Coherence, decoherence, and memory effects in the problems of quantum surface diffusion

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We consider surface diffusion of a single particle, which performs site-to-site under-barrier hopping, fulfils intrasite motion between the ground and the first excited states within a quantum well, and interacts with surface phonons. On the basis of quantum kinetic equations for one-particle distribution functions, we study the coherent and incoherent motion of the adparticle. In the latter case, we derive the generalized diffusion coefficients and study various dynamic regimes of the adparticle. The critical values of the coupling constant $G_{\rm cr}(T,\Omega)$, which separate domains with possible recrossing from those with the monotonic motion of the adparticle, are calculated as functions of temperature T and vibrational frequency Ω. These domains are found to coincide with the regions where the experimentally observed diffusion coefficients change their behavior from weakly dependent on T to quite a sensitive function of the temperature. We also evaluate the off-diagonal distribution functions both in the Markovian limit and when the memory effects become important. The obtained results are discussed in the context of the "long tails" problem of the generalized diffusion coefficients, the recrossing/multiple crossing phenomena, and an eventual interrelation between the adparticle dynamics at short times and the temperature dependence of the diffusion coefficients measured experimentally.

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I. INTRODUCTION

Quantum diffusion of light particles (mostly, hydrogen and its isotopes), adsorbed at solid surfaces, in the last decades has been a subject of joint efforts of investigators in various fields of science. The attention is dictated by its relevance in the technological processes like heterogeneous catalysis [1], fuel cell production [2], chemical reactions of hydrogen transfer [3], and series of physical phenomena occurring at the fluid-gas interfaces. On the other hand, the diffusion of hydrogen is of a fundamental interest, being a favorite system for theoretical analysis [4–6] and computer simulations [7,8]. Wide perspectives have been opened after creation of the scanning tunneling microscope (STM) [9]. At the same time, rapid development of powerful methods of computer experiments such as quantum molecular dynamics [10] or Monte Carlo Wave Function formalism [11] allows a direct analysis of the particle trajectories in real space and time. Recent results [12] showing that even such "heavy" atoms like Cr on the Au(111) surface manifest a great deal of the underbarrier tunneling bring us to a conclusion that the traditional viewpoint on the quantum diffusion as an inherent feature of light particles only is far from reality, and a fresh look at such processes is quite topical.

Theorists have put much effort into creation of reliable models of quantum diffusion and development of effective methods for calculation of the diffusion coefficients, taking into account all the interactions. In particular, a bulk quantum diffusion of light particles has been studied in [13–15]. Its description requires similar theoretical methods, and elaborated schemes can be considered as starting points for investigation of the surface quantum diffusion. Later, in Refs. [4–6,16–18], the quantum hopping was moved from the bulk to the surface. Generally, the concept of a small polaron [4,16,17] or its modification [6] has been applied with going beyond the linear "adatom-phonon" coupling to consider the anharmonic terms in "adsorbate-substrate" interaction [18]. The latter case together with consideration of electronic friction in the system [13,19] and direct "adsorbate-adsorbate" interactions [20] are very important because they provide additional channels of particle scattering and ensure finite values of the diffusion coefficients [21].

Diffusion coefficients are usually determined via the Green-Kubo relations [21], the low-frequency and small wave-vector limit of the dynamic structure factor [6,22], or zeroth moments of the "flux-flux" time correlation functions for classical [22,23] or quantum systems [7,8]. The latter approach is of particular interest because it allows one not only to study in detail the well-known "recrossing/multiple crossing" problem [7,8] but also to revise a quantum transition state theory (TST) [24,25].

The quantum diffusion coefficient is known to consist of two terms of a different physical origin. A coherent term [5,17] characterizes the way in which the dephasing limits the band motion of the adatom by destruction of the coherence of hopping probabilities, when the adatom-thermal bath coupling induces random fluctuations of each phase. This term is of a pure quantum origin and related to the competition between the tunneling mechanism, which tends to preserve the coherence, and the dephasing, which characterizes damping due to the scattering processes. The coherent part $D_{\rm coh}(T)$ of the diffusion coefficient weakly depends on temperature at low T in contrast to the incoherent one $D_{\rm in}(T)$, which tends to zero when $T \to 0$. The incoherent contribution describes processes in which the surface dynamics induces fluctuations of the tunneling matrix elements between two Wannier states, allowing the adparticle to perform a transition from one state to another by creating or annihilating surface phonons. Though the temperature dependence of the diffusion coefficients was studied profoundly for the small polaron model and its modification [6], some questions remain unclarified (especially, in the weak-coupling limit, where the contributions of $D_{\rm coh}(T)$ and $D_{\rm in}(T)$ are of the same order). The most challenging ones are dealt with: (i) justification of the multiphonon expansion; (ii) correct definition of the activation energies;

(iii) introduction of the additional channels of particles scattering; (iv) investigation of the memory effects influence on the temperature dependence of the diffusion coefficients and on the short-time dynamics of the adsorbate.

The last problem should be considered from several standpoints. First, a study of the short-time dynamics of the adparticle allows one to distinguish between various scenarios of the adsorbate motion (loss of coherence, presence of multiple or long hopping, etc.) that provides a deeper insight into the microscopic picture of the process [26]. Second, we can answer the question: What can enhance or suppress the particle motion? For instance, an eventual recrossing reduces the values of the diffusion coefficients, whereas a multiple crossing increases them. At last, such a theoretical analysis can give some recommendations for experimentalists as to how to evaluate the diffusion coefficients more efficiently. It is known [9] that at temperatures above 80 K, the diffusion rate of hydrogen is too fast to be followed by the standard atom-tracking technique, while below 50 K the opposite problem occurs, and it is necessary to minimize the influence of the STM tip on the adsorbate due to a prolonged interaction. Thus, it would be tempting to relate changes in the character of the short-time dynamics of the adsorbate to possible crossover from one typical temperature behavior of the diffusion coefficients to another. It could give us a possibility to prognose the temperature dependence of the diffusion coefficient, having only an information about the adatom dynamics at the initial stage of its motion.

In the present paper, which is a logical continuation of Ref. [26], we try to give an answer to the question about the interrelation between the process of the decoherence in the "adsorbate-substrate" system (leading to the dissipative dynamics of the adsorbate) and the memory effects. Here, we also use the method of the quantum kinetic equations [17,21,27].

The subject of our study is a single adsorbate that performs an underbarrier hopping to the nearest adsorption sites, moves between two different quantum states within a quantum well, and interacts with acoustic phonons. We define the conditions of memory damping, derive expressions for the generalized (time-dependent) diffusion coefficients, and study the influence of their long-time asymptotics on the temperature behavior of the transport coefficients measured experimentally. A particular emphasis is put on the critical regimes separating dynamics with either coherent or incoherent prevailing contribution to the diffusion coefficient. We show that the transition between oscillating and monotonic dynamics of the adparticle takes place at the same values of the critical coupling constant $G_{\rm cr}(T,\Omega)$, as those at which the temperature behavior of the diffusion coefficients changes from weakly dependent to quite a sensitive function of temperature.

A special attention is paid to evaluation of the off-diagonal (relative to the site labels) distribution functions, which describe the rate of the loss of coherence. While the study of the generalized diffusion coefficients allows one to make a conclusion about the recrossing phenomenon, behavior of the off-diagonal distribution functions shows us how a multiple crossing of the dividing surfaces (placed at the neighboring adsorption sites) by the moving adparticle can proceed. We discuss the obtained results in the context of some exisisting theoretical approaches: TST [24,25], description based on Fokker-Planck equation [22,23], and study of the frustrated longitudinal mode (T-mode) of the adsorbate [28,29].

The paper is organized in the following way. In Sec. II we define a basic Hamiltonian for a dissipative two-level system. In Sec. III using the obtained earlier [26] non-Markovian equations for nonequilibrium distribution functions, we investigate a long-time asymptotic of the kinetic kernels, determining a dissipative motion of the adsorbate. A particular case of a completely coherent dynamics is considered, which corresponds to zero coupling. The expressions for the generalized diffusion coefficients are obtained in the next section. In Sec. V, the Markovian approximation for these functions is considered, a temperature behavior of the diffusion coefficient is studied in a weak-coupling limit and compared with the experimentally observed surface diffusion in H/W(110) system [30]. In Sec. VI, a thorough analysis of the critical diagrams separating different kinds of the adparticle motion is performed, and the interconnection of the obtained results with those of the previous section is established. In Sec. VII, the off-diagonal nonequilibrium distribution functions are evaluated at different values of the tunneling amplitude under an assumption of continuous media; the obtained results are considered in the context of the multiple crossing, and a conclusion about validity of the Markovian approximation is made. In the last section we discuss briefly the obtained results and draw final conclusions.

II. SYSTEM HAMILTONIAN

To specify all interactions in the system, we choose the Hamiltonian, considered in Refs. [16,17],

$$H = H_A + H_{\rm int} + H_B, \tag{2.1}$$

where the adsorbate is described by the two-band constituent

$$H_A = \sum_{\langle ss'\rangle}(-t_0 a^\dagger_{s0}a_{s'0} + t_1 a^\dagger_{s1}a_{s'1}) + \sum_s \frac{\hbar\Omega}{2}(n_{s1} - n_{s0}). \tag{2.2}$$

Here, s denotes the site of the lattice; 0 and 1 are the ground and excited states within a given well, and $\langle ss'\rangle$ denotes a sum over the nearest-neighbor sites. The quantum states within a well are referred to as "vibrational" states with the vibrational frequency Ω, and we have taken zero of energy to lie midway between the two levels. $a^\dagger_{si}$ (a_{si}) creates (destroys) a particle on the site s in the vibrational state i; $n_{si} = a^\dagger_{si}a_{si}$ is the number operator for this state, and $n_s = n_{s0} + n_{s1}$. Hereafter, we will deal with a single adparticle only, hence the adparticle statistics becomes irrelevant. t_0 and t_1 are the nearest-neighbor tunneling amplitudes in the ground and the first excited states, respectively, and we expect that $t_1 \gg t_0$.

The coupling to phonons is considered to be local within each well. Phonons may couple both to the adsorbate density operators and to the vibrations within a quantum well. The interaction Hamiltonian is [16]

$$H_{\rm int} = \sum_s \Bigg\{ n_s \sum_q \gamma_{sq}(b_q + b^\dagger_q) + (a^\dagger_{s0}a_{s1} + a^\dagger_{s1}a_{s0}) \times \sum_q \chi_{sq}(b_q + b^\dagger_q) \Bigg\}, \tag{2.3}$$

where $b_q^\dagger$ (b_q) creates (destroys) a phonon with a normal mode frequency ω_q. The strengths γ_{sq} (χ_{sq}) describe coupling of phonons to the density (oscillation) modes of the adsorbate. The bandwidths t_0, t_1, and vibrational frequency Ω are evaluated in the framework of the eigenvector-eigenvalue problem for a periodic potential, felt by an adsorbate due to the static lattice. The coupling strengths are expressed via the mean values $\Gamma = \langle s,i|V_{\text{int}}^s|s,j\rangle$ of the lattice distortion potential V_{int}^s over the localized Wannier states $|s,j\rangle$ times the phase factor depending on site s and wave-vector q [16]. As in the cited paper, we suppose Γ to be the same for different quantum states $\{i,j\} = \{0,1\}$.

The last term in Eq. (2.1),

$$H_B = \sum_q \hbar\omega_q b_q^\dagger b_q, \tag{2.4}$$

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

It is convenient to use the hybrid set of states for each site:

$$a_{s\,{\scriptscriptstyle L \atop \scriptscriptstyle R}} \equiv \frac{1}{\sqrt{2}}(a_{s0} \pm a_{s1}), \tag{2.5}$$

and similarly for the creation operators. The designation L or R means that a single adparticle is now localized on the left or right side of the given well. We will refer to the transitions with $i \neq j, \{i,j\} = \{L,R\}$, as the end-changing processes, and transitions with $i = j$ will be termed as the end-preserving ones. If the tunneling part of Eq. (2.2) equals zero, then a Hamiltonian on the hybrid set of Eq. (2.5) is a generalization of the ubiquitous "spin-boson" model, which allows us to use some of the methods applied previously to the spin-boson case.

Usually, in the quantum diffusion problems, one can consider the "substrate-adsorbate" coupling to be arbitrary (either weak or strong). On the other hand, the one-particle characteristics of the system, described by Eq. (2.2), are treated as small parameters. In such a case, the further advance lies in performing a sequence of unitary transformations [16,17] on the Hamiltonian that has the effect of changing to a representation, in which the adsorbate is localized at the certain end of the adsorption site and in which there is a correlated displacement of the lattice.

To specify the "substrate-adsorbate" interaction, it is natural to introduce spectral weight functions:

$$J(\omega) = \sum_q \chi_{sq}^2 \delta(\omega - \omega_q), \tag{2.6}$$

$$\begin{aligned} J_{LR}(\omega) &= \sum_q [(\gamma_{sq} - \gamma_{s'q}) + (\chi_{sq} + \chi_{s'q})]^2\, \delta(\omega - \omega_q), \\ J_{RL}(\omega) &= \sum_q [(\gamma_{sq} - \gamma_{s'q}) - (\chi_{sq} + \chi_{s'q})]^2\, \delta(\omega - \omega_q), \end{aligned} \tag{2.7}$$

$$\begin{aligned} J_{LL}(\omega) &= \sum_q [(\gamma_{sq} - \gamma_{s'q}) + (\chi_{sq} - \chi_{s'q})]^2\, \delta(\omega - \omega_q), \\ J_{RR}(\omega) &= \sum_q [(\gamma_{sq} - \gamma_{s'q}) - (\chi_{sq} - \chi_{s'q})]^2\, \delta(\omega - \omega_q). \end{aligned} \tag{2.8}$$

The function of Eq. (2.6) describes the intrasite dynamics; the functions of Eq. (2.7) are related to the intersite end-changing processes, while Eq. (2.8) deals with the intersite end-preserving processes. The spectral weight function of Eq. (2.6) can be considered as site-independent if the system has a translational symmetry, whereas Eqs. (2.7) and (2.8) can be presented as dependent only on $s - s'$. This approximation is quite natural in the one-dimensional case (and if the labels s and s' refer to nearest neighbors) for the single particle diffusion, when the boundary effects are not essential. In the two-dimensional case, further crystal symmetries (e.g., of a geometrically isotropic square lattice) are required, and we consider them to be present yielding site-independent kinetic kernels. The opposite situation is briefly discussed in Sec. IV.

At low frequencies, the end-changing spectral weight functions (labeled by the subscript c) and the end-preserving ones (with the subscript p) are approximately given [17] by

$$J_c(\omega) \approx \eta_c \omega^{d-2}, \quad J_p(\omega) \approx \eta_c \omega^d \tag{2.9}$$

at $\omega_0 \leqslant \omega \leqslant \omega_{\text{max}}$ with

$$\eta_c = 10G, \quad \eta_p = 12.5G, \tag{2.10}$$

given in units of the dimensionless coupling constant

$$G = \frac{\Gamma^2}{M\omega_{\text{max}}^3}. \tag{2.11}$$

Here, $d = D$, where D is the lattice dimensionality, ω_{max} stands for the Debye frequency, M denotes the mass of the substrate atom, and the coupling strength Γ has been defined earlier. It is seen from Eq. (2.9) that for a 2D lattice the end-changing spectral weight functions are sub-Ohmic, while the end-preserving ones are super-Ohmic. Such a behavior is a consequence of the equality of the coupling strengths Γ for all the quantum states. On this point, it differs from the results of Refs. [14,21], where $d = D + 2$.

The lattice is assumed to possess a nonzero lowest frequency ω_0, which is introduced to take into account the finite size of the system. It not only removes the divergencies [31], when the sub-Ohmic spectral functions have the power index $n = 0$, but also allows one to describe the adsorbate-induced surface reconstruction [16], when the particles become self-trapped due to the overlap of lattice distortions.

It has been shown in Ref. [14] that for a 2D crystal there is a loss of the coherence even in absence of electronic friction and/or nonlinear phonon coupling. If both linear and nonlinear couplings are taken into account, the dynamical destruction of the band is enhanced due to the one-phonon interaction, but the decisive role in this destruction is still played by two-phonon processes. It is possible to show that the results, obtained within the framework of our model at the assumption of the gap $\omega_0 \neq 0$, reproduce those of Ref. [14], where a concept of finiteness of the particle life-time τ in a quantum well was adopted (though the underlying physics is different in the two cases). For instance, the band narrowing, to be presented in the next section, corresponds to the linear phonon contribution to the coherent transition amplitude obtained in Ref. [14]. We would like to note that the calculated surface quantum diffusion coefficients are quite insensitive to the value of ω_0, if temperature is much higher than $\hbar\omega_0/k_B$ [17,26].

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

The system of quantum kinetic equations for one-particle nonequilibrium distribution functions of the adsorbate can be obtained using the equation for the reduced density matrix $\rho_S(t)$ [21]. Considering the one-particle Hamiltonian [Eq. (2.2)] as a small perturbation, we can construct a closed system of kinetic equations up to the second order in one-particle parameters. These equations are nonlocal in time, so it is convenient to perform a Laplace transformation for the diagonal $f_{s,s}(t)=\sum_{i=L,R}\langle a^{\dagger}_{si}a_{si}\rangle^t_S$ and off-diagonal $f_{s,s'}(t)=\sum_{i=L,R}\langle a^{\dagger}_{s'i}a_{si}\rangle^t_S$ one-particle nonequilibrium distribution functions. In the single particle limit we obtain [26] the following chain of equations for the Laplace transforms $\tilde f_{s,s}(z)$, $\tilde f_{s,s+n}(z)$ (the index $s+n$ means the nearest neighboring site to s):

$$z\tilde f_{s,s}(z)-f_{s,s}(t=0)=-\frac{i}{\hbar}t_{\rm inter}\sum_n[\tilde f_{s,s+n}(z)-\tilde f_{s+n,s}(z)] -\tilde\gamma_{\rm inter}(z)\left[2\tilde f_{s,s}(z)-\sum_n\tilde f_{s+n,s+n}(z)\right], \tag{3.1}$$

$$\begin{aligned} z\tilde f_{s,s+n}(z)-f_{s,s+n}(t=0) &= -\frac{i}{\hbar}t_{\rm inter}[\tilde f_{s+n,s+n}(z)-\tilde f_{s,s}(z) \\ &\quad +\tilde f_{s-n,s+n}(z)-\tilde f_{s,s+2n}(z)] \\ &\quad -[\tilde\gamma_{\rm inter}(z)+\tilde\gamma_{\rm intra}(z)]\tilde f_{s,s+n}(z) \\ &\quad +\tilde\gamma^{+}_{LL}(z)\tilde f_{s+n,s}(z). \end{aligned} \tag{3.2}$$

The first terms of the r.h.s. of Eqs. (3.1) and (3.2) describe a coherent motion of the adsorbate with the renormalized tunneling amplitude [17,26]:

$$t_{\rm inter}=t_1\omega_0^{\eta_p k_B T}\left[2k_BT\sinh\left(\frac{1}{2k_BT}\right)\right]^{-\eta_p k_B T}. \tag{3.3}$$

In fact, $t_{\rm inter}$ corresponds to the polaron band narrowing due to the "substrate-adsorbate" interaction. Hereafter we use dimensionless frequencies in the units of $\omega_{\max}$ and temperatures in the units of $\hbar\omega_{\max}/k_B$.

The kinetic kernel

$$\tilde\gamma_{\rm inter}(z)=4\tilde\gamma_{LL}(z)+2\tilde\gamma_{LR}(z)+2\tilde\gamma_{RL}(z) \tag{3.4}$$

corresponds to the dissipative intersite motion of the adsorbate and describes processes, when the adparticle performs random site-to-site hoppings (with or without the change of its quantum state) owing to the interaction with the bath. The kinetic kernel $\tilde\gamma_{\rm intra}(z)$ in Eq. (3.2) describes a dissipative intrasite dynamic, 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 $\tilde\gamma_{\rm intra}(z)$, $\tilde\gamma_{\rm inter}(z)$ can be obtained from the Laplace transformation of the kinetic kernels

$$\gamma_x(\tau)=\omega_{\max}\lambda_x^2{\rm Re}\{\exp[-(\varphi_x(0)-\varphi_x(\tau))]-\exp[-\varphi_x(0)]\}, \tag{3.5}$$

$$\begin{aligned}\gamma^{+}_{LL}(\tau)=\omega_{\max}t_1^2{\rm Re}\{&\exp[-(\varphi_{LL}(0)+\varphi_{LL}(\tau))] \\ &-\exp[-\varphi_{LL}(0)]\},\end{aligned} \tag{3.6}$$

where

$$\varphi_x(\tau)=\int_{\omega_0}^{1}\frac{J_x(\omega)}{\omega^2}\left[\coth\left(\frac{\hbar\omega}{2k_BT}\right)\cos(\omega\tau)-i\sin(\omega\tau)\right], \tag{3.7}$$

and one-particle parameters $\lambda_x=\{t_1,\Omega\}$ are related to the corresponding end-changing/end-preserving spectral functions of Eq. (2.9) (see also table in Ref. [26]).

A study of the long-time asymptotics of the kinetic kernels allows us to establish a one-to-one correspondence between the low-frequency behavior of the spectral weight functions $J(\omega)$ and a damping of the kernels of Eqs. (3.5) and (3.6) at long times. These results are summarized in Table I, where the constants a_i, $i=\{0,\dots,3\}$, are introduced just to describe a particular time behavior of $\gamma(\tau)$ (in general case, these values are defined by the system parameters). It is seen from Table I that we pass from a fast relaxation of the kinetic kernels at $J(\omega)\sim\omega^n$, $n=\{0,1\}$, through long tails at $n=2$ to the divergent transport coefficients at $n>2$.

Note, that the system dimensionality strongly influences the long-time asymptotics of the kinetic kernels: in the bulk, the linear "substrate-adsorbate" coupling alone does not ensure finite values of the diffusion coefficients. As it has been already mentioned, this divergency can be eliminated by introduction of additional channels of the particle scattering that change the low-frequency asymptotics of the spectral functions. For instance, taking into account the electronic friction and/or anharmonic terms in "adsorbate-substrate" interaction yields damping of the kinetic kernels as $\exp(-a_1t)$ [13,14,19].

Keeping in mind the data of Table I, we find the long-time asymptotics of the end-changing and end-preserving kinetic rates $\gamma_{\substack{c\\p}}(\tau)$ at $T\gg\hbar\omega_0/k_B$. Both rates in the strong-coupling limit ($G\geqslant 0.1$) decay as Gaussian functions

$$\gamma_c(\tau)\sim\exp[-\eta_c|\ln\omega_0|(k_BT\tau^2+i\tau)], \tag{3.8}$$

$$\gamma_p(\tau)\sim\exp\left[-\frac{\eta_p}{2}(k_BT\tau^2+i\tau)\right], \tag{3.9}$$

TABLE I. Relation between low-frequency asymptotics of the spectral weight functions and long-time relaxation of the kinetic kernels.

$J(\omega)\sim$	$\gamma(\tau)\sim$
ω^0	$\exp(-a_0\tau^2)$
ω^1	$\exp(-a_1\tau)$
ω^2	$1/\tau^{a_2}$
ω^n, $n>2$	$\exp(-a_3)$

while in the weak-coupling limit ($G \leqslant 0.01$) the first of them still decays as a Gaussian function, but the second of them behaves as

$$\gamma_p(\tau) \sim 1/\tau^{2\eta_p k_B T} - \omega_0^{2\eta_p k_B T}. \tag{3.10}$$

Again, the presence of the gap allowed us to obtain a power law dependence, which extends up to the finite times $\sim \omega_0^{-1}$, whereupon the damped oscillatory dynamics of $\gamma_p(\tau)$ around zero value begins. In this aspect our result differs from the nontruncated ($\omega_0 = 0$) "long tail" behavior of the kinetic kernels, leading to the infinite values of the diffusion coefficients, which can be eliminated only due to the electronic friction or nonlinear phonons coupling.

Let us make two remarks here. First, the limiting sub-Ohmic case with $n \to 0$ allows one to express the kinetic kernels in quite a simple way as the Gaussian functions of Eq. (3.8), which is essential when obtaining analytical expressions for activation energies of the diffusion coefficients. The generalization of our theory for the sub-Ohmic case $0 < n < 1$ is straightforward and does not require the introduction of ω_0. Second, in the zero-temperature limit in Eq. (3.7), one gets "the death of linear response" [32] for the sub-Ohmic case, when the particle becomes localized and its mean-square displacement $\langle \Delta r(t)^2 \rangle$ tends to a constant value at infinite time. However, this interesting aspect of the adsorbate dynamics, related to the intrinsic width of the T-mode [29], is beyond the scope of the present paper.

Now we consider a limiting case of the vanishing coupling constant, when the adparticle motion becomes completely coherent. For simplicity, we limit ourselves to the 1D, single-band ($\Omega = 0$) approximation. In such a case, the kinetic Eqs. (3.1) and (3.2) can be rewritten as

$$\dot{f}_{s,s}(t) = -\frac{i}{\hbar} t_0 \sum_n [f_{s,s+n}(t) - f_{s+n,s}(t)], \tag{3.11}$$

$$\dot{f}_{s,s+n}(t) = -\frac{i}{\hbar} t_0 [f_{s+n,s+n}(t) - f_{s,s}(t) + f_{s-n,s+n}(t) - f_{s,s+2n}(t)]. \tag{3.12}$$

It is seen that in the site representation we have a coupled chain of equations involving all the lattice labels s. It can be solved in the wave-vector representation (the details can be found in the Appendix), giving the final result via the s-th order Bessel functions J_s as follows:

$$f_{s,s}(\tau) = J_s^2(2t_0\tau/\hbar), \tag{3.13}$$

$$f_{s,s+1}(\tau) = \mathrm{Re}[f_{s,s+1}(0)] + i J_s(2t_0\tau/\hbar) J_{s+1}(2t_0\tau/\hbar). \tag{3.14}$$

The real part of the off-diagonal distribution function can be evaluated by the methods of equilibrium statistical mechanics. It defines the transition strength and does not evolve in time. Instead, the imaginary part of the $f_{s,s+n}(\tau)$ is shifted by the quarter-period with respect to the diagonal distribution functions (see Fig. 1). A particle, initially located, say, at $s = 0$, starts its motion toward the nearest adsorption site $s = 1$. At that time, the probability to find the adparticle at the site $s = 0$ reduces, whereas the probability to find it at the site $s = 1$ increases. When the particle approaches the site $s = 1$ at $\tau^* = 2$, and the value of $f_{1,1}(\tau)$ is maximal, the inverse motion of the part of wave packet toward the site $s = 0$ begins, giving the negative branch of $\mathrm{Im}[f_{0,1}(\tau)]$ at the subsequent period of time. The other part of the wave packet keeps moving toward the site $s = 2$, yielding positive branches of $\mathrm{Im}[f_{0,2}(\tau)]$ and $\mathrm{Im}[f_{1,2}(\tau)]$ (not presented in Fig. 1).

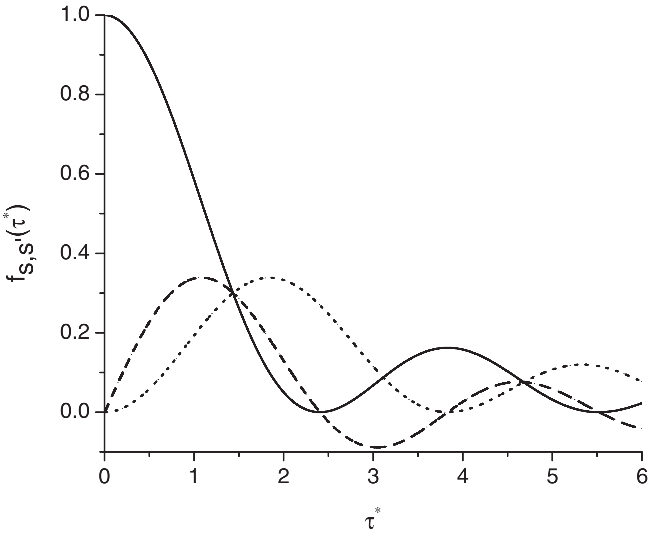

FIG. 1. Time dependence of the one-particle nonequilibrium distribution functions $f_{0,0}(\tau^*)$ (solid line), $f_{1,1}(\tau^*)$ (dotted line), and imaginary part of $f_{0,1}(\tau^*)$ (dashed line), given by Eqs. (3.13) and (3.14). The symbol τ^* denotes a time in the units $\hbar/(2t_0)$.

In contrast to the classical picture, when a free particle performs quasicontinuous motion over the barriers, the oscillations of the distribution functions are of a purely quantum mechanical origin: a superposition of the wave packets reflection from the potential barriers and tunneling through them.

IV. GENERALIZED DIFFUSION EQUATION FOR THE ADPARTICLE AT THE SURFACE

Our further advance is in the manner of the generalized collective modes approach [33,34]. To find the generalized diffusion coefficient, let us solve Eq. (3.2) with respect to the hopping probabilities $\tilde{f}_{s,s+n}(z)$ and insert the obtained result into Eq. (3.1). After grouping the terms, one obtains the following equation:

$$\begin{aligned} z\tilde{f}_{s,s}(z) - f_{s,s}(0) &= \left\{ \frac{2t_{\text{inter}}^2 \hbar^{-2}}{z + \tilde{\gamma}_{\text{inter}}(z) + \tilde{\gamma}_{\text{intra}}(z) + \tilde{\gamma}_{LL}^{+}(z)} + \tilde{\gamma}_{\text{inter}}(z) \right\} \\ &\quad \times \left[\sum_n \tilde{f}_{s+n,s+n}(z) - 2\tilde{f}_{s,s}(z) \right] \\ &\quad + \frac{t_{\text{inter}}^2 \hbar^{-2}}{z + \tilde{\gamma}_{\text{inter}}(z) + \tilde{\gamma}_{\text{intra}}(z) + \tilde{\gamma}_{LL}^{+}(z)} \\ &\quad \times \mathrm{Re}[2\tilde{f}_{s-n,s+n}(z) - \tilde{f}_{s,s+2n}(z) + \tilde{f}_{s,s-2n}(z)]. \end{aligned} \tag{4.1}$$

The ratio in the braces describes a coherent contribution,

$$\tilde{D}_{\text{coh}}(z) \sim \frac{2t_{\text{inter}}^2}{\hbar^2} \frac{1}{z + \tilde{\gamma}_{\text{total}}(z)}, \tag{4.2}$$

to the generalized diffusion coefficient. It can be interpreted [17,26] in terms of a simple model of band-type motion limited by scattering from the lattice at temperatures large relative to the bandwidth:

$$\tilde{D}_{\mathrm{coh}}(0) \sim v^2/\tilde{\gamma}_{\mathrm{total}}(0), \tag{4.3}$$

where $v = at_{\mathrm{inter}}/\hbar$ is the average velocity of the adsorbate, a stands for the substrate interatomic spacing, and

$$\tilde{\gamma}_{\mathrm{total}}(z) = \tilde{\gamma}_{\mathrm{inter}}(z) + \tilde{\gamma}_{\mathrm{intra}}(z) + \tilde{\gamma}^{+}_{LL}(z) \tag{4.4}$$

means the total rate of scattering from the lattice. The coherent contribution $\tilde{D}_{\mathrm{coh}}(z)$ characterizes the way in which the dephasing limits the band motion of the adatom by destruction of the coherence of the hopping probabilities $\tilde{f}_{s,s+n}(z)$. Whereas the eigenstate of a free particle on the surface is described by a superposition of localized Wannier states (this limiting case corresponds to the ballistic regime of motion), the coupling with the thermal bath induces random fluctuations of each phase, which destroys the coherence of the state.

The second term $\tilde{D}_{\mathrm{in}}(z) \equiv \tilde{\gamma}_{\mathrm{inter}}(z)$ in the braces in Eq. (4.1) is an incoherent contribution to the generalized diffusion coefficient. This is the result expected from the random walk model for diffusion with site-to-site hopping rate $\tilde{\gamma}_{\mathrm{inter}}(z)$, describing processes of the surface phonon creation/annihilation when the particle performs a transition from one Wannier state to another.

When the coupling between the adparticle and the surface is strong enough, the time scales for the two mechanisms of dissipation are different. Thus one can use the exponential approximation

$$\tilde{D}^{m}_{\mathrm{coh}}(z) = \frac{a^2}{4}\left(\frac{2t_{\mathrm{inter}}}{\hbar}\right)^2 \frac{1}{z + \tilde{\gamma}_{\mathrm{total}}(z=0)} \tag{4.5}$$

for $\tilde{D}_{\mathrm{coh}}(z)$ and a zero-width approximation for the Gaussian functions of Eqs. (3.8) and (3.9) to obtain the Telegrapher's equation for the nonequilibrium distribution function $n(r,t)$ in the continuous media limit [26].

The last term in the r.h.s of Eq. (4.1) involves the long hopping ($|s - s'| > a$) transition probabilities. As shown in the Appendix, it does not contribute to the total diffusion coefficient. The factor $\sum_n \tilde{f}_{s+n,s+n}(z) - 2\tilde{f}_{s,s}(z)$ at the braces in Eq. (4.1) in the continuous media limit 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 absence of the next-to-nearest-neighbor hopping) times $4a^2$.

Let us remind that in Sec. II we assumed the site-independent spectral weight functions that leads to a spatial locality of the generalized diffusion coefficients of the single adsorbate. At finite adsorbate coverage, the interparticle interaction can break the symmetry of jumps in the systems. It Ref. [35], the corrections to the tracer and chemical diffusion coefficients were reported, which are proportional to the squared gradient of the coverage. The most general case of the wave-vector-dependent diffusion coefficients also with the time nonlocality is a challenging topic of the surface diffusion theory but lies beyond the scope of the present paper.

At the end of this section, we would like to make the following remark. We call time-dependent diffusion coefficients $D(t)$ the generalized ones, even though this denotation is usually [34,36] used for the Laplace-transforms of $D(t)$. The generalized diffusion coefficient $D(t)$ is directly related to the velocity autocorrelation function, determined at the adsorption site s, and investigation of its temporal behavior can help to visualize the adparticle motion both at short and long times.

V. TEMPERATURE BEHAVIOR OF THE DIFFUSION COEFFICIENTS

Experimentally measured diffusion coefficients D_{exp} are usually associated with zeroth moments of the generalized diffusion coefficients $D_0 = \int_0^\infty D(t)dt$, which is nothing but the Markovian approximation $D_0 = \tilde{D}(z=0)$ for their Laplace transforms. In fact, in experimental conditions one deals with evaluation of the mean square displacement of the adparticle at times much larger than $1/\tilde{\gamma}_{\mathrm{total}}(0)$. Thus, measuring $D_{\mathrm{exp}} = 1/4 \lim_{t\to\infty}\langle \Delta r(t)^2\rangle/t$ one has to be sure that the influence of the transient states is excluded, and duration of the atom-tracking procedure [9] is large enough to fall into the hydrodynamic region $t \to \infty$. Otherwise, the value D_{exp} will differ from its theoretical prediction [6].

It is believed [6,26] that memory effects can be neglected if the time scales of the adsorbate motion and of the lattice dynamics are well separated, that is $\omega_{\mathrm{max}}/\Omega \gg 1$. A stronger substrate-adsorbate coupling favors the Markovian approximation, while the weak-coupling limit usually requires consideration of the memory effects at the initial stage of the adparticle motion. Using the Markovian approximation, the diffusion coefficient can be determined from Eq. (4.1) as

$$\tilde{D}(0) = \frac{a^2}{4}\left(\tilde{\gamma}_{\mathrm{inter}}(0) + \frac{8t^2_{\mathrm{inter}}\hbar^{-2}}{\tilde{\gamma}_{\mathrm{total}}(0)}\right). \tag{5.1}$$

Validity of the Markovian approximation at arbitrary values of Ω does not contradict the condition $\omega_{\mathrm{max}}/\Omega \gg 1$, as long as we are not interested in the adsorbate motion at short time scales. We will see in the next section that the situation changes if one investigates the intermediate regimes $t \sim 1/\tilde{\gamma}_{\mathrm{total}}(0)$, and it is necessary to consider a diffusion equation which is nonlocal in time.

Taking into account Eqs. (3.3) for the renormalized tunneling amplitude and Eqs. (3.5), (3.6), and (4.4) for the kinetic kernels, and noting their time dependence from Eqs. (3.8)–(3.10), it is easy to integrate over τ and to obtain the final result. Thus, in a strong-coupling limit, $G \geqslant 0.1$, the diffusion coefficient is completely defined by the incoherent term

$$D_{\mathrm{strong}} = \tilde{D}_{\mathrm{in}}(0) = \frac{a^2}{\omega_{\mathrm{max}}}\left(\frac{t_1}{2\hbar}\right)^2 \sqrt{\frac{2\pi}{\eta_p}}\,\frac{\exp(-\eta_p/8k_BT)}{\sqrt{k_BT}}, \tag{5.2}$$

which, in its turn, is being determined by the end-preserving processes.

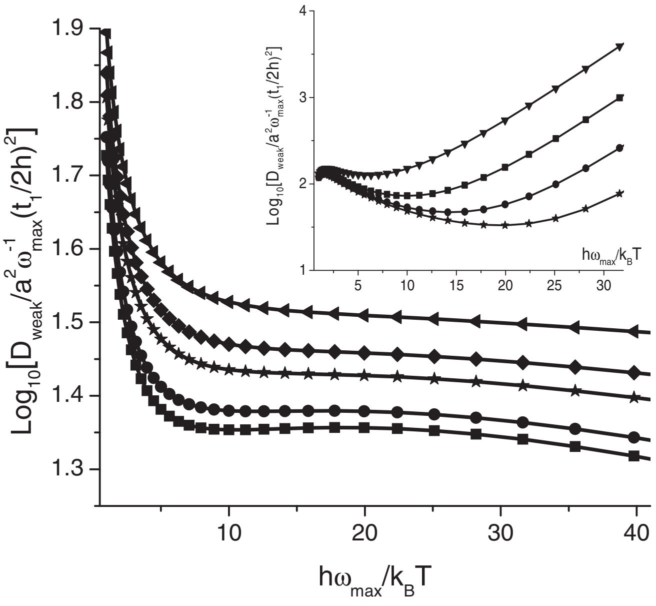

FIG. 2. Temperature dependence of the diffusion coefficient in a weak-coupling limit. Model parameters: $G = 10^{-3}$, $\omega_0/\omega_{\max} = 5 \times 10^{-4}$, $t_1/\hbar\omega_{\max} = 10^{-5}$. Lines with triangles, diamonds, stars, circles, and squares denote, correspondingly, the values of $\Omega/\omega_{\max} = 0.2$, 0.25, 0.3, 0.5, and 1. In the inset: the same but with the coupling constant $G = 10^{-2}$; lines with triangles, squares, circles and stars denote, correspondingly, the values of $\Omega/\omega_{\max} = 0.25$, 0.5, 1, and 2.

In the weak-coupling limit $G \leqslant 0.01$, and at a reasonable assumption $t_1 \ll \hbar\Omega$, the diffusion coefficient

$$D_{\text{weak}} = \frac{a^2}{\omega_{\max}}\left(\frac{t_1}{2\hbar}\right)^2\left[(\gamma_p + \gamma_c) + \frac{2\exp(-\varphi_p(0))}{\Omega^2\gamma_c}\right] \tag{5.3}$$

is determined by both incoherent [the first term of Eq. (5.3)] and coherent [the last term of Eq. (5.3)] contributions. The end-changing γ_c and the end-preserving γ_p rates can be presented in the following form:

$$\gamma_c = \sqrt{\frac{\pi}{\eta_c|\ln\omega_0|}}\frac{\exp(-\eta_c|\ln\omega_0|/4k_BT)}{\sqrt{k_BT}}, \tag{5.4}$$

$$\gamma_p = \frac{2\eta_p k_B T\omega_0^{2\eta_p k_B T - 1}}{1 - 2\eta_p k_B T}. \tag{5.5}$$

It has to be noted that the expressions for γ_c in both limits coincide with those of Ref. [17], while the expression for γ_p in the weak-coupling limit differs from the result of the cited paper, which was obtained as the multiphonon expansion of the end-preserving rates. Keeping in mind the power law behavior [Eq. (3.10)] of the end-preserving kernel at weak-coupling, one can show that a multiphonon expansion is not valid in this particular case.

In Fig. 2 we present the Arrhenius plot of the diffusion coefficients in the weak-coupling limit. It is seen that at low temperatures and for all shown values of Ω the overall diffusion coefficient is a relatively insensitive function of temperature. The obtained results are in good agreement with the experimentally observed temperature-independent diffusion of the H/W(110) system [30]. Indeed, taking the interatomic spacing for tungsten to be equal to 2.55 Å, the lattice Debye temperature $\hbar\omega_{\max}/k_B$ equal to 310 K and estimating $t_1 \sim 5 \times 10^{-5}$ meV, $\hbar\Omega = 15.7$ meV, $G \sim 10^{-3}$ (these parameters were evaluated in Ref. [17] by the analysis of the hydrogen-tungsten interaction potential), we obtain the low-temperature value of the diffusion coefficient $D_{\text{weak}}(T = 10 \div 80K) \sim 10^{-14}$ cm^2/s. This is close enough to the experimental data reported in Ref. [30]. Of course, we cannot reproduce correctly the regime above the quantum crossover temperature T_0 [24], when both underbarrier hopping and thermally activated diffusion take place.

At stronger coupling to the lattice but still in the weak-coupling regime, the temperature dependence is quite different (see the inset in Fig. 2). According to Eqs. (5.3) and (5.4), the main contribution at high temperatures comes from the incoherent term, and D_{weak} is a slowly increasing function of T. Contrary, at low temperatures the diffusion coefficient is dominated by the coherent contribution and behaves as $\exp(E_c/k_BT)$.

A qualitatively similar increase of the diffusion rate of H on Cu(001) below 20 K was observed experimentally [9]. However, in our case this behavior is just a result of the used two-level dissipative model, whereas in Ref. [9] it was attributed to the change of nonadiabatic response of the thermally excited e-h pairs to the diffusing particle. In Ref. [5], where the study of hydrogen self-diffusion on Cu(100) surface was performed by means of a similar method of quantum kinetic equations, a power law $D(T) \sim T^{-\alpha}$ increase of the diffusion coefficient at low temperatures was reported with $\alpha \approx 3.2$, which resembles the low-temperature behavior of the muonium diffusion in solids [15]. We can reproduce this result, taking the super-Ohmic spectral weight functions for the end-changing processes with the power index $n \approx 5/3$.

As we have pointed out in Sec. III, we can extrapolate the results to zero temperature. In that case, only end-preserving (super-Ohmic) processes contribute to the incoherent part of the diffusion coefficient, whereas the coherent part is dealt with the intrinsic width of the T-mode peak [29]. The friction coefficient is not zero in this limit because the excited adsorbate can transfer its energy to the lattice, induce excitations from the zero-point motions of the lattice modes, or create e-h excitations in the electron distribution.

Summarizing this section, we emphasize that a transition from one kind of temperature dependence of the diffusion coefficient to another takes place even in a relatively simple model. In the next section, we will show that this transition coincides perfectly (regarding to the coupling constant G) with the change of the character of adparticle dynamics at short times, when the memory effects have to be taken into account.

VI. TRANSITION REGIMES OF THE GENERALIZED DIFFUSION COEFFICIENTS

For visualization of the processes of adparticle motion at short and intermediate times, it is much more convenient to perform an inverse Laplace transformation of the generalized diffusion coefficients

$$D_{\rm coh}(t) = {\rm Re}\left[\frac{(at_{\rm inter})^2}{2\pi i\hbar^2}\lim_{\epsilon\to 0}\int_{\epsilon-i\infty}^{\epsilon+i\infty} dz\,\exp(zt)\frac{1}{z+\tilde{\gamma}_{\rm total}(z)}\right]$$
$$= \left(\frac{at_{\rm inter}}{\hbar}\right)^2 {\rm Re}\left[\sum_{i=1}^{\infty}\exp(-z_i t)\frac{1}{1+\tilde{\gamma}'_{\rm total}(z_i)}\right]. \quad (6.1)$$

The summation in Eq. (6.1) in accordance with the residue theorem runs over all poles z_i of the integrand, which obey the condition ${\rm Re}[z_i] < 0$. Equation (6.1) resembles the results of the generalized collective modes theory [33,34], postulating additive contributions of each collective excitation to a particular time correlation function. In our case, the summation is extended to the infinite number of poles, and major contribution comes from terms with maximal values of ${\rm Re}[z_i]$ and weight factors $[1+\tilde{\gamma}'_{\rm total}(z_i)]^{-1}$. The expression for $D_{\rm coh}(t)$ can be even more complicated if one deals with higher-order poles.

The expression for $D_{\rm in}(t)$ follows from Eq. (3.4) of the kernel $\tilde{\gamma}_{\rm inter}(z)$ and can be presented via the end-changing/end-preserving Eqs. (3.8)–(3.10) as

$$D_{\rm in}(t) = (at_1/h)^2 {\rm Re}[\gamma_c(t) + \gamma_p(t)]. \quad (6.2)$$

We evaluate the generalized diffusion coefficients in the weak-coupling regime when the memory effects are important at the initial stage of the adparticle motion.

In Fig. 3, we present the time dependence of $D(t) = D_{\rm in}(t) + D_{\rm coh}(t)$ at different temperatures. It is nonmonotonic, and the oscillations become more pronounced when the system temperature decreases. The lattice distortion caused by interaction of the adsorbate with the phonon subsystem has no time to relax, and the initial profile of the lattice potential has no time to be restored after the particle passage. As a result, the effective barrier is higher than its adiabatic value, and the particle starts to oscillate being caged in the deformed potential well. Such a behavior of $D(t)$ is observed even at temperatures comparable with $\hbar\omega_{\max}/k_B$.

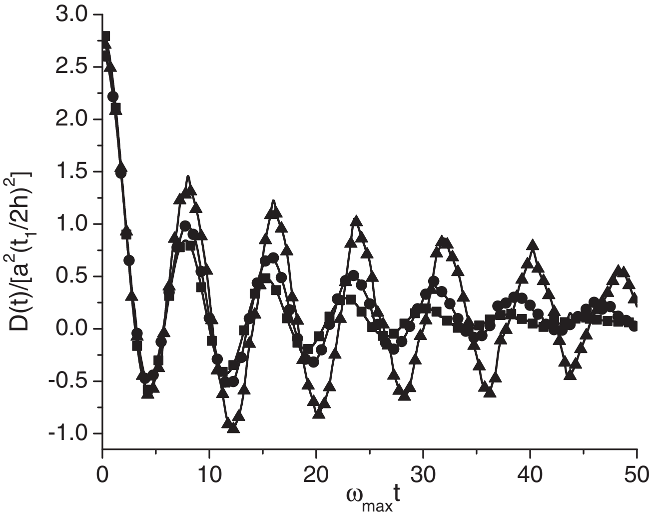

FIG. 3. Generalized diffusion coefficients calculated at $G = 10^{-3}$, $t_1/\hbar\omega_{\max} = 10^{-5}$, $\Omega/\omega_{\max} = 1$, and different temperatures: $k_BT/\hbar\omega_{\max} = 0.5$ (triangles), 0.75 (circles), and 1 (squares).

At temperatures $k_BT/\hbar\omega_{\max} < 0.5$ (not shown in Fig. 3), these oscillations persist on the time scales, which are by two orders of magnitude higher than the inverse Debye frequency. In Ref. [26], we calculated the generalized diffusion coefficients at different values of T and Ω. The general tendencies observed in Ref. [26] can be formulated as follows: low temperature T and a high vibrational frequency Ω favor the oscillation dynamics of the particle, and so does a weak "substrate-adsorbate" interaction.

It would be interesting to relate this nonmonotonic behavior of $D(t)$ to a possible recrossing phenomenon [7,8,24,25]. One can attribute the negative branches of $D(t)$ to the backward motion of the adsorbate: the particle may cross the dividing surface, located at the adsorption site s, due to the lattice distortions that "push" the particle in the opposite direction (with respect to that at the initial instant of motion). The nature of oscillations of $D(t)$ is different from that of $f_{s,s}(t)$, presented in Fig. 1. While in the coherent regime the only reason for the oscillating behavior of $f_{s,s}(t)$ is an interplay between the processes of transition and reflection of the wave packet, the nonmonotonic dissipative motion is determined by the adsorbate scattering from the substrate atoms. Indeed, one can easily verify that only $D_{\rm coh}(t)$ contributes to the oscillatory adparticle dynamics.

It should be emphasized that at weak coupling we are in the energy-diffusion-controlled regime from the viewpoint of TST [24] and in the dotted region of the "Thomas diagram," where the nonequilibrium effects are important. In such a case, a description using the Smoluchowski equation is no longer valid [23], and one has to use the Fokker-Planck equation instead [22,24]. An alternative way is to study a time behavior of the "velocity-velocity" autocorrelation functions or, as in our case, the generalized diffusion coefficients. In the weak-coupling limit it gives us a possibility to "visualize" the recrossing phenomenon in the coordinate representation, although in the energy-diffusion-controlled regime one normally has to use the concept of recrossing through the dividing surface in the energy space [25]. Investigation of the recrossing is complicated by the memory friction, for which, up to our knowledge, there is no reliable approach in the framework of TST.

Another interesting example of the short-time dynamics of the adsorbate is the onset of the T-mode [28,29]. The latter is known to appear when adparticle moves between two stable positions at the surface within one adsorption site due to the interaction with phonons or electronic subsystem of the substrate. The above presented model admits small longitudinal displacements of the particle, when it performs L-R transitions within the given well. At low temperatures, the shape of the T-mode is believed to be dominated by frictional damping characterized by the nonadiabatic coupling to the substrate excitations. At high temperatures, the anharmonicity of the static lattice potential plays a dominant role.

Though the analysis of the frequency-dependent diffusion coefficients would be more convenient in this case, since it allows us to relate the T-mode position to the maximum of ${\rm Re}[\tilde{D}(i\omega)]$, the main conclusions can be drawn from the time behavior of $D(t)$ as well. Some noticeable temperature-dependent changes of the generalized diffusion coefficients are seen in Fig. 3: a frequency shift toward the higher values and an increase of the damping with the temperature take place.

A detailed investigation of the temperature dependence of the T-mode features can be the subject of a separate study. One remark is to the point: whereas for the dynamic structure factor the T-mode analysis is often complicated due to overlap of the elastic and inelastic peaks [22], the method of generalized diffusion coefficients allows one to study the T-mode in more detail, being focused on the adsorbate motion at the well bottom.

Now let us ask the question: what happens if one increases the value of coupling constant G? An intuitive answer would state that oscillations of $D(t)$ disappear at a moderate-to-strong coupling. Indeed, at the strong coupling, when the energy exchange between the particle and the substrate atoms is faster, one can use the approximation Eq. (4.5), which leads to the exponential relaxation of $D_{\rm coh}(t)$. However, fine features of such transition regimes, when the character of the adparticle motion changes from oscillatory to monotonic, need to be analyzed in the framework of the non-Markovian approach.

Thus, if one increases the coupling constant until the oscillations of $D(t)$ disappear, one finds a certain critical value $G_{\rm cr}(T,\Omega)$ (as a function of the temperature and vibrational frequency), which separates two dynamic regimes: a plain relaxation of $D(t)$ at $G > G_{\rm cr}(T,\Omega)$ and a nonmonotonic behavior at $G < G_{\rm cr}(T,\Omega)$. A detailed analysis shows that, at first, the negative branch of $D(t)$ rises over the time axis; at that, oscillations of the generalized diffusion coefficients still remain. So recrossing is vanishing, but the particle moves toward the nearest adsorption site with altering absolute value of the velocity as if meeting obstacles.

We present the above-mentioned transition regimes of the adparticle motion in Figs. 4 and 5 as plots of $G_{\rm cr}$ vs. temperature (at the fixed value of vibrational energy) and vs. vibrational energy (at the fixed value of temperature). When inspecting these curves, one can observe a remarkable feature: the transition domains of different dynamic regimes of $D(t)$ with respect to the coupling constant G coincide with the regions, where the temperature behavior of the diffusion coefficients changes from a weakly dependent function of T to quite a sensitive function of temperature. Namely, the region with a recrossing (the C-domain in Fig. 4) maps to a weakly dependent temperature regime (see Fig. 2), and the region with the monotonic motion of the adparticle (the A-domain in Fig. 4) corresponds to a strongly dependent temperature regime (see inset in Fig. 2). The domain B in Fig. 4, evidently, corresponds to the transition of the temperature behavior of the diffusion coefficient from weakly to strongly dependent function of T.

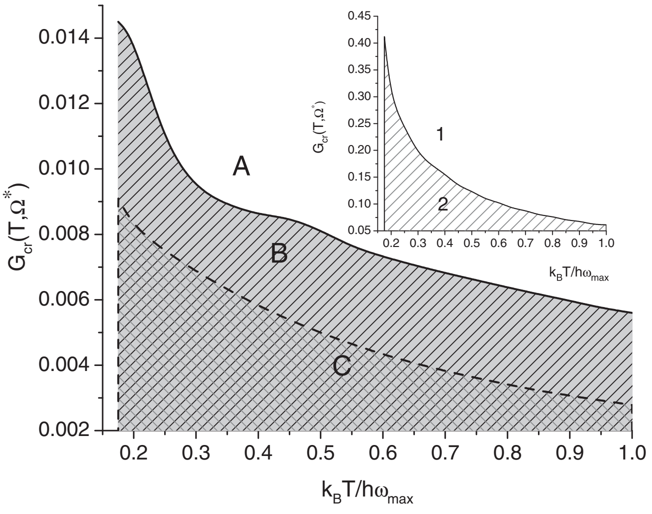

FIG. 4. The critical values of the coupling constants $G_{\rm cr}(T,\Omega^*)$ at $\Omega^*/\omega_{\max} = 1$, as functions of temperature T, that separate domains of the monotonic adparticle dynamics (A), oscillations without recrossing (B), and an eventual recrossing (C). The inset shows the temperature dependence of $G_{\rm cr}(T,\Omega^*)$ that separates the strong-coupling (1) and weak-coupling (2) domains.

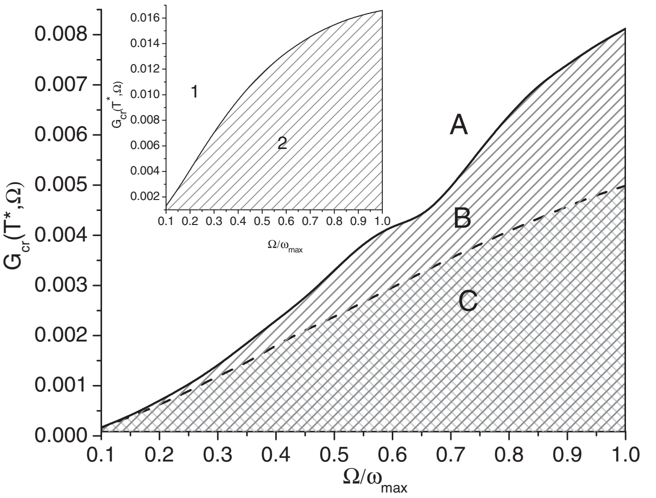

FIG. 5. The critical values of the coupling constants $G_{\rm cr}(T^*,\Omega)$ at $k_B T^*/\hbar\omega_{\max} = 0.5$, as functions of the vibrational frequency Ω, that separate domains of the monotonic adparticle dynamics (A), oscillations without recrossing (B), and an eventual recrossing (C). The inset shows the frequency dependence of $G_{\rm cr}(T^*,\Omega)$ that separates domain (1), where $D_{\rm coh}(t)$ decays as an exponential function [see Eq. (4.5)], from that with essentially non-Markovian behavior of $D_{\rm coh}(t)$.

At higher values of G the oscillations completely disappear, and the adsorbate motion is governed mainly by the incoherent term $D_{\rm in}(t)$. At $G \sim 0.1$ no coherent contribution is evident. Only the end-preserving rate $\gamma_p(t)$ defines the adparticle dynamics, and the temperature dependence of the diffusion coefficient is given by Eq. (5.2). It can be evaluated from the Smoluchowski equation [6,26] that the intermediate distribution function $\tilde{n}(k,t)$ [a Fourier transform of the nonequilibrium particle density $n(r,t)$] decays exponentially $\sim \exp(-k^2 D_{\rm strong} t)$ in this domain of the coupling constants. This behavior is consistent with the results for the dephasing rate, obtained recently [37] for the diffusion in the H/Pt(111) system. However, a quantitative estimation of the damping rate $z(k) = k^2 D_{\rm strong}$ using Eq. (5.2) for the diffusion coefficient yields the value $z(k)$, which is lower than that reported in Ref. [37]. Having not taken into account the influence of the thermal activation processes, we cannot describe correctly the system behavior at temperatures above the quantum crossover [24].

The same tendencies can be traced in Fig. 5. High values of the vibrational frequency extend the domains (B and C) of the nonmonotonic adparticle dynamics. The insert in Fig. 5 shows that a transition from essentially non-Markovian dynamics to the case, when $D_{\rm coh}(t)$ decays as an exponential function [see Eq. (4.5)], occurs in a moderate-to-strong coupling domain.

One of the assumptions inferred, when comparing these figures with Fig. 2, can be formulated as follows. If the tendencies, presented in the "critical diagrams" in Figs. 4 and 5, remain in more sophisticated models for quantum surface diffusion, and a correspondence between the transition "recrossing-monotonic motion" and the change of the T-dependence of the experimentally measured diffusion coefficients $D_{\rm exp}$ is valid in general, then we can give a prognosis about the temperature behavior of $D_{\rm exp}$, having only the information about the dynamics of the adsorbate at the initial stage of its motion. Otherwise, one has to measure the mean square displacement of the particle at times large enough to be sure that all remnants of the transition regimes are excluded. As it has been already mentioned, due to slow quantum diffusion at low temperatures (where the aforesaid transition regimes are the most pronounced and durable), it would be useful to reduce the time of atom-tracking measurement.

VII. TIME DEPENDENCE OF THE TRANSITION PROBABILITIES $f_{s,s+n}(t)$

In this section we study the off-diagonal nonequilibrium distribution functions $f_{s,s+n}(t)$. The decay rate of $f_{s,s+n}(t)$ defines the time scales at which the contribution of $D_{\rm coh}(t)$ vanishes. On the other hand, $f_{s,s+n}(t)$ can be related to the time-dependent "flux–flux" cross-correlation functions, determined at the adjacent sites s and $s+n$. These time correlation functions are known to describe a multihopping regime [7,8]. The multihopping facilitates an increase of the transport coefficients in contrast to the recrossing, which reduces the total rate of the adparticle escape and lowers the value of the diffusion coefficient.

We evaluate the nonequilibrium transition probabilities $f_{s,s+n}(t)$, solving Eq. (3.1) with respect to the diagonal distribution functions $f_{s,s}(t)$ and inserting the obtained result in Eq. (3.2). The expressions for the real and imaginary parts of $f_{s,s+n}(t)$ are the following:

$$\mathrm{Re}[\tilde f_{s,s+n}(z)] = \frac{f_{s,s+n}(0)}{z+\mathrm{Re}[\tilde\gamma_{\rm inter}(z)+\tilde\gamma_{\rm intra}(z)-\tilde\gamma^{+}_{LL}(z)]}, \tag{7.1}$$

$$\mathrm{Im}[\tilde f_{s,s+n}(z)] = -\frac{t_{\rm inter}}{\hbar}\,\frac{\tilde f_{s+n,s+n}(z)-\tilde f_{s,s}(z)}{z+\mathrm{Re}[\tilde\gamma_{\rm total}(z)]}, \tag{7.2}$$

where only linear terms in the tunneling amplitude t_1 are retained. Comparing denominators in Eqs. (4.2) and (7.1) one can observe that at small tunneling amplitudes the inverse decoherence time $\tau^{-1}_{\rm decoh} = \tilde\gamma_{\rm inter}(z)+\tilde\gamma_{\rm intra}(z)-\tilde\gamma^{+}_{LL}(z)$ is close to the decay rate of the "velocity-velocity" autocorrelation function.

Obviously, in the zero-coupling limit, Eq. (7.1) reproduces the value of $\mathrm{Re}[f_{s,s+n}(t)]$, which does not depend on time in the coherent regime of motion, and the inverse Laplace transformation of (7.2) gives the expression (3.14) for $\mathrm{Im}[f_{s,s+n}(t)]$.

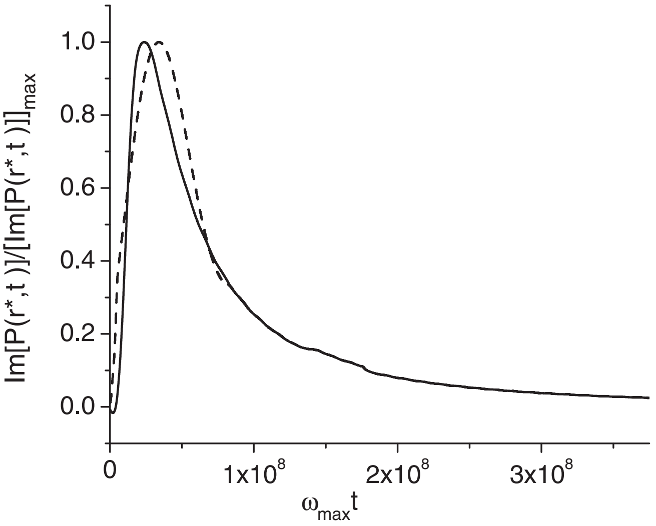

FIG. 6. Time dependence of the normalized function $\mathrm{Im}[P(r^*,t)]/[\mathrm{Im}[P(r^*,t)]]_{\rm max}$ at $r^* = r/a = 1$, $G = 10^{-3}$, $\Omega/\omega_{\rm max} = 1$, $k_BT/\hbar\omega_{\rm max} = 1$, and tunneling amplitude $t_1/\hbar\omega_{\rm max} = 10^{-5}$. Solid and dashed lines correspond to the Markovian and non-Markovian approximations.

To study the time dependence of the transition probabilities in detail, we use the continuous media approximation. In such an approximation, we are not bounded to a special geometry of the lattice any more and can rewrite Eq. (7.2) in the wave-vector-frequency representation for the imaginary part of the transition probability $\tilde P(k,z)$ as follows:

$$\mathrm{Im}[\tilde P(k,z)] = \frac{\hbar k}{2t_{\rm inter}}\,\frac{\mathrm{Re}[\tilde D_{\rm coh}(z)]}{z+k^2\mathrm{Re}[\tilde D_{\rm coh}(z)+\tilde D_{\rm in}(z)]}. \tag{7.3}$$

Then, performing inverse Fourier and Laplace transformations, we find the (r,t)-dependence of the imaginary part of the transition probability. In Figs. 6 and 7, we present the time dependence of this function (normalized per its maximum value) at $r^* = r/a = 1$. The time dependence of the real part of transition probability is the same as that of $D_{\rm coh}(t)$ (see Fig. 3).

The evaluation is performed for two different values of the tunneling amplitude $t_1/\hbar\omega_{\rm max} = 10^{-5}$ and 10^{-2}. In the first

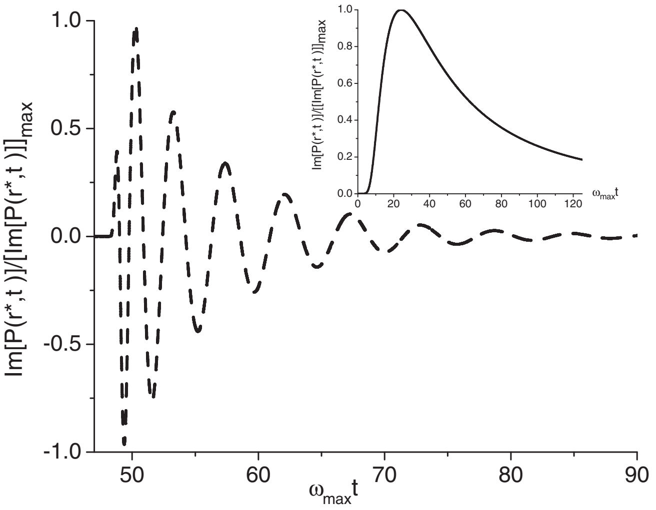

FIG. 7. Time dependence of the normalized function $\mathrm{Im}[P(r^*,t)]/[\mathrm{Im}[P(r^*,t)]]_{\rm max}$ at $r^* = r/a = 1$, $G = 10^{-3}$, $\Omega/\omega_{\rm max} = 1$, $k_BT/\hbar\omega_{\rm max} = 1$, and tunneling amplitude $t_1/\hbar\omega_{\rm max} = 10^{-2}$ in the non-Markovian approximation. Inset: the same in the Markovian approximation.

case, the adparticle approaches the point r^* at times of about $10^7 \omega_{\max}^{-1}$, when the imaginary value of the transition probability reaches its maximum. The adparticle motion is very slow, the lattice has plenty of time to relax at such huge times, and there is no qualitative difference between the Markovian approximation and the case, when the memory effects are taken into account.

The situation changes drastically (Fig. 7) when the tunneling amplitude increases by three orders of magnitude. The decay time of $\mathrm{Im}[P(r^*,t)]$ is then comparable with that of the generalized diffusion coefficients (see Fig. 3). The adparticle arrives at the point r^* at times of about seven Debye periods $2\pi/\omega_{\max}$, when the lattice has not relaxed completely, and the memory effects are still important. A transition state that originally obstructs a multihop from the site s to the nearest neighboring one is stabilized by the lattice fluctuations: the height of the effective barrier at $s+n$ can be lower than its adiabatic value at some instant of time, allowing the particle to perform a multiple crossing. Note the oscillating aperiodic behavior of the transition probability in contrast to the smooth relaxation in the Markovian case. The negative branches of $\mathrm{Im}[P(r^*,t)]$ mean that the "transition window" for the multiple crossing is not always open, and at other instants of time the barrier height can exceed its adiabatic value, prohibiting multihops of the particle. On the other hand, the width of oscillations grows in time while their amplitude reduces. It means that with increasing t the multiple hops become less probable, but the period favorable for them to proceed becomes longer.

At the end of this section, let us discuss the problem of multiple jumps in the relation to the existing theories. According to TST [24], at T lower than the quantum crossover temperature T_0 the quantum rate is so small that weak friction has no impact on deviation from a thermalized Boltzmann weighting. The validity of the low-temperature quantum-Kramers rate starts to break only at extremely weak dissipation.

On the other hand, the nonthermalized particles can exhibit multiple jumps, as it has been shown in Refs. [22,23] using the Fokker-Planck equation for the nonequilibrium distribution function, depending on both position and velocity of the adparticle. The onset of multihops was associated with the inelastic peak of the dynamic structure factor at nonzero frequency ω_{osc}. At low temperatures and high barriers, the long jumps are believed to be activated, when the velocity correlation time τ_v is the largest among the other typical times of the system: the period of oscillation $\omega_{\mathrm{osc}}^{-1}$ at the well bottom and the time τ_{th} taken by the particle to cross over a lattice spacing with a mean thermal velocity v_{th}. However, no additional studies of the temperature dependence of the inelastic peak were performed in Refs. [22,23] to attribute it to the T-mode features.

In our case, we face a T-mode onset, too. Thus, a question about the fraction of the multiple hops in the total diffusion can be answered only after an additional analysis of the T-mode behavior. If an eventual temperature-induced shift of the T-mode toward lower frequencies and its broadening are not so large (quasi- and inelastic peaks of the dynamic structure factor are well resolved), one can state that there is a portion of multihops in the system. The computer simulations within the Monte Carlo wave function formalism [11] and direct evaluation of the "flux-flux" time correlation functions [7,8] support this suggestion.

VIII. CONCLUSIONS

In this paper, we analyze the dynamics of the adparticle, which performs an underbarrier tunneling from one adsorption site to another as well as the vibrational transitions between two levels inside a quantum well, when its motion changes from coherent to incoherent due to interaction with acoustic surface phonons.

We investigate the short-time dynamics of the particle, when its vibrational frequency is comparable with the Debye frequency, and the memory effects have to be taken into account. Though the latter are traditionally thought to be important only at transition regimes, when the adparticle motion is neither ballistic nor purely diffusive, and the total rate of escape does not have to remember the details of intermediate period, we show that there is a close relation between the adparticle dynamics at intermediate times $\tau \sim \tau_{\mathrm{decoh}}$ and the temperature dependence of diffusion coefficients. Namely, as the coupling constant increases, the adparticle motion (initially oscillatory) becomes more and more smooth, indicating that the temperature behavior of the diffusion coefficients $D(T)$ should change from weakly dependent on T to quite a sensitive function of the temperature. Though we restricted ourselves by a comparatively simple model, we believe that the above-mentioned correspondence between the short-time dynamics of the adsorbate and the temperature behavior of the diffusion coefficients is valid for more sophisticated systems. If so, this "T vs. t" correspondence could be helpful at experimental evaluation of the diffusion coefficients because it would allow us to give a prognosis about their temperature behavior, having only an information about the adatom dynamics at the initial stage of its motion.

We show that the coherent term of the generalized diffusion coefficient, which is defined by the adparticle scattering from the lattice, is responsible for the recrossing phenomenon at weak-coupling. At high-coupling regime its contribution diminishes, and the particle motion is completely determined by the incoherent term. We perform a quantitative analysis of such transition regimes in terms of the critical coupling constants $G_{\mathrm{cr}}(T,\Omega)$, which depend on the temperature and vibrational frequency.

While the generalized diffusion coefficients are connected to the "velocity-velocity" autocorrelation functions, the transition probabilities $f_{s,s'}(t)$ can be related to the "velocity-velocity" cross-correlation functions. We investigated the time dependence of the transition probabilities in the model case of continuous media. It is shown that at very small values $t_1/\hbar\omega_{\max} = 10^{-5}$ of the tunneling amplitude the real part of the transition probability (which defines a multihop strength) decays at the same rate as the generalized diffusion coefficients. However, the particle approaches the nearest adsorption site much later. It moves very slowly; the lattice has plenty of time to relax, and the Markovian approximation is quite applicable. Contrary, at $t_1/\hbar\omega_{\max} = 10^{-2}$ the times of decay for real and imaginary parts of the transition probability are of the same order, and remnants of the memory effects influence the multiple crossing.

A study of the transition probabilities is interesting for two reasons: one, it shows how fast a loss of the adparticle coherence occurs; two, it allows us to draw a conclusion about the possibility of multiple crossing. The contribution of multiple jumps to the diffusion coefficient, being enhanced by the fact that in a double jump the random walker goes a double distance, can be essential even if its jump rate is much smaller than that of a single jump. We discuss the long-jump possibility in the context of the existing theories, pointing out that computer simulations [6–8,11] predict a noticeable portion of the multihops.

It can be argued that the memory effects preserve a particle coherence to a certain extent: part of relaxation energy of the lattice is delivered to the adparticles, preventing them from thermalization and maintaining the transition regimes from the coherent (ballistic) motion to the incoherent (diffusive) one. This tendency will persist after introduction of additional interactions (an electronic friction [13,19], a nonlinear "adsorbate-substrate" interaction [14,18], or a direct "adsorbate-adsorbate" interaction [20]).

Such a generalization will render the model more realistic. First of all, this would solve the "long tails" problem of the kinetic kernels [21] and ensure the convergence of the diffusion coefficients. On the other hand, additional interactions introduce new typical time scales, which could be well separated (the Markovian picture is then valid) or close to each other (then the non-Markovian approach is necessary). Investigation of the frustrated longitudinal mode becomes especially interesting in this case, giving more information on the lateral potential-energy surface and the frictional damping, experienced by the adsorbate due to e-h pair creation or phonon coupling to the metal substrate. So far there is no unique viewpoint which factors (phonon and/or e-h excitations, anharmonic contributions or memory effects) are predominant in the T-mode development at different temperatures, couplings, and interaction regimes. We believe that all these directions are quite interesting from a viewpoint of the study of transition regimes of the adsorbate and could be the subject of future investigations.

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APPENDIX

To solve Eqs. (3.11) and (3.12) we perform at first a Fourier transformation for the creation/annihilation operators

$$a_s^\dagger = \frac{1}{\sqrt{N}}\sum_k \exp(iks)a_k^\dagger, \quad a_s = \frac{1}{\sqrt{N}}\sum_k \exp(-iks)a_k, \tag{A1}$$

passing from the site representation $a_s^\dagger$, a_s to wave-vector representation $a_k^\dagger$, a_k with $k = (2\pi/N)m$ [$k = (2\pi/N)(m + 1/2)$] for the lattice with the odd [even] numbers of adsorption sites and $m = -N/2, -N/2+1, \ldots, N/2-1$ [if N is even] or $m = -(N-1)/2, -(N-1)/2+1, \ldots, (N-1)/2$ [if N is odd].

Inserting (A1) in Eqs. (3.11) and (3.12) for the coherent motion, we obtain the following equation for the intermediate distribution function $F_{k,k'}(t) \equiv \langle a_{k'}^\dagger a_k\rangle^t$:

$$\frac{\partial F_{k,k'}(t)}{\partial t} = -\frac{2it_0}{\hbar}(\cos k - \cos k')F_{k,k'}(t), \tag{A2}$$

which is easily solved, giving

$$F_{k,k'}(t) = \exp\left[\frac{-2it_0}{\hbar}(\cos k - \cos k')t\right]. \tag{A3}$$

In the infinite lattice limit $N \to \infty$, we can pass from summation over k to integration over continuous wave-vector according to $\frac{1}{\sqrt{N}}\sum_k \cdots \longrightarrow \frac{1}{2\pi}\int_{-\pi}^{\pi} \cdots dk$. Then we obtain an integral representation for the diagonal one-particle nonequilibrium distribution function as follows:

$$f_{s,s}(\tau) = \frac{1}{4\pi^2}\left|\int_{-\pi}^{\pi} dk[\cos(ks) + i\,\sin(ks)] \times \exp\left[\frac{-2it_0}{\hbar}\tau\cos k\right]\right|^2 = J_s^2(2t_0\hbar^{-1}\tau), \tag{A4}$$

which is nothing but the squared s-th order Bessel function. Similarly, we can obtain the Eq. (3.14) for the imaginary part of the transition probability $f_{s,s+1}(t)$.

To show that the last term in Eq. (4.1) does not contribute to the mean square displacement $\langle \Delta r(t)^2\rangle = a^2\sum_{s=1}^N s^2 f_{s,s}(t)$ of the particle, let us perform for simplicity the Markovian approximation in Eq. (4.1). Using Fourier transformation (A1), we obtain the evolution equation for the intermediate distribution function in the following form:

$$\begin{aligned}\frac{\partial F_{kk'}(t)}{\partial t} = -\frac{F_{kk'}(t)}{a^2}\{&2[\tilde{D}_{\text{coh}}(0) + \tilde{D}_{\text{in}}(0)][1 - \cos(k-k')] \\ &+ \tilde{D}_{\text{coh}}(0)[\cos 2k + \cos 2k' - 2\cos(k+k')]\},\end{aligned} \tag{A5}$$

where the lower line is related to the last term in the r.h.s of Eq. (4.1), which involves the "long distance" transition probabilities $f_{s\pm n,s\mp n}(t)$, $f_{s,s\mp 2n}(t)$.

The evolution equation for the mean square displacement can be written down as follows:

$$\begin{aligned}\frac{d\langle\Delta r(t)^2\rangle}{dt} &= a^2\sum_{s=1}^{N}\sum_{k,q} s^2\exp(iqs)\dot{F}_{k,k-q}(t) \\ &= -a^2\sum_{k,q}\dot{F}_{k,k-q}(t)\frac{d^2}{dq^2}\left(\sum_{s=1}^{N}\exp(iqs)\right).\end{aligned} \tag{A6}$$

Note that the sum in the brackets yields N times Kronecker delta-symbol, which in the infinite lattice limit converts to Dirac delta-function $\delta(q)$. Then integrating (A6) by parts with taking into account (A5), one can verify that only the first term in braces of Eq. (A5) contributes to the evolution equation for $\langle\Delta r(t)^2\rangle$:

$$\begin{aligned}\frac{d\langle\Delta r(t)^2\rangle}{dt} &= [\tilde{D}_{\text{coh}}(0) + \tilde{D}_{\text{in}}(0)]/\pi\int_{-\pi}^{\pi}dk\int_{-\pi}^{\pi}dq[1 - \cos q] \\ &\quad\times F_{k,k-q}(t)\frac{d^2}{dq^2}\delta(q) = 2[\tilde{D}_{\text{coh}}(0) + \tilde{D}_{\text{in}}(0)],\end{aligned} \tag{A7}$$

while the second term vanishes at the integration over k:

$$\int_{-\pi}^{\pi}\int_{-\pi}^{\pi} dk dq\{\cos(2k)+\cos(k-q)-2\cos(2k-q)\} \times F_{k,k-q}(t)\frac{d^2\delta(q)}{dq^2} = \int_{-\pi}^{\pi} dk[2\cos(2k)-\cos k]F_{k,k}(t)=0, \tag{A8}$$

because $F_{k,k}(t)\equiv 1$ and all derivatives of $F_{k,k}(t)$ with respect to wave-vector vanish.

The presented above calculation can be generalized to the 2D lattice or to the case when the memory effects are taken into account. As for the 2D coherent regime, the only modification of Eqs. (3.13) and (3.14) consists in doubling of the power indexes at Bessel functions.

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