Kinetic equation approach to the description of quantum surface diffusion: Non-Markovian effects versus jump dynamics

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We consider surface diffusion of a single particle, which performs site-to-site underbarrier hopping, fulfils intrasite motion between the ground and the first-excited states within a quantum well, and interacts with surface phonons. We obtain a chain of quantum-kinetic equations for one-particle distribution functions and nonequilibrium hopping probabilities. The generalized diffusion coefficients are derived, and the generic non-Markovian diffusion equation is written down both for the infinite lattice model and in the continuous media limit. In the latter case, the one-particle distribution function obeys the telegrapher's equation, which could give us a nonmonotonic behavior of the intermediate distribution functions at large spatial gradients. In a weak-coupling limit, if the energy of level splitting is comparable with the temperature, there are also pronounced oscillations of the generalized diffusion coefficients. The recrossing/multiple crossing phenomena, a problem of long tails of the generalized diffusion coefficients, as well as a mapping into the next- to the nearest-neighbors hopping regime, are discussed.

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I. INTRODUCTION

A description of the diffusion processes of particles adsorbed on metallic surfaces is a topical problem of surface physics and of a high interest both for experimentalists and theorists. It is well known that diffusion of the adparticle can proceed via two different mechanisms: (i) thermally activated one, when the adsorbed particle due to thermal fluctuations of the bath gets enough energy to surmount a potential barrier formed by static (or dynamic) location of the substrate atoms, or (ii) underbarrier quantum tunneling [1–3]. It is widely believed that the latter scenario is typical for light adatoms, such as a hydrogen and its isotopes, whose de Broglie wavelength is comparable with the substrate interatomic spacing a.

However, a class of the "adsorbate-substrate" systems to be described in a quantum-mechanical manner is much wider than that. For instance, in Ref. [4], on the basis of experimental (x-ray magnetic circular dichroism) and computer simulations (quantum Monte Carlo method) approaches, it has been shown that the jump rates of Cr adatoms on Au(111) surface by many orders exceed the values, expected for thermal overbarrier hopping at low temperatures. In Ref. [5], the authors showed that there are notable quantum corrections to the intermediate scattering function of another quite "heavy" atom Na on flat and corrugated Cu(001) surfaces and calculated their contributions in a wide region of temperatures and coverages. Furthermore, the phenomena, such as quantum-mechanical tunneling of a light impurity between interstitial sites of a host lattice [6], bulk diffusion of muonium in NaCl and KCl [7], μ^+ in metals [8], are similar to the problems of surface quantum diffusion, and their description requires similar theoretical methods [6,9,10].

From the theoretical point of view, the diffusion coefficients are traditionally determined via the Green-Kubo relations [9,10], the low frequency and small wave-vector limit of the dynamic structure factor [3,11], or zeroth moments of

the "velocity-velocity" autocorrelation functions [11,12]. A quantum analog of the latter approach is based on the calculation of "flux-flux" time correlation functions defined either on different sites of the lattice [13] or on different eigenfunctions of the dividing surface, which crosses a top of the barrier [14]. It is possible to study the well-known "recrossing/multiple crossing" problem [15,16], describe effectively the dynamics of the adsorbed particle, or even to derive a new quantum transition state theory [14,17].

The method of quantum-kinetic equations is somewhat distant from other theoretical approaches. Traditionally, this method is thought to be less promising because it requires an existence of a small parameter in the system under consideration. Thus, if there is no way to restrict oneself by the equation for one-particle distribution functions only, one has to keep some equations of the hierarchy and decouple them when appropriate. Such a situation emerges, for instance, when one deals with collective diffusion, and many-particle interactions cannot be treated in the framework of the mean-field approximation [18] or a nonequilibrium behavior of the phonon subsystem is evident [19].

In the problems of the tracer diffusion, there is much less limitation for the application of the quantum-kinetic equations. Even better results can be obtained if one deals with a single adparticle, which interacts only with electron and/or phonon subsystems of the surface. In this case, it is possible to obtain expressions for the diffusion coefficients, which are valid up to the second-order approximation with respect to the tunneling amplitudes. Many reliable results were obtained in the framework of the reduced density-matrix method in its application to the problems of surface [20,21] or bulk quantum diffusion [6]. For instance, the mean-square displacement $\langle \Delta r(t)^2 \rangle$ of the adparticle, performing random motion between lattice sites, has been calculated, a temperature dependence of the diffusion coefficients in a wide region of T in the limits of both weak and strong couplings has been obtained, and a detailed analysis of multiphonon contributions to the hopping rates has been carried out. However,

some questions related to the dynamic behavior of the system remained out of the examination.

Even in the case of the tracer diffusion, memory effects can be present, if the substrate has no time to relax during the adparticle motion. In fact, the leading memory effect is the backward correlation of the second jump with respect to the first one since the first jump leaves a vacancy behind. Besides, the memory effects are stronger for the single-particle motion than for a collective motion, where most of the above backward correlations cancel out. To answer the question whether non-Markovian effects are important, one has to estimate the ratio between the time scales of the surface excitations, electronic excitations, and adparticle motion. Usually, it is believed that the electronic excitations are too fast to contribute to the memory effects [3] though they should be taken into account to obtain a proper long-time behavior of the kinetic kernels [10] and reliable values of the quantum diffusion coefficients [22]. The Markovian approximation is applicable if $\omega_{max}/\Omega \gg 1$, where ω_{max} stands for the Debye frequency of the substrate, and Ω means the vibrational frequency of the adparticle at the bottom of the potential well. Usually, the above-mentioned time scales are well separated that justifies the application of the Markovian limit both in the problems of thermally activated and quantum diffusion.

In the present paper on the basis of a simple model of a single-particle diffusion, we study the conditions, when the memory effects play an important role and cannot be excluded from consideration. It will be shown that in a weak-coupling limit, when the energy exchange between the adparticle and the substrate (which plays a role of the thermal bath) is very slow, the relaxation times of the generalized (time-dependent) diffusion coefficients exceed the inverse Debye frequency by two orders of magnitude. If the vibrational frequency Ω is comparable with ω_{max}, this slow relaxation of the generalized diffusion coefficients is accompanied by an oscillatory behavior.

Once a dominant influence of memory effects on the dynamic of the system "substrate adsorbate" is recognized, a problem of correct determination of the generalized diffusion coefficients emerges. There are several ways to introduce them. The first one consists in the generalization of the Green-Kubo relations to the non-Markovian case [9]. The second one is dealt with the calculation of the mean-square displacement of the tagged particle at short times, while a long-time limit by means of the Einstein's relation gives us the value of the usual tracer diffusion coefficient [3,21]. Recent achievements in the atom-tracking technique [23] allow one to connect the experimentally obtained mean-square displacement of the adparticle with the values calculated theoretically.

In our paper, we define the generalized diffusion coefficient in a different way. We make use of the generalized collective modes approach, whose cornerstone is the time hierarchy of the dynamic processes. This method has manifested its efficiency in numerous problems of the condensed-matter theory [24–27]. In our point of view, in the problems of the single-particle diffusion this method is much more preferable due to the following reasons. First of all, there is no need to solve the system of kinetic equations to obtain the mean-square displacement of the particle and, correspond-

ingly, the diffusion coefficients, as it was done in Ref, [21]. Quite contrary, the expressions for the transport coefficients arise in a consistent way—by the elimination of nonequilibrium transition probabilities from the chain of quantum-kinetic equations with subsequent renormalization of the kinetic kernels. One can attribute the renormalized term to the coherent diffusion coefficient and to impart it a plain physical meaning. Second, our approach allows to consider both nearest-neighbor hopping and possible long jumps of the adparticle on equal footing. Last but not least, it is possible to point out and to investigate, in detail, two reasons of different nature, leading to the oscillatory dynamics of the intermediate distribution function $n(k,t)$: (i) considerable spatial gradients in the system in the presence of the processes of different time duration and (ii) nonmonotonic behavior of the generalized diffusion coefficients themselves that leads to the oscillations of $\langle \Delta r(t)^2 \rangle$ at short times. In the case (i), the dynamics of the adparticle is governed by the telegrapher's equation [3,28], which (to our knowledge) was introduced in a semiphenomenological way only. The case (ii) could be mapped into the next- to the nearest-neighbors hopping regime that results in a similar (oscillatory) dynamics of the mean-square displacement of the adparticle.

Our paper is organized in the following way. In Sec. II, we present a Hamiltonian of the "adsorbed particle-substrate" system, which has been used in Ref. [21], for the description of the temperature behavior of the diffusion coefficient of the H/W(110) system. In Sec. III, following the suggested procedure there, the initial Hamiltonian by a sequence of unitary transformations is rewritten in the form without an explicit interaction between subsystems. In Sec. IV, a chain of non-Markovian equations for one-particle distribution functions and nonequilibriun hopping probabilities is derived on the basis of the reduced density-matrix method. The generalized diffusion coefficients are obtained by the standard "rolling-up" procedure. The continuous media limit $a \rightarrow 0$ is performed and a generic non-Markovian diffusion equation is written down. In Sec. V, we consider two different problems, leading to the oscillatory behavior of the intermediate distribution function $n(k,t)$. Relationship between the parameters of the model that leads to the transition from monotonic to oscillatory behavior of the generalized diffusion coefficients is established. In two last sections, we discuss the obtained results, point out some related problems to be solved, and draw final conclusions.

II. SYSTEM HAMILTONIAN

To specify all interactions in the "metallic surface-adparticles" system, we choose a Hamiltonian, which allows site-to-site tunneling of an adsorbate, intrasite oscillations of the adparticle between ground and excited states within the potential well and an interaction of the adparticles with a lattice (coupling with substrate is both by density and oscillation modes). We use Hamiltonian considered in Refs. [20,21].

$$H = H_A + H_{int} + H_B, \qquad (2.1)$$

where the adsorbate is described by the two-band Hubbard Hamiltonian H_A,

$$H_A = \left\{ \sum_{\langle ss' \rangle, \sigma} (- t_0 a_{s0\sigma}^{\dagger} a_{s'0\sigma} + t_1 a_{s1\sigma}^{\dagger} a_{s'1\sigma}) + \sum_s \left[\frac{\Omega}{2}(n_{s1} - n_{s0}) \right. \right.$$

$$\left. \left. + U \frac{n_s(n_s - 1)}{2} \right] \right\}, \quad (2.2)$$

with

$$n_{si} = \sum_\sigma n_{si\sigma}, \quad n_s = n_{s0} + n_{s1}.$$

Here s denotes the site in the lattice, 0 and 1 are two states (ground and excited) within a given well, σ is the spin label, and $\langle ss' \rangle$ denotes a sum over the nearest-neighbor sites. Quantum states within a well are referred to as "vibrational" states, with vibrational frequency Ω, and we have taken zero of the energy to lie midway between the two levels. $a_{si\sigma}^{\dagger}(a_{si\sigma})$ creates (destroys) a particle on the site s, in the vibrational state i, and with spin σ; $n_{si\sigma} = a_{si\sigma}^{\dagger} a_{si\sigma}$ is the number operator for this state. Depending on the spin of the adparticles, the creation and destruction operators obey either Bose or Fermi commutation relations; since we will deal with single adparticle only, the spin label in all subsequent expressions is omitted. t_0 and t_1 are the nearest-neighbor tunneling amplitudes in the ground and first-excited states, respectively (note that both quantities are positive in the convention used here, and we expect that $t_1 \gg t_0$). For the adparticles obeying Bose statistics, U means on-site Hubbard repulsion, which is assumed to be independent of vibration.

The coupling to phonons described by the term H_{int} is considered to be local within each well. Phonons may couple both to the adsorbate density operators and also to the vibrations within a quantum well. The interaction Hamiltonian is [21]

$$H_{int} = \sum_s \left\{ n_s \sum_q \gamma_{sq}(b_q + b_q^{\dagger}) + (a_{s0}^{\dagger} a_{s1} + a_{s1}^{\dagger} a_{s0}) \sum_q \chi_{sq}(b_q \right.$$

$$\left. + b_q^{\dagger}) \right\}, \quad (2.3)$$

where $b_q^{\dagger}$, (b_q) creates (destroys) a phonon with a normal-mode frequency ω_q. Strengths γ_{sq} (χ_{sq}) describe coupling of phonons to the density (oscillation) modes of the adsorbate. We present the substrate-adsorbate interaction potential $\mathcal{V}_{int}(r;\{u_s\})$, parametrized by the particle position r and the lattice displacements $\{u_s\}$, in the form

$$\mathcal{V}_{int}(r;\{u_s\}) = V^{eq}(r) + \sum_{s=1}^{N} u_s V^s(r),$$

up to the linear terms in the lattice displacements. While the bandwidths t_0, t_1, and vibrational frequency Ω are assumed to be evaluated in the framework of eigenvector-eigenvalue problem for the periodic potential $V_{eq}(r)$ felt by the adsorbate due to the static lattice, the coupling constants are expressed as the mean values of lattice distortion potential $V^s(r) = \frac{\partial \mathcal{V}_{int}(r;\{u_s\})}{\partial u_s}\big|_{\{u'_s = 0\}}$ over the localized Wannier states, $|s;0\rangle$, $|s;1\rangle$, and are supposed to be the same for all quantum states [20]. For a one-dimensional (1D) case, the strengths γ_{sq}, χ_{sq} could be written explicitly via the lattice parameters [20]; for

a two-dimensional (2D) infinite lattice (which is considered in our paper), we introduce in the next section the lattice spectral weight functions [20,21] to describe substrate-adsorbate interaction.

The last term in Eq. (2.1),

$$H_B = \sum_q \hbar \omega_q b_q^{\dagger} b_q, \quad (2.4)$$

corresponds to the phonon bath; only longitudinal-acoustic phonons are taken into account in this model.

III. UNITARY TRANSFORMED HAMILTONIAN

Usually, in the quantum diffusion problems, one can consider the substrate-adsorbate coupling to be arbitrary (either weak or strong one). On the other hand, one-particle characteristics of the system described by the first term of the Hamiltonian (2.1) are treated as small parameters. In such a case, it is useful [6,20,21] to start from a unitary transformed Hamiltonian on a new correlated basis, which provides a better zeroth-order representation: the sequence of unitary transformations has the effect of changing to a representation in which the adsorbate is localized at one end of an adsorption site or the other, and in which there is a correlated displacement of the lattice. Before performing the unitary transformation, we pass to the hybrid set of states for each site according to the following rule:

$$a_{s_{R}^{L}} \equiv \frac{1}{\sqrt{2}}(a_{s_0} \pm a_{s_1}) \quad (3.1)$$

and similarly for the creation operators. The designation L or R means that a single adparticle is now localized on the left or on the right side of the given well. Then, applying a procedure of double unitary transformation [20,21] $\tilde{H} = \mathcal{U} H \mathcal{U}^{\dagger}$ with the operator $\mathcal{U} = \mathcal{U}_1 \mathcal{U}_2$, where

$$\mathcal{U}_1 = \prod_s \exp\left[-n_s \sum_q \frac{\gamma_{sq}}{\omega_q}(b_q^{\dagger} - b_q) \right],$$

$$\mathcal{U}_2 = \prod_s \exp\left[-(n_{sL} - n_{sR}) \sum_q \frac{\chi_{sq}}{\omega_q}(b_q^{\dagger} - b_q) \right], \quad (3.2)$$

a transformed Hamiltonian of the system of adparticles is obtained in the following form [20]:

$$\tilde{H} = H_{intra} + H_{inter} + H_{pp} + H_B \equiv H' + H_{pp} + H_B. \quad (3.3)$$

The term H_{intra} describes the lattice-modified intrasite dynamics of the adparticle,

$$H_{intra} = \sum_s \frac{U}{2} n_s(n_s - 1) - \left(\frac{\Omega}{2} B_s a_{sL}^{\dagger} a_{sR} + \text{H.c.} \right), \quad (3.4)$$

$$B_s = \exp\left[-2 \sum_q \frac{\chi_{sq}}{\hbar \omega_q}(b_q - b_q^{\dagger}) \right] \quad (3.5)$$

with the lattice-induced operator exponent B_s, and denotation H.c. means Hermitian conjugation. The second term in Eq. (3.3)

$$H_{inter} = \sum_{\langle ss' \rangle} t_{ch}(B_{ss'}^{LR} a_{sL}^\dagger a_{s'R} + B_{ss'}^{RL} a_{sR}^\dagger a_{s'L}) + t_{pr}(B_{ss'}^{LL} a_{sL}^\dagger a_{s'L}$$
$$+ B_{ss'}^{RR} a_{sR}^\dagger a_{s'R}) \tag{3.6}$$

is the intersite tunneling term with end-changing (end-preserving) amplitudes t_{ch} (t_{pr}), which are the linear combinations $t_{pr}^{ch} = \frac{1}{2}(t_1 \pm t_0)$ of the initial tunneling amplitudes, while operators B are of the structure

$$B_{ss'}^{LR,RL} = \exp\left[- \sum_q (\Delta_q^{ss'} \pm {}^{(+)}\delta_q^{ss'})(b_q - b_q^\dagger) \right],$$

$$B_{ss'}^{LL,RR} = \exp\left\{ - \sum_q [\Delta_q^{ss'} \pm {}^{(-)}\delta_q^{ss'}](b_q - b_q^\dagger) \right\},$$

$$\Delta_q^{ss'} = \frac{\gamma_{sq} - \gamma_{s'q}}{\hbar \omega_q}, \quad {}^{(\pm)}\delta_q^{ss'} = \frac{\chi_{sq} \pm \chi_{s'q}}{\hbar \omega_q}, \tag{3.7}$$

where an upper sign in Eq. (3.7) corresponds to the first superscript.

The last but one term of the Hamiltonian (3.3)

$$H_{pp} = - \sum_{\langle ss' \rangle} \{ C_{s,s'}^{DD} n_s n_{s'} + 2 C_{s,s'}^{DO} n_s (n_{s'L} - n_{s'R})$$
$$+ C_{s,s'}^{OO} (n_{sL} - n_{sR})(n_{s'L} - n_{s'R}) \} \tag{3.8}$$

describes the particle-particle lattice-induced interaction with strengths

$$C_{s,s'}^{DD} = \sum_q \frac{\gamma_{sq} \gamma_{s'q}}{\hbar \omega_q}, \quad C_{s,s'}^{DO} = \sum_q \frac{\gamma_{sq} \chi_{s'q}}{\hbar \omega_q},$$

$$C_{s,s'}^{OO} = \sum_q \frac{\chi_{sq} \chi_{s'q}}{\hbar \omega_q}. \tag{3.9}$$

Coefficients $C_{s,s'}^{DD} \equiv C_{|s-s'|}^{DD}$ correspond to the short-range attractive interaction between adparticles at adjacent sites and, therefore, oppose the Hubbard on-site repulsion. Terms with $C_{s,s'}^{DO} \equiv C_{|s-s'|}^{DD}$ give a mutual repulsion between particles. The long-range $C_{s,s'}^{OO} \equiv C_{|s-s'|}^{DD}$ interactions (determined by the overlap of the lattice distortions associated with each particle) stabilize the system, when the particles are on the sites s and s' and at the same ends (L or R) of their respective wells [20]. In the single adsorbate limit, the Hubbard repulsing term vanishes, and H_{pp} contributes only to a site-independent lattice stabilization energy [21] $E_{stab} = C_0^{DD} + C_0^{OO}$ and has no effect on the dynamics of the adsorbate. Hereafter, we use a condition of the translational symmetry of the lattice. As a result, the interaction strengths depend only on the distance between the particles. For the same reason, we consider site-independent end-changing spectral weight functions,

$$J(\omega) = \sum_q \chi_{sq}^2 \delta(\omega - \omega_q), \tag{3.10}$$

$$J_{LR}(\omega) = \sum_q [(\gamma_{sq} - \gamma_{s'q}) + (\chi_{sq} + \chi_{s'q})]^2 \delta(\omega - \omega_q),$$

$$J_{RL}(\omega) = \sum_q [(\gamma_{sq} - \gamma_{s'q}) - (\chi_{sq} + \chi_{s'q})]^2 \delta(\omega - \omega_q) \tag{3.11}$$

and end-preserving ones,

$$J_{LL}(\omega) = \sum_q [(\gamma_{sq} - \gamma_{s'q}) + (\chi_{sq} - \chi_{s'q})]^2 \delta(\omega - \omega_q),$$

$$J_{RR}(\omega) = \sum_q [(\gamma_{sq} - \gamma_{s'q}) - (\chi_{sq} - \chi_{s'q})]^2 \delta(\omega - \omega_q). \tag{3.12}$$

The function (3.10) describes the intrasite dynamics, the functions (3.11) are related to intersite end-changing processes, while Eqs. (3.12) are dealt with intersite end-preserving processes. At low frequencies, the end-changing spectral weight functions (labeled by the subscript c) are approximately given by

$$J_c(\omega) \approx \begin{cases} 0, & \omega < \omega_0 \\ \eta_c \omega^{D-2}, & \omega > \omega_0, \end{cases} \tag{3.13}$$

and the end-preserving (with the subscript p) ones by

$$J_p(\omega) \approx \begin{cases} 0, & \omega < \omega_0 \\ \eta_p \omega^D, & \omega > \omega_0, \end{cases} \tag{3.14}$$

with

$$\eta_c = 10G, \quad \eta_p = 12.5G \tag{3.15}$$

given in units of the dimensionless coupling constant [20,21]

$$G = \frac{\Gamma^2}{M \omega_{max}^3}. \tag{3.16}$$

In Eqs. (3.13)–(3.16), D labels a dimension of the lattice, M denotes the mass of a substrate atom, ω_{max} stands for a Debye frequency, and the coupling strength Γ is expressed via the mean value of the distortion potential over localized Wannier states. Moreover, the lattice is allowed to possess a nonzero lowest frequency ω_0. Though the presence of a gap in the spectrum of acoustic phonons on the infinite lattice seems to be rather controversial, the evaluation of the diffusion coefficient of a hydrogen atom on a tungsten surface showed [21] that the obtained results are quite insensitive to the value of ω_0 provided the temperature is much greater than $\hbar \omega_0 / k_B$. Besides, a low-frequency approximation for the spectral weight functions shows similar tendencies in the case of a bulk diffusion of a light inclusion assisted by optical phonons [6,9,10]. The only difference is the value of the parameter D, which is found to be equal to 5.

Now we have all constituents of the Hamiltonian (3.3) to investigate the dynamical properties of the system "adparticle-substrate" and, in the next section, we will construct the system of quantum-kinetic equations.

IV. KINETIC EQUATIONS FOR ONE-PARTICLE NONEQUILIBRIUM FUNCTIONS OF ADSORBATE

We consider the first two terms of the Hamiltonian (3.3) as a small perturbation H', which allows us to construct a

closed systems of kinetic equations for one-particle nonequilibrium distribution functions up to the second order in H'. Using the method of the reduced density matrix [9], we present the equation for nonequilibrium statistical operator $\rho_S(t)$ of the adsorbate as follows:

$$\frac{\partial \rho_S(t)}{\partial t} + \frac{1}{i\hbar}[\rho_S(t), H_S] = -\frac{1}{\hbar^2}\int_{t_0}^{t} dt' \exp[-\epsilon(t-t')]$$
$$\times \mathrm{Tr}_B\{[H',[H'(t-t'),\rho_B\rho_S(t')]]\}.$$
(4.1)

In Eq. (4.1) $\epsilon \to +0$, and $H(t')$ stands for the operator H' in the Heisenberg picture,

$$H'(t') = \exp[it'(H_S + H_B)/\hbar]H' \exp[-it'(H_S + H_B)/\hbar],$$

$$H' = H_{intra} + H_{inter} - \langle H_{intra} + H_{inter}\rangle_B,$$
(4.2)

with the Hamiltonian

$$H_S = -E_{stab}\sum_s n_s + \langle H_{intra} + H_{inter}\rangle_B.$$
(4.3)

The first term in Eq. (4.3) is, in fact, a single adsorbate limit for the particle-particle lattice-induced interaction H_{pp} and, as have been already said, can be omitted. In a many-particle case [29] but at low coverage, one has to use the mean-field approximation H_{pp}^{mf} for Eq. (3.8) instead of the first term in Eq. (4.3). The term with H_{pp}^{mf} can be quite relevant, if one deals with additional many-particle interactions, such as chemical reactions, or if there is a spatial inhomogeneity in the system. The remaining part of Eq. (4.3) corresponds to the renormalized tunneling and intrasite terms averaged over the phonon bath. It can be shown that only end-preserving spectral weight functions give nonzero contributions. The expression for this term will be presented later.

One more point deserves mentioning. In the expression (4.1), we intentionally retained an initial time t_0 in the integral part instead of performing the Markovian limit $t - t_0 \to \infty$. As will be shown in subsequent sections, such a limit is not well justified if the coupling constant is weak enough, and one has to deal with kinetic equations, which are essentially nonlocal in time.

Using the equation for $\rho_S(t)$ after straightforward but somewhat lengthy calculations, one obtains the system of linear kinetic equations for the Laplace transforms $\tilde{f}_{s,s}(z)$ and $\tilde{f}_{s,s+n}(z)$ of the one-particle nonequilibrium distribution functions $f_{s,s}(t) = \sum_{i=L,R}\langle a_{si}^\dagger a_{si}\rangle_S^t$ and hopping probabilities $f_{s,s+n}(t) = \sum_{i=L,R}\langle a_{s+ni}^\dagger a_{si}\rangle_S^t$, where the index $s+n$ means the nearest neighboring site with respect to s. We present this system of equations in the following form (see the Appendix for some details of its derivation):

$$z\tilde{f}_{s,s}(z) - f_{s,s}(t=0) = -\frac{i}{\hbar}t_{inter}\sum_n [\tilde{f}_{s,s+n}(z) - \tilde{f}_{s+n,s}(z)]$$
$$- \tilde{\gamma}_{inter}(z)\left[2\tilde{f}_{s,s}(z) - \sum_n \tilde{f}_{s+n,s+n}(z)\right],$$
(4.4)

$$z\tilde{f}_{s,s+n}(z) - f_{s,s+n}(t=0) = -\frac{i}{\hbar}t_{inter}[\tilde{f}_{s+n,s+n}(z) - \tilde{f}_{s,s}(z)]$$
$$- [\tilde{\gamma}_{inter}(z) + \tilde{\gamma}_{intra}(z)]\tilde{f}_{s,s+n}(z)$$
$$+ \tilde{\gamma}_{LL}^+(z)\tilde{f}_{s+n,s}(z).$$
(4.5)

A similar chain of equations has been obtained in Ref. [21]; however, the authors applied a Markovian approximation for the kinetic kernels and did not study the short-time dynamics of the adsorbate.

Linearity of Eqs. (4.4) and (4.5) is the result of a single-particle approximation, and the question about statistics of the adparticle loses its significance. Note that a similar linear approximation could be performed also at low coverage of the adsorbate. However, at low-to-moderate coverage, one has to retain all nonlinear terms and at high coverage to include nonequilibrium correlation functions into the set of dynamical variables of the abbreviated description [9].

Let us analyze in detail all constituents of the kinetic Eqs. (4.4) and (4.5). The first terms of in right-hand side describe a nondissipative coherent motion of the adsorbate with the renormalized tunneling amplitude

$$t_{inter} = t_{pr}\exp\left[-\frac{1}{2}\int_{\omega_0}^{1}d\omega\frac{J_p(\omega)}{\omega^2}\coth\left(\frac{\hbar\omega}{k_BT}\right)\right]$$
$$= t_{pr}\omega_0^{\eta_p k_B T}\left[\eta_p k_B T \sinh\left(\frac{1}{2\eta_p k_B T}\right)\right]^{-\eta_p k_B T}.$$
(4.6)

Hereafter, we use dimensionless frequencies in the units of ω_{max} and temperatures in the units of $\hbar\omega_{max}$. The kinetic kernel

$$\tilde{\gamma}_{inter}(z) = 4\tilde{\gamma}_{LL}(z) + 2\tilde{\gamma}_{LR}(z) + 2\tilde{\gamma}_{RL}(z)$$
(4.7)

corresponds to the dissipative intersite motion of the adsorbate and describes processes, when the adparticle performs series of random site-to-site hoppings (with or without the change in its quantum states) owing to the interaction with a bath. The kinetic kernel $\tilde{\gamma}_{intra}(z)$ describes dissipative intrasite dynamics, when the adsorbate during its scattering from the lattice gets enough energy from the bath to be excited from the ground state to the upper level within one adsorption site (the opposite process of particle de-excitation with a phonon emission is also taken into consideration). The rates $\tilde{\gamma}_{intra}(z)$, $\tilde{\gamma}_{inter}(z)$ can be obtained from the Laplace transformation of the kinetic kernels

$$\gamma_x(\tau) = \omega_{max}\lambda_x^2 J_0^4(2t_{inter}\tau)\{\exp[-(\varphi_x(0) - \varphi_x(\tau))]$$
$$- \exp[-\varphi_x(0)]\},$$
(4.8)

$$\gamma_{LL}^+(\tau) = \omega_{max}t_{pr}^2 J_0^4(2t_{inter}\tau)\{\exp[-(\varphi_{LL}(0) + \varphi_{LL}(\tau))]$$
$$- \exp[-\varphi_{LL}(0)]\},$$
(4.9)

where

TABLE I. Rate functions γ_x, amplitudes λ_x, and spectral weight functions $J_x(\omega)$ along with their low-frequency limits (3.13) and (3.14).

γ_x	λ_x	$J_x(\omega)$
γ_{intra}	$\Omega/2$	$J_{intra}(\omega) = J_c(\omega)$
γ_{LR}	$-(t_1+t_0)/2$	$J_{LR}(\omega) = J_c(\omega)$
γ_{RL}	$-(t_1+t_0)/2$	$J_{RL}(\omega) = J_c(\omega)$
γ_{LL}	$(t_1-t_0)/2$	$J_{LL}(\omega) = J_p(\omega)$
γ_{RR}	$(t_1-t_0)/2$	$J_{RR}(\omega) = J_p(\omega)$

$$\varphi_x(\tau) = \int_{\omega_0}^{1} \frac{J_x(\omega)}{\omega^2}\left[\coth\left(\frac{\hbar\omega}{2k_BT}\right)\cos(\omega\tau) - i\,\sin(\omega\tau)\right].$$
$$(4.10)$$

In Table I, we present the amplitudes λ_x and the spectral weight functions $J_x(\omega)$, relevant to the rates (4.8) and (4.9) appearing in the kinetic Eqs. (4.4) and (4.5). The functions [Eq. (4.10)] yield lattice contributions to the kinetic kernels, and the zeroth-order Bessel function $J_0(2t_{inter}\tau)$ in Eqs. (4.8) and (4.9) accounts for the particle contribution. The latter function ensures a convergence of the time integrals of Eqs. (4.8) and (4.9) at any value of the coupling constants, though from the mathematical point of view, it exceeds the required accuracy, being higher than the second order in tunneling amplitudes. We will touch upon this problem later when discussing the results for generalized diffusion coefficients.

Our further advance is in the manner of the generalized collective modes approach [24,27]. To find the generalized diffusion coefficient, let us solve Eq. (4.5) with respect to the hopping probabilities $\widetilde{f}_{s,s+n}(z)$ and insert the obtained result into Eq. (4.4). After grouping the similar terms, one obtains the following equation:

$$z\widetilde{f}_{s,s}(z) - f_{s,s}(0) = \left\{ \frac{2t_{inter}^2}{z + \widetilde{\gamma}_{inter}(z) + \widetilde{\gamma}_{intra}(z) + \widetilde{\gamma}_{LL}^+(z)} + \widetilde{\gamma}_{inter}(z) \right\}\left[\sum_n \widetilde{f}_{s+n,s+n}(z) - 2\widetilde{f}_{s,s}(z)\right].$$
$$(4.11)$$

The ratio in the braces describes a coherent contribution $\widetilde{D}_{coh}(z)$ to the generalized diffusion coefficient and can be interpreted in terms of a simple model of band-type motion limited by scattering from the lattice at temperatures large as compared to the bandwidth. Indeed, in the framework of this model [21]

$$\widetilde{D}_{coh}(0) \sim v^2/\widetilde{\gamma}(0),\qquad (4.12)$$

where v denotes the average velocity of the adsorbate, and $\widetilde{\gamma}(0)$ means the total rate of scattering from the lattice. In the two-band model, v is proportional to at_{inter}, where a denotes a substrate interatomic spacing, and the total scattering rate is given by $\widetilde{\gamma}_{inter}(0) + \widetilde{\gamma}_{intra}(0) + \widetilde{\gamma}_{LL}^+(0)$. Hence, the coherent diffusion coefficient is really of the form given in Eq. (4.12). On the other hand, $\widetilde{D}_{coh}(z)$ characterizes the way in which

the dephasing limits the band motion of the adatom by the destruction of the coherence of the hopping probabilities $\widetilde{f}_{s,s+n}(z)$. If the adparticle moves on the surface in a coherent manner, not interacting with the substrate, then its eigenstate is described by a superimposition of localized Wannier states. This limiting case corresponds to the ballistic (collisionless) regime of motion, when the mean-square displacement of the particle is proportional to the squared time. However, the coupling with the thermal bath induces random fluctuations of each phase, which destroys the coherence of the state. Thus, $\widetilde{D}_{coh}(z)$ is related to the competition between the tunneling mechanism, which tends to preserve the coherence, and the dephasing constant $\widetilde{\gamma}(z)$, which characterizes damping due to the scattering process.

The second term $\widetilde{\gamma}_{inter}(z) \equiv \widetilde{D}_{in}(z)$ in Eq. (4.11) is an incoherent contribution to the diffusion coefficient. This is the result expected from the random-walk model for diffusion with site-to-site hopping rate $\widetilde{\gamma}_{inter}(z)$; it describes processes in which the surface dynamics induces fluctuations of the tunneling matrix elements between two Wannier states [30]. As a result, the adparticle is allowed to perform a transition from one Wannier state to another by creating or annihilating surface phonons.

It has to be noted that the terms of "coherent" and "incoherent diffusion coefficients" are introduced just to distinguish the contributions of $\widetilde{D}_{coh}(z)$ and $\widetilde{D}_{in}(z)$ to the generalized diffusion coefficient and are widely used in the literature [6,21,30]. In reality, no coherent motion is possible if the adatom interacts with a thermal bath since a dephasing limited band motion destroys the coherence.

The last multiplier of Eq. (4.11) in a continuous media limit, when the interatomic spacing tends to zero, converts to the second derivative with respect to the space variable (for 1D lattice) times a^2 or to the Laplace operator (for 2D lattice in the absence of the next- to the nearest-neighbors hopping) times $4a^2$. Then, performing the inverse Laplace transformation, one can write down a non-Markovian diffusion equation for the one-particle nonequilibrium distribution function $n(r,t)$ as follows:

$$\frac{\partial n(r,t)}{\partial t} = \int_{t_0}^{t} D(t-t')\Delta n(r,t')dt',\qquad (4.13)$$

where Δ denotes the Laplace operator (obviously, this result is valid rather for many-particle system at low coverage, when there are gradients of the adparticles concentration, than for the $N \to 1$ limit). Let us remind that in the previous section, we assumed the kinetic kernels to be independent of the site label s. It is a very essential assumption, and it leads to the absence of spatial nonlocality in the expressions for generalized diffusion coefficients, so the memory effects only are taken into consideration. The case when there is a spatial inhomogeneity, which results from the site-dependent interaction strengths (3.9) and spectral weight functions (3.10)–(3.12), is the subject of separate studies. For instance, in Ref. [31], the generalized diffusion coefficients in the presence of large spatial gradients have been calculated using the lattice-gas model of the nonequilibrium diffusion. Both

tracer D_{tr} and chemical diffusion D_{ch} coefficients have been shown to depend on the surface coverage Θ and its spatial derivative; at that D_{tr} decreases by the value proportional to the $(\nabla\Theta)^2$ in comparison with its equilibrium value. The most general case of the wave-vector-dependent diffusion coefficients also with the time nonlocality is a challenging topic of nonequilibrium surface diffusion theory. It allows one to get a deeper insight into the dynamics of the system at various time-spatial scales, and, undoubtedly, deserves much attention from the researches but lies beyond the scope of the present paper.

We call $D(t)$, entering Eq. (4.13), the generalized diffusion coefficients, even though this denotation is usually [27,32] attributed to the Laplace transforms of $D(t)$. It should be stressed that the time dependence of the kinetic kernels is much more informative than the frequency one: the generalized diffusion coefficient $D(t)$ is directly related to the flux-flux time correlation function $C_{s,s}^{JJ}(t)$ determined on the adsorption site s. The investigation of its temporal behavior can help to visualize a motion of the adparticle both at short and long times.

V. ADPARTICLE DYNAMICS AT VARIOUS VALUES OF THE COUPLING CONSTANTS

A. Intermediate and strong-coupling limits

In the intermediate to strong-coupling limit, when $G \geq 0.01$, the functions (4.8) could be approximated as follows:

$$\frac{\gamma_c(\tau)}{\omega_{max}\lambda_c^2} \approx \exp[-\eta_c|\ln\omega_0|(k_BT\tau^2 + i\tau)], \quad (5.1)$$

$$\frac{\gamma_p(\tau)}{\omega_{max}\lambda_p^2} \approx \exp\left[-\frac{\eta_p}{2}(k_BT\tau^2 + i\tau)\right], \quad (5.2)$$

while Bessel functions $J_0(2t_{inter}\tau)$ can be taken equal to unity. On the other hand, keeping in mind that the vibrational frequency Ω is much greater than tunneling amplitudes t_{ch}, t_{pr} [21], and performing the Markovian approximation $\tilde{\gamma}_{intra}(z) \approx \tilde{\gamma}_{intra}(0)$, one can obtain the following expression for the coherent part of the generalized diffusion coefficient:

$$\tilde{D}_{coh}(z) = a^2\left(\frac{t_1}{2}\right)^2\frac{t_{inter}}{z + \frac{1}{4}\Omega^2\tilde{\gamma}_c(z=0)}. \quad (5.3)$$

In time representation, it corresponds to an exponential damping. On the contrary, according to Eqs. (5.1) and (5.2), kinetic kernels that form the incoherent term $D_{in}(t)$ decay as Gaussian functions. If, in addition, the values of multipliers at the corresponding powers of t are of the same order (the choice of the parameters of our model at which all numerical calculation have been performed, indeed, provides such a situation), then it is a good reason to perform the Markovian approximation for $D_{in}(t)$, while leaving $D_{coh}(t)$ under the integral in Eq. (4.13). Thus, the diffusion (4.13) turns into

$$\frac{\partial n(r,t)}{\partial t} = D_{in}\Delta n(r,t) + \int_{t_0}^{t}D_{coh}(t-t')\Delta n(r,t')dt',$$

$$(5.4)$$

where $D_{in} = \tilde{D}_{in}(0) = \int_0^\infty D_{in}(t)dt$ denotes the Markovian limit of the generalized diffusion coefficient $D_{in}(t)$ and has a simple physical meaning of the incoherent part of the experimentally observed diffusion coefficient [21]. Differentiating both sides of Eq. (5.4) with respect to time, one obtains a telegrapher's equation

$$\frac{\partial n(r,t)}{\partial t} + \tau_r\frac{\partial^2 n(r,t)}{\partial t^2} = D\Delta n(r,t),$$

$$\tau_r = \frac{4}{\Omega^2\tilde{\gamma}_c(0)}, \quad D = \tilde{D}_{in}(0) + \tilde{D}_{coh}(0). \quad (5.5)$$

This equation is known to describe a correlated random walk [28] and, usually, is obtained phenomenologically by introducing special relaxation flux terms to the original diffusion equation. We derived Eqs. (5.5) rigorously by the Markovian approximation for the incoherent part of the generalized diffusion coefficient as a result of different decay rates of $D_{in}(t)$ and $D_{coh}(t)$.

A solution of Eq. (5.5) can be either diffusionlike or propagating (wavelike). The first regime is being realized at wave numbers $k < k_{min}$. Here, k_{min} is the smallest root of the corresponding characteristic equation for the intermediate distribution function $\tilde{n}(k,t)$, which is a Fourier transform of $n(r,t)$. On the other hand, in the domain $k_{min} < k$, the intermediate distribution function starts to oscillate. It can be shown that at intermediate and strong coupling, we have $k_{min}a \geq 1$, i.e., the oscillations occur far away from the hydrodynamic region. Quite contrary, at weak coupling with $G \leq 10^{-2}$, the following relation is valid: $k_{min}a \ll 1$, i.e., the oscillations of $\tilde{n}(k,t)$ occur in the hydrodynamic region. Nevertheless, recalling the relation between the mean-square displacement $\langle\Delta r(t)^2\rangle$ of the adparticle and the intermediate distribution function $\tilde{n}(k,t)$

$$\langle\Delta r(t)^2\rangle = -\left.\frac{\partial^2\tilde{n}(k,t)}{\partial k^2}\right|_{k=0}, \quad (5.6)$$

one can conclude that no oscillation is evident in the mean-square displacement, and we have a diffusion with $\langle\Delta r(t)^2\rangle \to 4(D_{in}+D_{coh})t$ coming out monotonically to the Einstein's law at long times. Anyway, a reason for the formation of a wavelike solutions of Eq. (5.5) is a presence of spatial inhomogeneities in the adsorbate-substrate system rather than the nonmonotonic behavior of the generalized diffusion coefficients. In the next subsection, we will show what happens at a very weak coupling, when it is not possible to perform the Markovian approximation in Eq. (5.3).

B. Weak-coupling limit

It could be shown [21] that in the weak-coupling limit, when $G < 10^{-2}$, the approximation (5.1) for the end-changing kernels is still valid while this is not true for the end-
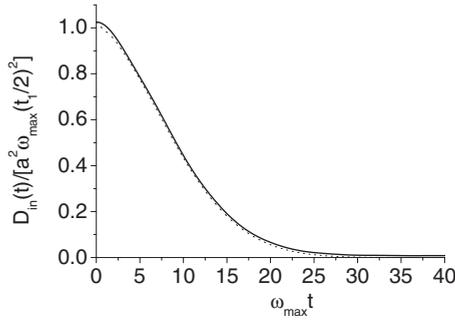
FIG. 1. The incoherent part of the generalized diffusion coefficient as a function of the dimensionless time $\omega_{max}t$ calculated at the coupling constant $G=10^{-3}$ and the temperature $k_BT/\hbar\omega_{max}=0.1$. A solid curve is obtained when omitting Bessel function in the kinetic kernel.

preserving [Eq. (5.2)] ones. This is due to the different low-frequency behavior of the weight spectral functions (3.13) and (3.14): only $J(\omega) \sim \omega^\alpha$ with $\alpha < 2$ provides a time convergence of the integral for $\tilde{\gamma}(z=0)$; hence we have to take $J_0(2t_{inter}\tau)$ into account to eliminate an eventual divergency.

On the other hand, it could be shown that in the weak-coupling regime the approximation (5.3) fails, and we have to take into consideration the exact expression for the coherent generalized diffusion coefficient

$$\tilde{D}_{coh}(z) = a^2\left(\frac{t_1}{2}\right)^2 \frac{t_{inter}}{z + \frac{1}{4}\Omega^2\tilde{\gamma}_c(z)}. \quad (5.7)$$

Again, performing the Laplace transformation for the kinetic kernel $\gamma_c(t)$, we make use of expression (5.1). Thus, an exponential decay of $D_{coh}(t) \sim \exp(-t/\tau_r)$, occurring at the intermediate and strong couplings, could change to more complicated behavior such as "long tails" [power-law relaxation $D_{coh}(t) \sim \frac{D_{coh}(t_0)}{1+(t-t_0)^\alpha}$] or oscillation regime.

We performed numerically the inverse Laplace transformation to Eq. (5.7) to calculate the coherent contribution to the generalized diffusion coefficient in a time representation. For the incoherent part defined by Eq. (4.7), the expressions (5.1) and (5.2) were used, and we ensured the proper time decay of the $D_{in}(t)$ multiplying Eq. (5.2) by the factor $J_0^4(2t_{inter}\tau)$.

In Figs. 1 and 2, we present the incoherent and coherent parts of the generalized diffusion coefficient at a low value of the vibrational frequency $\Omega/\omega_{max}=0.1$. Hereafter, all generalized diffusion coefficients are expressed in the dimensionless units $(t_1/2)^2 a^2 \omega_{max}$.

It is seen from Fig. 1 that the incoherent part of the generalized diffusion coefficient decays comparatively fast at times about $3\tau_D$, where $\tau_D=2\pi/\omega_{max}$ stands for the period of the fastest lattice vibration, and there is a good reason to perform the Markovian approximation like it was done in Eq. (5.4). Moreover, both solid and dotted curves almost coincide, meaning that a nonstationarity of the site-localized states [characterized by $J_0(2t_{inter}\tau)$], which leads to the uncertainty in their energy of the order of magnitude of the renormalized bandwidth t_{inter}, are taken into account. Thus, it
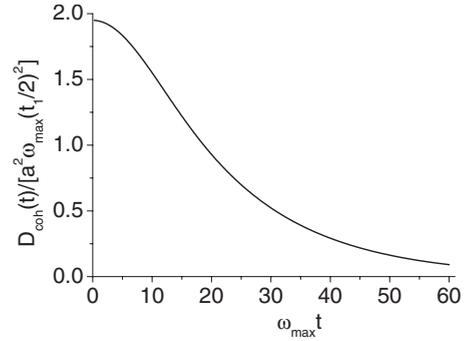

FIG. 2. The coherent part of the generalized diffusion coefficient calculated at $G=10^{-3}$, $k_BT/\hbar\omega_{max}=0.1$, and $\Omega/\omega_{max}=0.1$.

is possible to get a one-phonon contribution to the rates $\tilde{\gamma}_x(0)$, $\tilde{\gamma}_{LL}^+(0)$ without violation of the conservation law of the energy. The one-phonon contribution is known to occur mainly at low temperatures [6], while at higher temperatures many-phonon processes have to be taken into account [10]. Note that only one-phonon processes have been taken into consideration in the initial Hamiltonian (2.1), and many-phonon contributions are the results of its unitary transformation, leading to the appearance of the phonon-assisted terms (3.4)–(3.6).

The coherent contribution presented in Fig. 2 decays much slower than $D_{in}(t)$, and there is no reason to perform the Markovian limit in the diffusion equation: the time of decay of $D_{coh}(t)$ could be comparable with the relaxation time of the one-particle nonequilibrium distribution function $n(r,t)$. The lattice has no time to relax after the adsorbate motion, and the memory effects become of high importance. On the other hand, little could be concluded from Fig. 2 about the law of time relaxation of the generalized diffusion coefficient $D_{coh}(t)$, and additional studies are to the point.

At higher temperature but still at low vibrational frequency, the time evolution of the incoherent term (Fig. 3) is similar to the case $k_BT/\hbar\omega_{max}=0.1$, but the problem of a slow decay appears when one neglects the factor $J_0^4(2t_{inter}\tau)$. As for the coherent contribution to the generalized diffusion coefficient (Fig. 4), one can observe much slower relaxation as compared to the low-temperature case. When temperature rises, the phonon bath delivers more energy to the adparticle, and the generalized diffusion coefficient, which can be re-
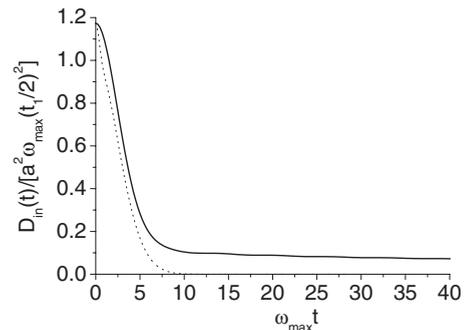

FIG. 3. The incoherent part of the generalized diffusion coefficient calculated at $G=10^{-3}$ and $k_BT/\hbar\omega_{max}=1$. A solid curve is obtained when omitting Bessel function in the kinetic kernel.
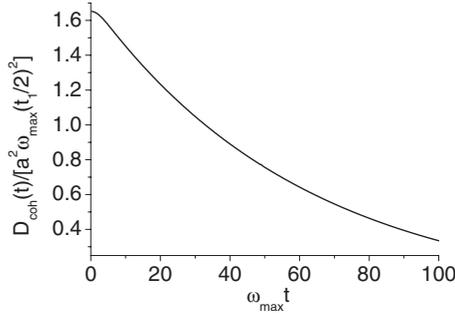
FIG. 4. The coherent part of the generalized diffusion coefficient calculated at $G=10^{-3}$, $k_B T/\hbar\omega_{max}=1$, and $\Omega/\omega_{max}=0.1$.

FIG. 6. Generalized diffusion coefficients calculated at $G = 10^{-3}$, $\Omega/\omega_{max}=1$, and different temperatures: $k_B T/\hbar\omega_{max}=0.5$ (triangles), 0.75 (circles), and 1 (squares).

lated to the flux-flux time correlation function [9,10], decays much slower.

The behavior of $D_{coh}(t)$ changes drastically when the vibrational frequency increases. In Fig. 5, we present the time evolution of the coherent part of the generalized diffusion coefficient at Ω, comparable with the Debye frequency. There are profound long-live oscillations with a period of about $2\pi/\Omega$.

These oscillations become even more pronounced when the system temperature decreases. In Fig. 6, we present the generalized diffusion coefficients $D(t)=D_{in}(t)+D_{coh}(t)$ calculated at different temperatures. At low temperatures, thermal fluctuations of the lattice are very small. Therefore, a lattice distortion caused by the interaction of the adsorbate with the phonon subsystem, when the adparticle initially resides at the top of the barrier, has no time to relax, and the initial (unperturbed) profile of the static lattice potential has no time to be restored after the particle passage. As a result, the effective barrier has a higher value than its adiabatic one, and the particle starts to oscillate being caged in the deformed potential well. This leads to the pronounced damped oscillations regime. Such a behavior of $D(t)$ is observed even at the temperatures comparable with $\hbar\omega_{max}/k_B$. At lower temperatures about $k_B T/\hbar\omega_{max}=0.1$ (which are not presented in Fig. 6), these oscillations persist on the time scales, which are by two orders of magnitude higher than the inverse Debye frequency.

It would be interesting to relate this nonmonotonic behavior of $D(t)$ to the possible recrossing phenomenon [13,14,16,17]. It is seen from the last figure that the time evolution of the generalized diffusion coefficient cannot be
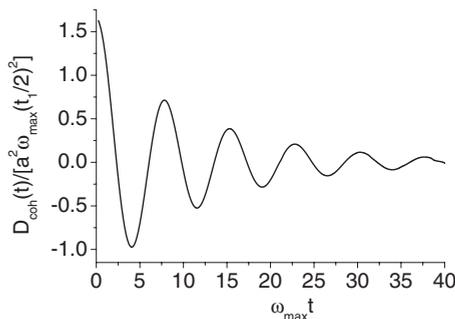
approximated by a damped cosine function. On the contrary, from Fig. 6 one can conclude that such a behavior is inherent to the damped inharmonic oscillator: the period of oscillations rises with a decrease in the decrement; while for the damped harmonic oscillator, the situation is quite opposite. It is not strange because the large value of Ω could be associated with the motion of the adsorbate far from the bottom of the quantum well. But how "far" is that far: is the energy large enough so that adparticle, which is weakly coupled with a substrate and dissipates its energy very slowly, can traverse several potential barriers and perform multiple (or long) hopping?

This question can be partially answered when one calculates a mean-square displacement of the particle. In Fig. 7, we plot the time evolution of $\langle\Delta r(t)^2\rangle$. It is seen that even in the high-temperature regime the mean-square displacement at short times exceeds a^2. Nevertheless, we cannot with certainty attribute this result to eventual multiple hopping (or long jumps) without an additional study. One of the possible ways consists in calculation of the flux-flux time correlation function $C_{s,s+n}^{jj}(t)$ determined on the neighboring sites [13,17]. An attempt to estimate it without a direct calculation of the quantum correlation functions could be performed in the framework of our approach: one has to solve Eq. (4.4) with respect to the distribution functions $\tilde{f}_{ss}(z)$ and to insert the obtained result in Eq. (4.5) for nonequilibrium jump probabilities. After regrouping of the corresponding terms, it is possible to obtain the kinetic kernel related to $C_{s,s+n}(t)$ similarly, as it was done when obtaining Eq. (4.11). As for

FIG. 5. The coherent part of the generalized diffusion coefficient calculated at $G=10^{-3}$, $k_B T/\hbar\omega_{max}=1$, and $\Omega/\omega_{max}=1$.
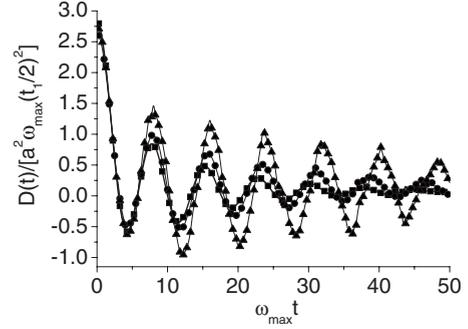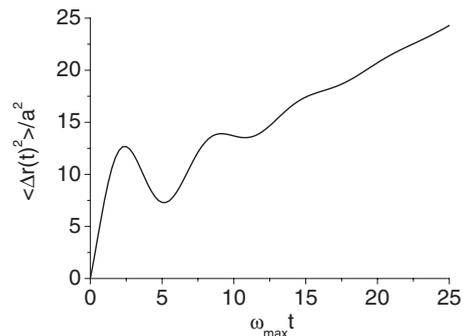

FIG. 7. A mean-square displacement $\langle\Delta r(t)^2\rangle$ of the adparticle calculated at $G=10^{-3}$, $k_B T/\hbar\omega_{max}=1$, and $\Omega/\omega_{max}=1$.

the investigation of the recrossing problem dealt with the study of the $C_{s,s}^{JJ}(t)$, our approach allows to obtain reliable estimations.

Finally, let us consider the crossover from purely monotonic relaxation of the generalized diffusion coefficients to the damped oscillations regime. If one lowers the coupling constant G until the oscillations in $D(t)$ appear, one can obtain a critical value $G_{cr}(T,\Omega)$ as a function of temperature and vibrational frequency, which separates these two regimes of time evolution: there is a plain relaxation of the $D(t)$ at $G > G_{cr}(T,\Omega)$ and a nonmonotonic behavior at $G < G_{cr}(T,\Omega)$. It can be shown that at the fixed temperature T^*, a critical value of the coupling constant is scaled as $G_{cr}(T^*,\Omega) \sim \Omega^2$. If one fixes a vibrational frequency Ω^*, a critical value of the coupling constant $G_{cr}(T,\Omega^*)$ becomes a nonmonotonic slightly varying function of the temperature. Undoubtedly, a detailed study of the behavior of $G_{cr}(T,\Omega)$ can shed more light on the nature of adparticle dynamics.

VI. DISCUSSION

First, we would like to discuss the relation of the used model to the commonly accepted scenarios of the quantum tunneling mechanism. Usually, it is believed that coupling to phonons could lead to an activated behavior even in the tunneling regime, with an activation energy E_A obtained in the Markovian limit from the so-called small polaron model, when the local lattice distortion is carried from site to site by the tunneling particle [22,33–35]. However, the small polaron energy was found to be only a fraction of the relaxation energy of the lattice and has the order of a few meV. This is in contradiction with recent experimental data [36], showing a much higher value of E_A and possibly pointing to a different mechanism of the underbarrier hopping, which occurs through thermal excitation to the first vibrational excited state and then tunneling to the neighboring sites.

When the memory effects are taken into consideration, the lack of relaxation of the substrate during the adparticle motion increases the effective barrier, so it is higher than the adiabatic one. The increase in the barrier is proportional to the relaxation energy of the substrate atoms and can be a significant fraction of the barrier height. The particle is caged in the deformed potential well, and the long-live oscillations of the generalized diffusion coefficient appear.

To pursue further discussion and to relate the generalized diffusion coefficients with quantities directly measurable in the experiments, we would like to underline some important points. As have been already said, in the Markovian limit, the zeroth moment $D_0 = \int_0^\infty D(t)dt$ of the generalized diffusion coefficient is usually associated with the experimentally observed diffusion coefficient D_{exp}. However, it is no longer true if the memory effects are taken into account. A mathematical manifestation of the Markovian approximation failure consists in the fact that D_0 becomes larger than D_{exp} [3].

In the considered case, when the memory effects are taken into account, the temperature behavior of the experimental diffusion coefficient D_{exp} should be compared with that of the quantity $D = \frac{1}{4}\lim_{t\to\infty}\langle\Delta r(t)^2\rangle/t$, which is the long-time limit of the mean-square displacement (5.6). To find it, one has, in

particular, to solve the non-Markovian equation for the intermediate distribution function $n(k,t)$. The obtained result will strongly depend on the time behavior of the generalized diffusion coefficients, which play the role of the kinetic kernels in the corresponding nonlocal diffusion equations: the eventual oscillations of $D(t)$ reduce the mean-square displacement, while possible long tails increase this value.

The obtained results can differ from (i) those of the Markovian approximation for the small polaron model and from (ii) those of the model of activated diffusion through the higher vibrational states [3,36]. The case (i) has been already analyzed: the weaker the substrate-adsorbate coupling in the system is, the more the relaxation energy of the substrate increases the effective barrier. As for the case (ii), it should be noted that the term "activation energy" loses its sense if one cannot obtain an explicit Arrhenius-like form for the temperature behavior of the diffusion coefficients. For the model similar to ours, it has been shown [30] that no activated regime is possible for the coherent diffusion coefficient at low temperatures, and the temperature dependence of the coefficient is then governed by that of the dephasing constant and given by the power law in T. The common feature of our results and those obtained in Ref. [30] is a scaling of the generalized coherent diffusion coefficient as Ω^{-2} and inverse dependence of $\widetilde{D}_{coh}(z)$ on the kinetic kernel related to the dephasing constant. However, little can be said about a temperature dependence of the diffusion coefficient D, which can be calculated as described above, without an additional study. Thus, the question of the temperature behavior of the diffusion coefficients in the problems of quantum non-Markovian diffusion is in no way a trivial one.

Our model yields the correct results in the limiting cases, and this serves as an additional criterion of its consistency. Thus, in the limit of vanishing coupling constant, the calculated mean-square displacement oscillates with the frequency Ω (if the relation $\hbar\Omega \gg t_0, t_1$ is valid) or steadily arrives at the asymptotics given by the Einstein's law at long times (in the opposite case of a single-band model).

However, the adparticle located in the quantum well usually has several vibrational states [30], and the coupling of the adsorbate with the substrate is different in different eigenstates [21]. Therefore, the two-level model can be improved by taking into account not only the first-excited level but also some higher vibrational states coupled to the phonon degrees of freedom. As soon as it is done, and one deals with a set of different vibrational frequencies, a more accurate interpretation of the obtained results can be given in the context of the recrossing problem. In particular, a controversial result (see Fig. 7) of large oscillations of the mean-square displacement at short times could be eliminated, and the amplitude of $\langle\Delta r(t)^2\rangle$ should be reduced. It is also reasonable to introduce different coupling constants for different states, though it can complicate a derivation of the kinetic equations to a great extent.

The obtained results look quite interesting in the context of comparison with a multiple hopping during thermally activated surface diffusion [11,12]. At weak coupling and high enough barriers, the adparticle performs a good portion of the oscillations inside the potential well and, having been not

thermalized and trapped at the adsorption site, can carry out a series of multiple hoppings. A nonmonotonic behavior of the mean-square displacement is a manifestation of such a hopping regime. It should be noted that, according to designations of Ref. [12], the regime of the adparticle motion, being studied in our paper (small G, large Ω), is close to the zone 2: low friction, considerable probability of the multiple jumps. A natural question appears: what happens if one lowers the barrier height (that corresponds to the decrease of Ω)? Will the regime of the quasicontinuous diffusion be reached? Our quantum lattice model allows to take into consideration the next- to the nearest-neighbor tunneling in the initial Hamiltonian (2.1). Very preliminary studies dealt with the "multiple jumps or long jumps" dilemma showed that the onset of the oscillation regime in presence of tunneling on large distances is observed in the limit $\Omega \rightarrow 0$ and at large G, i.e., close to the domain of high friction, low barriers, and quasicontinuous diffusion (domain 5 reported in Ref. [12]). It would be also interesting to investigate which contribution to the diffusion coefficient (coherent or incoherent one) dominates during multiple or long hopping. The study of quantum diffusion for the H/Ni(111) system by the Monte Carlo wavefunction method (which enables visualization of the trajectories in a real space) has been carried out in Ref. [37], showing a good fraction of long coherent tunneling processes; hence the investigation of the long underbarrier hoppings is a worthwhile problem.

We would like also to touch upon the consideration of anharmonicities in the adsorbate-substrate interaction. It was shown in the previous section that there are some problems with ensuring of the proper time decay of the kernels dealt with the end-preserving processes. In our point of view, taking into consideration the multiphonon processes (exceeding the limits of small lattice displacements) in the initial Hamiltonian is more promising (though more complicated from the computational point of view) than the way followed in Refs. [6,21], when the multiphonon contributions are evaluated by expanding the kinetic kernels (4.8) and (4.9) in the series in $\varphi(\tau)$. Taking into account the anharmonic terms provides an additional channel of the energy dissipation in the adsorbate-substrate system, though the intensity of such kind of interaction itself could be relatively small [10]. Nevertheless, in the case of dielectric solids, when there is no electronic friction in the system, consideration of multiphonon processes is indispensable to obtain convergent values of the diffusion coefficients [38,39].

VII. CONCLUSIONS

In this paper, we use the quantum-kinetic approach for the description of surface diffusion of a light particle adsorbed on a metallic surface and interacting with substrate vibrations. In a single adsorbate limit, we obtained the system of coupled equations for the one-particle nonequilibrium distribution functions and nonequilibrium tunneling probabilities. These equations have phonon-modified kernels, which depend on the lattice parameters, and are nonlocal in time. The Laplace transformation allows to pass from the initial integro-differential equations to the chain of linear algebraic

equations with frequency-dependent coefficients.

The generalized diffusion coefficient was calculated by the standard rolling-up procedure (by elimination of hopping probabilities from the set of equation) with subsequent inverse Laplace transformation and turned out to consist of two terms: a coherent contribution, which can be interpreted in terms of a simple model of band-type motion limited by scattering from the lattice, and incoherent one, following from the random-walk model for diffusion with site-to-site hopping. These two terms have been found to decay on different time scales; in the intermediate to strong-coupling limit, this allows us to obtain the telegrapher's equation governing the dynamics of the adsorbed particle, which has either diffusionlike or wavelike solutions. If the substrate-adsorbate interaction is weak enough and the energy of the level splitting is comparable with temperature of the lattice, the generalized diffusion coefficient itself has pronounced long-live oscillations that lead to the nonmonotonic behavior of the mean-square displacement of the adparticle at short times. If the vibrational energy is not too large, the time decay of the generalized diffusion coefficients is also very slow, though there is no oscillation of $D(t)$. Thus, in the weak-coupling limit when the energy exchange between the adsorbate and the substrate is slowed down, the memory effects start to play an essential role and change the jump dynamics of the adparticle considerably.

APPENDIX

To obtain the system of quantum-kinetic equations for the one-particle nonequilibrium distribution functions $f_{c\varkappa,c\varkappa}(t)$ and hopping probabilities $f_{c\varkappa,c'\varkappa'}(t)$, let us multiply Eq. (4.1) by $a^{\dagger}_{c'\varkappa'}a_{c\varkappa}$ and average this product over $\rho_S(t)$. The second term in the left-hand side yields the coherent (nondissipative) contributions to the kinetic equations (4.4) and (4.5). To obtain the incoherent contributions, which is formed by the integral term in Eq. (4.1), one has to find, at first, the Heisenberg representation for the operators $a^{\dagger}_{k\mu}(a_{k\mu})$ and $b^{\dagger}_q(b_q)$. Calculation of the latter is quite simple,

$$b^{\dagger}_q(t) = \exp[i\omega_q t]b^{\dagger}_q, \quad b_q(t) = \exp[-i\omega_q t]b_q. \quad (A1)$$

To calculate the operators $a^{\dagger}_{c\varkappa}(t)$, $a_{c\varkappa}(t)$, one has to note that because of the different behavior of the corresponding spectral weight functions in the low-frequency limit the term $\langle H_{\text{intra}} \rangle_B$ vanishes, while $\langle H_{\text{inter}} \rangle_B$ equals to Eq. (4.6). This term forms the off-diagonal elements of the dynamic matrix, while the diagonal ones in the low coverage limit are formed via the mean-field energy E^{mf}_{pp} [see Eq. (3.8)] (in the one-particle limit, it transforms to the stabilization energy $E_{stab} = C^{DD}_0 + C^{OO}_0$). It can be shown that the three-diagonal dynamic matrix of $\exp(\frac{i}{\hbar}H_S t)$ yields

$$a_{k\mu}^{\dagger}(t) \equiv (e^{(i/\hbar)H_S t})_{k\mu,l\mu} a_{l\mu}^{\dagger} = J_{|k-l|}^D(2t_{inter}t) e^{(i/\hbar)E_{pp}^{mf}t} a_{l\mu}^{\dagger},$$

$$a_{k\mu}(t) \equiv (e^{-(i/\hbar)H_S t})_{k\mu,l\mu} a_{l\mu} = J_{|k-l|}^D(2t_{inter}t) e^{-(i/\hbar)E_{pp}^{mf}t} a_{l\mu},$$
$$(A2)$$

where D means the dimension of the lattice, and $J_{|k-l|}(2t_{inter}t)$ are the $|k-l|$th order Bessel functions. Having calculated the time evolution of all quantum-mechanical operators, after some straightforward algebra we can express the integrand which forms the incoherent terms of the kinetic equations as

$$
\begin{aligned}
J_{|k-l|}^D & (2t_{inter}\tau) J_{|k'-l'|}^D(2t_{inter}\tau) \{ [\langle \Delta \bar{B}_{cs}^{\varkappa\nu} \Delta \bar{B}_{kk'}^{\mu\mu'}(\tau) \rangle_B \\
& - \langle \Delta \bar{B}_{kk'}^{\mu\mu'}(\tau) \Delta \bar{B}_{cs}^{\varkappa\nu} \rangle_B] \\
& \times [f_{s\nu,c'\varkappa'}(t') f_{l'\mu',l\mu}(t') \pm f_{s\nu,l\mu}(t') f_{l'\mu',c'\varkappa'}(t')] \\
& + \langle \Delta \bar{B}_{cl}^{\varkappa\mu} \Delta \bar{B}_{kk'}^{\mu\mu'}(\tau) \rangle_B f_{l'\mu',c'\varkappa'}(t') \\
& - \langle \Delta \bar{B}_{sc}^{\nu\varkappa'} \Delta \bar{B}_{kk'}^{\mu\mu'}(\tau) \rangle_B f_{l'\mu',s\nu}(t') \delta_{cl} - \{ \dots \}_{c\varkappa\leftrightarrow c'\varkappa'}^* \}.
\end{aligned}
$$
$$(A3)$$

In Eq. (A3), a summation over repeated indexes is assumed; the upper (lower) sign corresponds to the case of Bose (Fermi) statistics, and $\{\dots\}_{c\varkappa\leftrightarrow c'\varkappa'}^*$ stands for the complex conjugate of all preceding it terms in the parentheses with the replaced indexes $c\varkappa \to c'\varkappa'$, $c'\varkappa' \to c\varkappa$. The other notations in Eq. (A3) are the following: $\tau = t - t'$, $\bar{B}_{ss'}^{\varkappa\nu} = \{\frac{1}{2}\Omega B_s, t_{ch}B_{ss'}^{LR,RL}, t_{pr}B_{ss'}^{LL,RR}\}$, where $B_{ss'}^{\varkappa\nu}$ are defined in Eqs. (3.5) and (3.7).

When obtaining Eq. (A3), we took into account the fact that the system Hamiltonian in the mean-field approximation is a bilinear form of the operators $a^\dagger$, a. This allowed us to perform the Wick's decomposition of the higher operator products and to express the kinetic equations in the closed form via the nonequilibrium distribution functions and hopping probabilities.

In the one-particle limit, Eq. (A3) becomes linear in $f(t')$, and the adparticle statistics is no longer relevant. To simplify Eq. (A3) further, one has to note that it contains kinetic ker-

nels of two types: (i) those which are finite at $\tau = 0$ and (ii) those which are zero at $\tau = 0$. It can be shown that the most important contributions to the kernels are those with nonzero values at $\tau = 0$. They are proportional to the zeroth-order Bessel functions $J_0(2t_{inter}\tau)$ and to one of the following correlation functions: $\langle \Delta B_{ss}^{\varkappa\varkappa'} \Delta B_{ss}^{\varkappa'\varkappa}(\tau) \rangle_B$, $\langle \Delta B_{ss'}^{\varkappa\varkappa'} \Delta B_{s's}^{\varkappa'\varkappa}(\tau) \rangle_B$, $\langle \Delta B_{ss'}^{\varkappa\varkappa} \Delta B_{s's}^{\varkappa'\varkappa'}(\tau) \rangle_B$, and $\langle \Delta B_{ss'}^{\varkappa\varkappa} \Delta B_{ss'}^{\varkappa\varkappa}(\tau) \rangle_B$, corresponding to the cases with the same lattice displacements and without a cross correlation between the different types of processes. In other words, the intrasite and intersite processes are separated, whereas the intersite end-changing processes do not correlate with the intersite end-preserving ones.

Then we calculate the lattice time correlation functions by using the Baker-Campbell-Hausdorff formula

$$e^A e^{A(\tau)} = e^{A + A(\tau) + [A, A(\tau)]/2 + [A, [A, A(\tau)]]/12 + \dots} \quad (A4)$$

for the operators $A_{cc'}^{\varkappa\varkappa'} = -\Sigma_q \alpha_{cc'}^{\varkappa\varkappa'}(q)(b_q - b_q^\dagger)$ and $A_{cc'}^{\varkappa\varkappa'}(\tau) = -\Sigma_q \alpha_{cc'}^{\varkappa\varkappa'}(q)(b_q e^{-i\omega_q \tau} - b_q^\dagger e^{i\omega_q \tau})$. Here $\alpha_{cc'}^{\varkappa\varkappa'}(q) = \{2\frac{\chi_{cq}}{\hbar\omega_q}, \Delta_q^{cc'} \pm^{(+)} \delta_q^{cc'}, \Delta_q^{cc'} \pm^{(-)} \delta_q^{cc'}\}$ [see Eqs. (3.5) and (3.7)]. Using the cumulant expansion

$$\langle \exp[A + A(\tau)] \rangle_B = \exp\left[\sum_{n=1}^{\infty} \frac{1}{n!} \mathcal{K}_n(\tau) \right], \quad (A5)$$

taking into account the symmetry properties of $\alpha_{cc'}^{\varkappa\varkappa'}$ with respect to the site permutation along with the definitions (3.10)–(3.12) of the spectral weight functions, and noting that only the cumulants $K_n(\tau)$ with $n \le 2$ contribute to the lattice correlation functions, one obtains the expressions (4.8) and (4.9) for the kinetic kernels with the function $\varphi(\tau)$ in the form (4.10). Note that the kernel (4.9), in contrast to the kernels (4.8), is not a "golden-rule" rate and can be negative [21].

The basic expressions (4.4) and (4.5) appear after the Laplace transformation of the obtained kinetic equations for the one-particle nonequilibrium distribution functions $f_{s,s}(t) = \Sigma_{i=L,R} \langle a_{si}^\dagger a_{si} \rangle_S^t$ and hopping probabilities $f_{s,s+n}(t) = \Sigma_{i=L,R} \langle a_{s+ni}^\dagger a_{si} \rangle_S^t$.

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