwise very similar surface of Pt(111) values a hundred times smaller are reported.$^{21}$ Using typical values for the wave vectors and assuming that the prefactor in the Arrhenius parametrization of the desorption rate varies between $10^{13}$–$10^{15}$/sec we find that the desorption and diffusion contribution to the decay rate of the adsorbate density fluctuation becomes comparable for temperatures in the range of 600 to 2000 K. That range of temperature should be accessible to all experiments using a LITD to study surface diffusion.

The above discussion suggests that the combined effect of desorption and diffusion can be observed away from equilibrium, for example in LITD experiment. Our model assumes conventional fluctuation dissipation relations resulting in the expression for the dynamic structure factor $S(q,\omega)$ exhibiting two time scales. This should not raise any concerns since recent experiments on light scattering from nonequilibrium fluid systems$^{12}$ indicate that the conventional form of the fluctuation dissipation holds far away from equilibrium. Therefore experimental measurement of $S(q,\omega)$ during LITD should access both time scales and provide an independent measurement of the relatively high-temperature diffusion coefficient and desorption rate.

In conclusion, we have provided a linear master-equation model for combined diffusion and desorption phenomena occurring on surfaces with complex geometrical arrangements of adsorption sites. We have shown that under conditions similar to those realizable in the LITD experiment those two phenomena combine in a nontrivial way leading to the occurrence of several comparable time scales in the evolution of the density fluctuations. We have chosen for our analysis relatively simple but experimentally relevant crystal surfaces for which diffusion is isotropic. Choosing other experimentally investigated surfaces, like W(211), would result not only in several time scales we have discussed, but also in anisotropic diffusion.

The analysis presented in this work assumed that the transition probabilities, Eq. (2.8), have fairly general properties. Actual quantitative predictions require detailed knowledge of these rates. Therefore, the microscopic theory of interstitial atomic jumps on realistic crystal surfaces is of great importance and should be vigorously pursued. Work along this line is now in progress.

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