A temperature behavior of the frustrated translational mode of adsorbate and the nature of the “adsorbate–substrate” interaction

V.V. Ignatyuk
Institute for Condensed Matter Physics, 1 Svientsitskii Street, 79011, Lviv, Ukraine
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A temperature behavior of the frustrated translational mode (T-mode) of a light particle, coupled by different regimes of ohmicity to the surface, is studied within a formalism of the generalized diffusion coefficients. The memory effects of the adsorbate motion are considered to be the main reason of the T-mode origin. Numerical calculations yield a thermally induced shift and broadening of the T-mode, which is found to be linear in temperature for Ohmic and super-Ohmic systems and nonlinear for strongly sub-Ohmic ones. We obtain analytical expressions for the T-mode shift and width at weak coupling for the systems with integer “ohmicity” indexes \( n = 0 \div 2 \) in zero temperature and high temperature limits. We provide an explanation of the experimentally observed blue- or red-shifts of the T-mode on the basis of a comparative analysis of two typical times of the system evolution: a time of decay of the “velocity–velocity” autocorrelation function, and a correlation time of the thermal bath random forces. A relation of the T-mode to the multiple jumps of the adsorbate is discussed, and generalization of conditions of the multiple hopping to the case of quantum surface diffusion is performed.

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I. INTRODUCTION

Among a number of problems dealt with the surface diffusion, which occurs either due to thermally activated \([1, 2]\) or tunnelling mechanisms \([2, 3]\), one can single out the investigation of the frustrated translational mode (T-mode) of the adsorbate \([4, 5]\). The T-mode is known to appear when the adparticle moves between two stable positions at the surface within one adsorption site (for instance, between the atop position and the saddle point \([6]\) due to interaction with phonons or electronic subsystem of the substrate. This motion of the adsorbate is being detected during inelastic helium atom scattering (IHAS) \([6, 7]\) as an additional peak in the dynamic structure factor \([5, 8, 9]\). The vibrational nature of the T-mode allows to refer this excitation to the external (low frequency) modes of the adsorbate \([10, 11]\), which are more or less temperature dependent and dispersionless with homogeneous broadening at low coverages \([5]\).

In the last years the T-mode became a subject of the intensive studies of both experimentalists and theorists. For instance, in the recent scanning tunnelling spectroscopy experiments \([12]\) the excitation of the T-mode in polyatomic molecules CO/Pd(110) has been explained in terms of the energy transfer from the C-O stretch mode to the frustrated translational one due to the anharmonic coupling between normal modes. A certain intrigue is introduced by the fact that the T-mode is observed even in such “classical” systems as CO/Cu(001) and CO/Pt(111) \([13]\), though the underlying mechanism of the T-mode formation is purely quantum mechanical: the transitions between ground and excited states within a well. This stimulated a creation of the models based on classical \([14]\) or quantum \([15]\) Langevin equations, the transition state theory (TST) \([15]\), where anharmonicity of the lattice potential is taken into account, leading to the temperature induced shift and broadening of the T-mode \([4]\).

At the same time, a theoretical approach for the T-mode description has been proposed \([2]\) from purely quantum mechanical concepts. This method allows to extrapolate the results obtained at \( T \neq 0 \) to the zero temperature limit, yielding information about the “adsorbate-substrate” interaction strength and vibrational frequency from the IHAS data. Much effort has been put \([5]\) into description of the T-mode temperature dependence. It is known that unlike diffusion the vibrational damping is not an activated process \([5, 10]\). Nevertheless, the temperature induced T-peak shifts towards lower frequencies, and almost linear broadening is observed \([13]\) for the Na/Cu(001) system in a region between 0 K and 200 K, while for the CO/Cu(001) and CO/Pt(111) systems the T-mode is blue-shifted with temperature. It is believed that at low temperatures the shape of the T-mode is dominated by a frictional damping, characterized by the nonadiabatic coupling to the substrate excitations \([5]\). At high temperatures the anharmonicity of the static lattice potential plays a dominant role \([4]\). Summarizing, it could be stated that up to now 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.

Last but not least, one can relate the existence of the T-mode to multiple jumps of the adsorbate. The onset of multi-hops was associated with an inelastic peak of the dynamic structure factor at frequency \( \omega_{\text{osc}} \) of the adparticle oscillations at the well bottom \([1, 17]\). If the T-mode is well resolved on the dynamic structure factor and not overlapped by the central quasi-elastic peak, it could be said that thermalization of the adsorbate velocity has
not taken place yet, and multiple jumps contribute significantly to the diffusion coefficient.

In the present paper we study the conditions of the T-mode formation, its temperature dependence, and its connection with the nature of the “adsorbate–substrate” interaction. We explore a two-level model of the light particle coupled non-adiabatically to the surface phonons [18, 20]. The other kinds of “adsorbate–substrate” interaction, like electronic friction or nonlinear phonon coupling, will be also considered. The underbarrier hopping to the nearest adsorption sites is postulated to be a “driving force” of the surface motion of the adsorbate.

We consider non-Markovian effects of the adsorbate motion, dealt with retarded relaxation of the lattice excitations, to be the main reason of the T-mode origin. Since this one-particle excitation is very sensitive to the form of the kinetic kernels, rigorous numerical evaluation of the T-mode temperature behavior is carried out without any approximation (e.g., like Wigner-Weisskopff one [2, 14]). On the other hand, both zero temperature and semiclassical limits for the kinetic kernels are considered in our paper that allows us to obtain the analytical expressions for the T-mode characteristics at low “adsorbate–substrate” coupling.

We perform our analysis in terms of the generalized diffusion coefficients (which are related to the “velocity–velocity” autocorrelation functions) rather than dynamic structure factor. The latest approach is often complicated due to the overlap of quasi-elastic and inelastic peaks of the dynamic structure factor [3], while 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. We propose a physical interpretation of the observed temperature induced shift of the T-mode on the basis of a comparative analysis of two typical timescales of the system dynamics: a time of decay \( \tau_c \) of the generalized diffusion coefficients and a correlation time \( \tau_{cor} \) of the thermal bath random forces. The obtained results reveal a close connection between the direction of the T-mode shift and the nature of the “adsorbate–substrate” interaction.

Our paper is organized in the following way. In Sec. II we present the generalized diffusion coefficient of a light particle derived by the method of quantum kinetic equations [19, 20] on the basis of two-level dissipative model of adparticle coupled to substrate phonons. In Sec. III we consider different correlation functions of the thermal bath random forces, which depend on the nature of the “adsorbate–substrate” interaction. In the next Section we attribute the T-mode of the adsorbate to the coherent part of the generalized diffusion coefficient and calculate its temperature dependence numerically at different values of ohmicity index \( n \). A comparison of the obtained results with the experimental data and the results of similar theoretical approaches is provided in this Section. In Sec. V we calculate the T-mode frequency and width analytically in zero and high temperature limits for strongly sub-Ohmic (ohmicity index \( n = 0 \)), Ohmic, and the super-Ohmic systems with \( n = 2 \). In Sec. VI, according to Refs. [1, 17], we relate the T-mode to the onset of multiple jumps of the adsorbate and generalize the conditions of the multiple hopping to the case of quantum surface diffusion. In the last Section we discuss briefly the obtained results and draw final conclusions.

II. GENERALIZED QUANTUM SURFACE DIFFUSION COEFFICIENTS

We consider a light particle, which performs underbarrier hopping to the nearest adsorption site, oscillates between ground and excited states within the potential well, and interacts with the lattice vibrations. Hamiltonian of the system is chosen as follows [16, 13]

\[
H = H_A + H_{int} + H_B,
\]

where the adsorbate is described by the two-band constituent

\[
H_A = \sum_{\langle ss' \rangle} (-t_0 a_{s0}^\dagger a_{s'0} + t_1 a_{s1}^\dagger a_{s'1}) + \sum_{s} \hbar \Omega \frac{1}{2} (n_{s1} - n_{s0}).
\]

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” ones with the vibrational frequency \( \Omega \). \( a_{s0}^\dagger \) (\( a_{s1} \)) creates (destroys) a particle on the site \( s \) in the vibrational state \( i \); \( n_{si} = a_{si}^\dagger a_{si} \) 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 tunnelling 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 [18]

\[
H_{int} = \sum_{s} \left\{ n_s \sum_{q} \gamma_{sq} (b_q + b_q^\dagger) + (a_{s0}^\dagger a_{s1} + a_{s1}^\dagger a_{s0}) \times \sum_{q} \chi_{sq} (b_q + b_q^\dagger) \right\},
\]

where \( b_q^\dagger \) (\( b_q \)) creates (destroys) a phonon with a normal mode frequency \( \omega_q \). The strengths \( \gamma_{sq} \) (\( \chi_{sq} \)) describe coupling of phonons to the density (oscillation) modes of the adsorbate. The bandwidths \( t_0, t_1 \) and vibrational frequency \( \Omega \) can be 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 \( \Gamma = \langle s, i | V_{int}^s | s, j \rangle \) of the lattice distortion potential \( V_{int}^s \) over the localized Wannier states \( |s, j\rangle \) times the phase
factor depending on the site number $s$ and wave-vector $q$ \cite{18}. Likewise, we suppose $\Gamma$ to be the same for different quantum states $\{i,j\} = \{0,1\}$ and use the dimensionless coupling parameter

$$G = \frac{\Gamma^2}{M\omega_{\text{max}}^2} \quad (2.4)$$

to characterize the “adsorbate–substrate” interaction. Here $\omega_{\text{max}}$ stands for the Debye frequency, and $M$ denotes the mass of the substrate atom.

The last term in Eq. (2.1)

$$H_B = \sum_q \hbar \omega_q b_q^\dagger b_q \quad (2.5)$$
corresponds to the phonon bath; longitudinal acoustic phonons only are taken into account in this model.

Since the tunnelling amplitudes are always much smaller than the coupling strengths, the interaction part of Hamiltonian \cite{20} cannot be considered as a perturbation and has to be taken into account exactly. The most refined method consists in performing unitary transformations in order to exclude the linear over the interaction terms from the system Hamiltonian. In the unitary transformed Hamiltonian the tunnelling processes can be considered as those with emission/adsorption of the virtual phonons, and the same is true for the vibrational processes.

It is also useful to pass to the hybrid set of states for each site:

$$a_{s,L,R} = \frac{1}{\sqrt{2}} (a_s \pm a_{s}), \quad (2.6)$$

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 vibrational transitions with $i \neq j$, $\{i,j\} = \{L,R\}$, as the end-changing processes, supplying them afterwards by the subscript $(c)$, and transitions with $i = j$ will be termed as the end-preserving ones with the corresponding subscript $(p)$.

Using the method of the reduced density matrix \cite{21} it is possible \cite{16,19,20} to obtain the chain of quantum kinetic equations for diagonal $f_{s,s}(t) = \sum_i = L,R (a_{s,i}^\dagger a_{s,i})^\dagger \$ and off-diagonal $f_{s,s'}(t) = \sum_i = L,R (a_{s,i}^\dagger a_{s',i})^\dagger \$ one-particle non-equilibrium distribution functions, where the averaging is taken with the statistical operator $\rho_S(t)$ of the adsorbate. These integro-differential equations are linear in $f_{s,s}(t)$, $f_{s,s'}(t)$ but are non-local in time; hence it is useful to perform the Laplace transformation $\tilde{f}(z) = \int_0^\infty \exp(-zt)f(t)dt$. Solving the equations for the off-diagonal distribution functions and inserting the obtained results into the equation for the diagonal ones, one can obtain \cite{16,20} an expression for the generalized (frequency dependent) diffusion coefficient:

$$\tilde{D}(z) = \tilde{D}_{\text{coh}}(z) + D_{\text{in}}(z)$$

$$= \frac{a^2}{4} \left[ \frac{2t_{\text{inter}}^2/\hbar^2}{z + \gamma_{\text{inter}}(z) + \gamma_{\text{intra}}^+(z) + \gamma_{\text{inter}}(z)} \right] \quad (2.7)$$

The first term $\tilde{D}_{\text{coh}}(z)$ in (2.7) describes a coherent contribution to the generalized diffusion coefficient. It can be interpreted \cite{16,19} in terms of a simple model of band-type motion limited by scattering from the lattice (with interatomic spacing $a$) at temperatures large relative to the bandwidth $t_{\text{inter}}$, which is narrowed due to polaronic effect. The kinetic kernel

$$\tilde{\gamma}_{\text{inter}}(z) = 4\gamma_{LL}(z) + 2\gamma_{LR}(z) + 2\gamma_{RL}(z) \quad (2.8)$$
corresponds to the dissipative intersite motion of the adsorbate and describes processes, when the adparticle performs random site-to-site hopping (with or without the change of its quantum state) owing to the interaction with the bath. The kinetic kernel $\tilde{\gamma}_{\text{intra}}(z)$ in Eq. (2.7) describes a 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 the same adsorption site (the opposite process of particle de-excitation with a phonon emission is also taken into consideration).

The second term $\tilde{D}_{\text{in}}(z)$ in Eq. (2.7) 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 $\tilde{\gamma}_{\text{intra}}(z)$, describing processes of the surface phonon creation/annihilation, when the particle performs a transition from one Wannier state to another.

The rates $\tilde{\gamma}_{\text{intra}}(z)$, $\tilde{\gamma}_{\text{inter}}(z)$ can be obtained from the Laplace transformation of the kinetic kernels

$$\gamma_\tau(x) = \omega_{\text{max}} x_3 \Re \{ \exp[-(\varphi(x)-\varphi(x)(\tau))]-\exp[-\varphi(x)], \} \quad (2.9)$$

$$\gamma_{LL}^+(x) = \omega_{\text{max}} t_{\text{intra}}^2 \Re \{ \exp[-(\varphi_{LL}(x)+\varphi_{LL}(x))]-\exp[-\varphi_{LL}(0)], \} \quad (2.10)$$

where

$$\varphi(x) = \int_0^x \frac{f_x(\omega)}{\omega^2} \left[ \coth \left( \frac{\hbar \omega}{2k_B T} \right) \cos(\omega \tau) - \sin(\omega \tau) \right] \quad (2.11)$$

and one-particle parameters $\lambda_x = \{t_1, \Omega\}$ are related to the corresponding end-changing/end-preserving processes (see also Table in Ref. \cite{19}). The exponential form of the rates (2.9)–(2.11) is a result of averaging of the lattice time correlation functions \cite{16,19} over the bath variables that yields the temperature dependent factor in Eq. (2.11). Hereafter we use dimensionless frequencies in the units of $\omega_{\text{max}}$ and temperatures in the units of $\hbar \omega_{\text{max}}/k_B$.

The “adsorbate–substrate” interaction enters the kinetic rates via spectral weight functions \cite{16,18,20}

$$J(\omega) = \sum_q \chi_{sq}^2 \delta(\omega - \omega_q), \quad (2.12)$$

$$J_{LR}(\omega) = \sum_q [(\gamma_{sq} - \gamma_{sq'}) + (\chi_{sq} + \chi_{sq'})^2] \delta(\omega - \omega_q), \quad (2.13)$$

$$J_{RL}(\omega) = \sum_q [(\gamma_{sq} - \gamma_{sq'}) - (\chi_{sq} + \chi_{sq'})^2] \delta(\omega - \omega_q), \quad (2.14)$$
\[ J_{LL}(\omega) = \sum_q [(\gamma_{sq} - \gamma_{s'q}) + (\chi_{sq} - \chi_{s'q})]^2 \delta(\omega - \omega_q), \]  
(2.14)

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

The function (2.12) describes the intrasite dynamics; the functions (2.13) are related to the intersite end-changing processes, while (2.14) are dealt with the intersite end-preserving processes. The spectral weight function (2.12) can be considered as site-independent if the system has a translational symmetry, whereas the functions (2.13)-(2.14) depend only on the distance \(|s - s'|\) between the nearest neighbor sites \(s\) and \(s'\) [18, 20].

The system dynamics is governed by the low frequency behavior of the spectral weight functions (2.12)-(2.14). In Refs. [16, 18–20] they were chosen to be scaled as

\[ J_c(\omega) \approx \Theta(\omega - \omega_0)\Theta(\omega_{\text{max}} - \omega)\eta_c \omega^{D-2}, \]  
(2.15)

for the end-changing, and

\[ J_p(\omega) \approx \Theta(\omega - \omega_0)\Theta(\omega_{\text{max}} - \omega)\eta_p \omega^D, \]  
(2.16)

for the end-preserving processes with \(\eta_c = 10G\), \(\eta_p = 12.5G\), and \(\Theta(z)\) denoting the Heaviside step function.

In Eqs. (2.15)-(2.16) the power index \(D\) equals the system dimensionality. Thus, for a two-dimensional lattice the end-changing spectral weight functions are sub-Ohmic, while the end-preserving ones are super-Ohmic [22]. Such a behavior is a consequence of the equality of the coupling strengths \(\Gamma\) for all the quantum states. Moreover, the lattice is assumed to possess a nonzero lowest frequency \(\omega_0\), which is introduced to take into account the finite size of the system. It not only removes the divergencies [22], when the sub-Ohmic spectral functions have the power index \(n = 0\), but also allows one to describe the adsorbate-induced surface reconstruction [18], when the particles become self-trapped due to the overlap of lattice distortions.

We would like to note that a sharp cut-off of the spectral weight functions at the Debye frequency \(\omega_{\text{max}}\) is not a unique one, and plain exponential [22] or algebraic [23] cut-offs are also used. However, the obtained results are found to be rather insensitive to the cut-off form, being governed above all by the low frequency behavior of \(J(\omega)\).

In the next Section we will consider other values of the power index \(n\) in the expressions for spectral weight functions and discuss their relation to the processes of different physical nature. Here we would like to emphasize that there is a one-to-one correspondence between the low frequency behavior of \(J(\omega)\) and the long-time relaxation of the kinetic kernels (2.19). It was pointed out in Ref. [24] that at large times we pass from a Gaussian form for \(\gamma_{\text{coh}}(\tau)\) (for the sub-Ohmic processes with \(n = 0\)) through exponential relaxation of kinetic kernels (for the Ohmic processes) to the power law behavior (in the super-Ohmic case with \(n = 2\)).

To conclude this Section, let us note that at a reasonable assumption of an infinitesimal value of the tunneling amplitude in comparison with vibrational frequency, \(t_3 \ll \hbar \Omega\), the expression (2.7) for the generalized diffusion coefficient can be simplified and presented as follows

\[ \tilde{D}(z) \approx \frac{a^2 t_3^2}{2k_B} \left[ \frac{\exp(-\varphi(0))}{z + \Omega^2 \gamma_c(z)} + 2 \left( \tilde{\gamma}_c(z) + \tilde{\gamma}_p(z) \right) \right]. \]  
(2.17)

where \(\tilde{\gamma}_c(z)\) and \(\tilde{\gamma}_p(z)\) mean the Laplace transforms of the end-changing (evaluated with spectral weight functions (2.13)) and end-preserving (evaluated with spectral weight functions (2.16)) kernels times factor \(1/\omega_{\text{max}}^2\). A generic form for the coherent contribution to \(\tilde{D}(z)\) has a structure similar to Eq. (2.17) even if the other kinds of interaction (like electronic friction and/or anharmonic coupling to phonon subsystem) are taken into account. In the very general case, a denominator in the expression for \(D_{\text{coh}}(z)\) will consist of several terms of different physical origin, which describe the vibrational transitions of the adsorbate within the well. In Sec. IV we attribute the T-mode to the coherent part of the generalized diffusion coefficient, and explore Eq. (2.17) to study in detail its features at different types of the “adsorbate–substrate” interaction.

III. CORRELATION FUNCTIONS OF THE THERMAL BATH RANDOM FORCES

We can look at the problem of quantum surface diffusion from another viewpoint. Making use of the solution of the Heisenberg equations of motion for the external degrees of freedom [18] one can derive the so-called generalized quantum Langevin equation [25]

\[ M \ddot{q}(t) + M \int_0^t \gamma(t - \tau) \dot{q}(\tau) d\tau + \frac{dV(q, t)}{dq} = F_r(t) \]  
(3.1)

for the particle with the mass \(M\) and a generalized coordinate \(q(t)\) moving within the potential \(V(q, t)\), where the damping kernel \(\gamma(t)\) is expressed via spectral weight function in the following way

\[ \gamma(t) = \int_0^\infty \frac{J(\omega)}{\omega} \cos(\omega t) d\omega. \]  
(3.2)

The mean value of the operator-valued noise \(F_r(t)\) is zero

\[ \langle F_r(t) \rangle_{\text{bath}} = 0, \]  
(3.3)

whereas the time correlation function of the thermal bath random forces can be expressed as follows

\[ S_{FF}(t) = \frac{1}{2} \langle F_r(t) F_r(0) + F_r(0) F_r(t) \rangle_{\text{bath}} = M \int_0^\infty \frac{J(\omega)}{\omega} \hbar \omega \coth \left( \frac{\hbar \omega}{2k_B T} \right) \cos(\omega t) d\omega. \]  
(3.4)
In the classical limit it converts to the non-Markovian Einstein relation

\[ S_{FF}^q(t) = M k_B T \gamma(t), \]  

(3.5)

where the average in Eqs. (3.3)-(3.4) is taken with respect to a bath density matrix, which contains shifted oscillators.\(^\text{[23]}\)

The relation (3.4) implies that modelling of quantum dissipation in the system is possible in terms of macroscopic quantities such as the friction kernel \(\gamma(t)\) and temperature \(T\). A class of such systems is by no means restricted to the “adparticle – linear Debye phonons” coupling. One can give examples of several types of the “adsorbate-substrate” coupling, which are closely related to the low frequency behavior of the spectral weight functions. They range from the systems with a flicker noise\(^\text{[26, 27]}\) with \(J(\omega) \sim \omega^0\) (like the end-changing spectral functions (2.15)) through the Ohmic coupling with \(J(\omega) \sim \omega^1\), when one takes into account the electronic friction and/or anharmonic terms in “adsorbate-substrate” interaction\(^\text{[21, 23]}\), to the super-Ohmic systems with \(J(\omega) \sim \omega^2\), when coupling to surface Debye phonons is considered\(^\text{[18, 20]}\) (see also the end-preserving spectral functions (2.16)).

At any ohmicity it is useful to introduce the correlation time \(\tau_{cor}\), which defines the decay rate of correlation functions (3.4)-(3.5) of the thermal bath random forces. In other words, at times about \(\tau_{cor}\) the excess energy of the lattice relaxes. For instance, in the systems with flicker noise, the corresponding time correlation functions have the residual correlations \(\tau_{cor} \sim \omega_0^{-1}\) in damping kernels,

\[ \gamma(t) \sim -\eta_c C_i(\omega_0 t), \quad C_i(z) = \int_z^\infty dt \frac{\cos t}{t}. \]  

(3.6)

The sub-Ohmic case with the power index \(n = 0\) implies an introduction of the lower limit \(\omega_0\) of frequency, \(0 < \omega_0 < \omega_{max}\), which is related to the inverse time of the experiment duration\(^\text{[27]}\), or dealt with the finiteness of the system size\(^\text{[15, 21]}\) (see also Eqs. (2.15)-(2.16) and subsequent explanation).

The Ohmic systems have a white-noise-like behavior \(\gamma(t) \sim \eta_c \delta(t)\), and there are ultra-short range time correlations in the super-Ohmic case. The super-Ohmic coupling with the power indexes \(n > 2\) is beyond our consideration. The cases of non-integer \(n\), which are typical for fractal systems, will be considered solely for the reason of proper convergence of the numerical calculations. In particular, in the next Section we consider the Ohmicity indexes \(n = \epsilon\), and \(n = 2 - \epsilon\) with \(\epsilon \ll 1\). An alternative way is to use the lower bound cut-off frequency \(\omega_0\), as it is done in Sec. V, where the analytical expressions for the T-mode features in the quasi-classical limit are obtained.

There is also another typical time scale of the system dynamics – the relaxation time \(\tau_v\) of the velocity autocorrelation functions. This time will be introduced in the next Section, and along with \(\tau_{cor}\) will be used for explanation of the direction of the temperature induced shift of the T-mode on the basis of a comparative analysis between \(\tau_{cor}\) and \(\tau_v\).

IV. T-MODE AS A COHERENT PART OF THE GENERALIZED DIFFUSION COEFFICIENT

As has been already said, the T-mode of the adsorbate is being detected in IHAS experiments as an additional (inelastic) peak in the dynamic structure factor. Thus, to predict theoretically the T-mode features one has to evaluate the dynamic structure factor

\[ S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} I(k, t) dt = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle e^{-ik \cdot R(0)} e^{ik \cdot R(t)} \rangle dt, \]  

(4.1)

which is nothing but the Fourier transform of the intermediate scattering function \(I(k, t)\). In Ref.\(^\text{[2]}\), the model of a damped quantum harmonic oscillator bilinearly coupled to a bath of lattice oscillators has been proposed. Non-Markovian equations of motion for the creation/annihilation operators of the adsorbate have been derived, which have a form of the generalized Langevin equation (3.1). The dynamic structure factor of the adsorbate has been found with taking into consideration the memory effects. Temperature dependences of the frequency of the inelastic peak of \(S(k, \omega)\) and its full width on half maximum (FWHM) have been studied in detail.

Though an investigation of the T-mode features using the dynamic structure factor is closely related to scattering experiments, this approach can sometimes be complicated due to the overlap of quasi-elastic and inelastic peaks. It happens, for instance\(^\text{[1]}\), in the quasi-continuous regime of adsorbate motion, at small friction and high values of \(k\), when the quasi-elastic peak of \(S(k, \omega)\), dealt with diffusion of the adsorbate, becomes low and broad and cannot be well separated from the inelastic peak at the vibrational frequency \(\Omega\). The inelastic peak also becomes indistinguishable at strong coupling due to the inability of completing coherent oscillations in the wells.

In such a case, investigation of the T-mode features using the Fourier transform \(\tilde{C}_{vv}(\omega) = 1/2\pi \Re \left[ \int_{-\infty}^{\infty} e^{i\omega t} C_{vv}(t) dt \right]\) of the velocity autocorrelation function \(C_{vv}(t)\) looks more promising, being focused on the adsorbate motion at the bottom of the potential well. For instance, \(\tilde{C}_{vv}(\omega)\) reveals the adsorbate motion in the potential wells also in the overdamped regime at high barriers, when, in spite of large friction, the particle can perform small parts of oscillations with unthermalized velocity\(^\text{[1]}\). On the other hand, \(\tilde{C}_{vv}(\omega)\) can be easily
obtained from the dynamic structure factor by a simple relation \[17\]

\[
\tilde{C}_{vv}(\omega) = \omega^2 \lim_{k \to 0} \frac{S(k, \omega)}{k^2}.
\] (4.2)

It has been pointed out in our previous papers \[10, 20\] that the generalized diffusion coefficients are directly related to the velocity autocorrelation function \(C_{vv}(t)\), determined at the adsorption site \(s\). We will follow this rule, having dealt a time-dependent diffusion coefficient \(D(t)\) with \(C_{vv}(t)\). Such a definition of the generalized diffusion coefficient differs from that used in Ref. \[28\], where the relation \(D(t) = \int_0^\infty C_{vv}(u)du\) has been adopted. However, it is much more useful since it allows one to associate the time of decay of \(D(t)\) with the relaxation time \(\tau_v\) of the velocity autocorrelation function. On the other hand, the zero frequency limit \(D_{exp} = \pi \lim_{\omega \to 0} \widetilde{C}_{vv}(\omega) = \int_0^\infty D(t)dt\) determines the experimentally measured diffusion coefficients \(D_{exp}\), whose temperature dependence has been studied quite profoundly \[2, 3\].

In Ref. \[21\] it has been shown that there is a close relation (at least, within the model proposed) between the adparticle dynamics at intermediate times \(\tau \ll \tau_v\) and temperature dependence of the diffusion coefficients. Namely, as the coupling strength increases, the adparticle motion (initially oscillatory) becomes more and more smooth, indicating that the temperature behavior of the diffusion coefficients \(D_{exp}(T)\) should change from weakly dependent on \(T\) to quite a sensitive function of temperature. The oscillatory behavior of the generalized diffusion coefficient has been related to the T-mode onset. In the frequency representation, oscillations of \(C_{vv}(t)\) yield the side wings of \(\text{Re}[\widetilde{C}_{vv}(\omega)]\), localized in the vicinity of the vibrational frequency \(\Omega\). The T-mode frequency was found to increase with temperature (see Fig. 3 in Ref. \[24\]). The corresponding side peak of \(\text{Re}[\widetilde{C}_{vv}(\omega)]\) should be blue-shifted too.

Thus, there are two peaks of different physical origin in the Fourier transform \(\text{Re}[\widetilde{C}_{vv}(\omega)]\) of the velocity autocorrelation function, presented in Fig. 1. The central one, localized at \(\omega = 0\), is related to the processes of adsorbate site-to-site random hopping. This peak is determined by the incoherent contribution

\[
D_{in}(t) = \left(\frac{a t_1}{\hbar}\right)^2 \text{Re} \left[\gamma_c(t) + \gamma_p(t)\right]
\] (4.3)

to the generalized diffusion coefficient. In a weak coupling limit, at high temperatures, and at large times the end-changing kinetic kernels decay as

\[
\gamma_c(\tau) \sim \exp\left[-\eta_c \ln \omega_0 (k_B T \tau^2 + i \tau)\right],
\] (4.4)

while the end-preserving ones decay as

\[
\gamma_p(\tau) \sim \Theta(\omega_0^{-1} - t) \left(1/\tau^2 \eta_k k_B T - \omega_0^2 \eta_p k_B T\right).
\] (4.5)

It is seen from Eqs. \[4.3 - 4.5\] that the relaxation law of the kinetic kernels changes from the Gaussian behavior for the sub-Ohmic case with \(n = 0\) to the truncated long tails for the super-Ohmic case with \(n = 2\). It is also easy to show that the kinetic kernels in the Ohmic regime behave as

\[
\gamma_c(\tau) \sim \exp(-\pi \eta_c T \tau). \quad (4.6)
\]

In a weak coupling limit and at the vibrational frequency large enough there is also an additional maximum of \(\text{Re}[\widetilde{C}_{vv}(\omega)]\). This peak is determined by the adsorbate scattering from the substrate atoms \[10\] and corresponds to recrossing processes dealt with the adparticle nonmonotonic dissipative motion \[19, 20\]. Hence, a side peak arises due to the coherent contribution to the generalized surface diffusion coefficient \[2.17\]. The expression for frequency dependence of the T-mode, associated with the above mentioned maximum of \(\text{Re}[\widetilde{C}_{vv}(\omega)]\) can be easily obtained from Eq. \[2.17\], putting \(z = -i \omega + 0^+\)

\[
\tilde{C}_{vv}^{coh}(\omega) \equiv \text{Re} \left[\tilde{D}_{coh}(\omega)\right] = \frac{a^2 t_{\text{inter}}^2}{2R(\omega)} \frac{\Omega^2 R(\omega)}{\omega - \Omega^2 I(\omega)}.
\] (4.7)

It is seen from Eq. \[4.7\] that the T-mode localization in the vicinity of the vibrational frequency \(\Omega\) is determined by \(I(\omega)\), whereas the T-mode width depends on \(R(\omega)\).

Let us study the time dependence of the coherent contribution to the generalized diffusion coefficient in more detail. Performing the inverse Laplace transformation,
one can obtain the following expression:

\[
D_{coh}(t) = \text{Re} \left[ \frac{(at_{\text{inter}})^2}{2\pi i h^2} \lim_{\varepsilon \to 0} \int dz \exp(zt) \frac{1}{z + \Omega^2 \gamma(z)} \right]
\]

\[
= \left( \frac{a t_{\text{inter}}}{\hbar} \right)^2 \text{Re} \left[ \sum_{i=1}^{\infty} \exp(z_i t) \frac{1}{1 + \Omega^2 \gamma(z_i)} \right]. \quad (4.8)
\]

The summation in (4.8) in accordance with the residue theorem runs over all poles \(z_i\) of the integrand, which obey the condition \(\text{Re}[z_i] < 0\). In a general case, the summation is extended to the infinite number of poles, and the major contribution comes from terms with maximal values of \(\text{Re}[z_i]\) and weight factors \(1 + \gamma(z_i)^{-1}\).

The expression for \(D_{coh}(t)\) can be even more complicated if one deals with higher order poles. Indeed, when the temperature increases, the 2-nd order poles (with rather small weight factors) appear in the integrand. Even though these higher order contributions to \(D_{coh}(t)\) have a form similar to anharmonic corrections to the velocity autocorrelation function \([3]\), their physical nature is definitely different. Basically, they are of non-Markovian origin, while a skewness of the T-mode peak in Ref. [4] arises due to the anharmonicity of the local lattice potential.

Just as relaxation times of the incoherent contributions \(D_{coh}(t)\) to the generalized diffusion coefficients depend on the ohmicity of the system (see Eqs. (4.3)-(4.6)), the damping rates \(\text{Re} z_i\) in (4.8) also change over the large range of values depending on nature of the “adsorbate–substrate” interaction. An additional study shows that at fixed parameters of the model there is a strong inequality, \(\text{Max}\{\text{Re} z_i(n = 0)\} \ll \text{Max}\{\text{Re} z_i(n = 1)\}\ll \text{Max}\{\text{Re} z_i(n = 2)\}\ll \text{Re} z_i(n)\ll 0\), ordering the damping rates of the coherent term \(D_{coh}(t)\) subject to the ohmicity index \(n\).

Turning back to Fig. 1 let us point out that the T-mode width, which defines the inverse life-time of this one-particle excitation, can increase for two different reasons. At fixed temperature the T-peak is broadened when the “adsorbate–substrate” coupling increases, and the coherent motion of the adparticle diminishes. Contrary, one can keep the coupling fixed and increase the system temperature, “switching on” more and more bath oscillators until their number reaches the maximum at the Debye temperature \(T_D = \hbar \omega_{\text{max}} / k_B\). In such a case not only the T-mode width increases due to higher dissipation, but also the peak position shifts with temperature.

The temperature dependence of the T-mode frequency and its FWHM are shown in Figs. 2-4. In the sub- and super-Ohmic regimes we used the power indexes \(n = 0.03\) and \(n = 1.97\) (which slightly deviate from the corresponding integer values 0 and 2) to eliminate the lower bound cut-off frequency \(\omega_0\). The others fitting parameters (the vibrational frequency \(\Omega\) and the coupling strength \(\eta_c\)) are chosen to reproduce the experimental data [3].

It is seen from Fig. 2 that in a strong sub-Ohmic regime the T-mode frequency is blue-shifted with \(T\) up to temperatures of about \(\hbar \Omega / k_B\), where the T-mode frequency becomes a descending function of temperature.

The T-mode FWHM is found to be a nonlinear function of \(T\) at all temperatures studied. At \(k_B T / \hbar \omega_{\text{max}} \sim 0.4\) the T-mode becomes very broad in spite of very small coupling, and almost disappears from the spectrum function \(\text{Re}[C_{vv}(\omega)]\) (see next Section for analytic estimations).

To explain the T-mode blue-shift at low-to-moderate temperatures let us recall that in the sub-Ohmic regime with \(n = 0\) there are residual correlations of the flicker noise [27]. The correlation time \(\tau_{\text{cor}}\) of the thermal bath random forces is much larger than the relaxation time \(\tau_v\) of the velocity autocorrelation functions (see Eqs. (4.3), (4.8)). Thus, a non-relaxed energy of the lattice is being delivered to the adparticle increasing its effective vibrational energy until the inverse process begins at the temperatures of about \(\hbar \Omega / k_B\).

In Fig. 3 we present the results for the T-mode temperature induced shift and broadening in the strong super-Ohmic regime. There are ultra-short range time correlations \(\tau_{\text{cor}}\) of the thermal bath random forces at super-Ohmic coupling [28], and much longer times \(\tau_v\) at which

![Fig. 2: Left panel: temperature dependence of the T-mode frequency in the sub-Ohmic regime with \(n = 0.03\), dimensionless vibrational frequency \(\Omega / \omega_{\text{max}} = 0.2\) and coupling constant \(\eta_c = 0.002\). Right panel: temperature dependence of the T-mode FWHM at the same parameters.](image)

![Fig. 3: Left panel: temperature dependence of the T-mode frequency in the super-Ohmic regime with \(n = 1.97\), dimensionless vibrational frequency \(\Omega / \omega_{\text{max}} = 0.2\) and coupling constant \(\eta_c = 0.166\). Right panel: temperature dependence of the T-mode FWHM at the same parameters.](image)
the velocity of the adparticle decays (see Eqs. (1.5), (1.8)). In such a case the excess energy of the adsorbate is being transferred to the lattice, yielding a decrease of the effective vibrational energy of the adparticle with temperature and, consequently, the red-shift of the T-mode frequency. The FWHM of the T-mode accommodates to almost a linear function of temperature after a short transition regime at low $T$.

At the Ohmic coupling (see Fig. 4) the T-mode is slightly blue-shifted with temperature, and its FWHM is a linear function of $T$ like in the super-Ohmic case. At the Ohmic coupling the difference between two typical times $\tau_{cor}$ and $\tau_v$ is smaller than in the other regimes. As a result, the T-mode shift is also smaller than in the sub- or super-Ohmic regimes (at the same values of the parameters of the model), which will be shown in the next Section. Such a behavior is consistent with the experimental data of Ref. [29] where the e-h pair contribution (with a weak Ohmic coupling [21]) was found to be almost independent of temperature.

Summing up this Section, we would like to discuss the difference between our approach and the one used in Ref. [3] when studying the temperature behavior of the adsorbate T-mode. In Ref. [3] two fitting parameters were used, which characterize the behavior of the spectral weight function $J_x(\omega)$ times a thermal population factor in the vicinity of the T-mode frequency. These parameters were found to depend very weakly on the surface temperature for the three systems studied. Moreover, the dynamic structure factor itself has been calculated in the Wigner-Weisskopff approximation [14]. That introduced an additional inaccuracy in the description of the system dynamics at intermediate times, when the memory effects have to be taken into account rigorously [19, 20].

Even though in Ref. [3] the quantum model for the adsorbate motion has been proposed, further calculations were carried out in the impulsive collision approximation without reference to the driving Hamiltonian term. The influence of non-selective measurements (e.g. collisions) on the evolution of quantum system was considered more precisely in [30], where the short- and long-time dynamics of the adsorbate has been studied in the context of quantum Zeno and anti-Zeno effects, however, without taking into account the tunnelling-mediated surface diffusion and memory effects.

In our paper we consider a more general case when the “driving force” is dealt with slow underbarrier site-to-site hopping of the adsorbate and should be treated on equal footing with other interaction mechanisms. The interaction term [23] of Hamiltonian is not of a bilinear form in creation/annihilation operators. It takes into account coupling both to density and oscillation modes of the adsorbate that corresponds to more realistic systems [2, 18]. Neither a power series expansion for the spectral weight functions at vibration frequency $\Omega$ nor any approximation for the kinetic kernels (like the Wigner-Weisskopff one) are made in our paper. As a result, we manage to describe the T-mode behavior quite accurately using only one fitting parameter - the dimensionless coupling constant. It is shown in the next Section that its value can be extracted from the residual shift and broadening of the T-mode at zero temperature.

V. AN ANALYTICAL EVALUATION OF THE T-MODE TEMPERATURE DEPENDENCE

Analytical results can be obtained in the zero temperature and high temperature limits. In the first case, a thermal population factor from Eq. (2.11) is eliminated. On the other hand, at high temperatures the thermal population factor can be approximated as $\coth(\hbar\omega/2k_B T) \approx 2k_B T/\hbar\omega$. Then using the long time asymptotics (4.4)- (4.7) for the kinetic kernels instead of the exact expressions (2.9) we can obtain analytical expressions for the T-mode frequency and FWHM.

A. Zero temperature limit

In the Ohmic regime and in the weak coupling limit $\eta_c \ll 1$ the following expression for the T-mode frequency is valid

$$\omega_T(0) = \sqrt{\Omega^2 - \Delta(0)^2/4}, \quad (5.1)$$

that coincides with the expression for the frequency of the damped harmonic oscillator. The expression (5.1) for the T-mode localization frequency defines a shift that can be referred to as the residual one, insofar it is present even at 0 K. The corresponding residual (or intrinsic) FWHM in the sub- and Ohmic regimes ($n \leq 1$) is scaled as

$$\Delta(0) \sim \eta_c \Omega^n. \quad (5.2)$$

The damping coefficient is not zero in the $T \to 0$ 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.
Let us note that the scaling law (5.2) for the T-mode FWHM agrees completely with the results of Ref. [3] obtained in the zero temperature limit. Besides, a practical significance of such results becomes quite clear: inspecting the T-mode localization, one can draw a conclusion about the vibrational frequency $\Omega$ whereas FWHM includes the information about the “adsorbate–substrate” coupling strength $\eta_c$.

Our model does not admit a straight zero temperature limit in the super-Ohmic regime because there is no polaron band narrowing in such a case [13], and a new derivation of the coherent term of the generalized diffusion coefficient becomes indispensable. Nevertheless, the obtained results are quite reliable to be used for the analysis of the low temperature T-mode features from both theoretical and experimental viewpoints.

B. High temperature limit

1. Sub-Ohmic regime with $n = 0$

Taking into account the Gaussian form (4.4) of the long time asymptotics for the kinetic kernels and Eq. (4.7) for the frequency dependence of the T-mode it is straightforward to obtain the expansion for the T-mode frequency

$$\omega_T(T) = \Omega + \frac{\eta_c \Omega}{\sqrt{\eta_c T} \ln \omega_0} \left\{ 1 - \frac{5 \eta_c T \ln \omega_0}{2 \Omega^2} \right\}$$  \hspace{0.5cm} \text{(5.3)}

as a series in the coupling strength $\eta_c$. The corresponding FWHM $\Delta(T)$ can be written down as

$$\Delta(T) = \frac{\Omega^2 \exp(-\Omega^2/4\eta_c T \ln \omega_0)}{2 \sqrt{\eta_c T} \ln \omega_0};$$  \hspace{0.5cm} \text{(5.4)}

it does not admit the $\eta_c$ series expansion. The T-mode FWHM is found to be a nonlinear function of temperature, which agrees completely with the results presented in Fig. 2.

Analyzing the T-mode temperature dependence (5.3) it is possible to find the temperature

$$T^* = \frac{\Omega^2}{5 \eta_c \ln \omega_0}.$$  \hspace{0.5cm} \text{(5.5)}

at which a maximal shift of the T-mode

$$\Delta \omega_T(T^*) = \omega_T(T^*) - \Omega = \frac{1}{10} \Omega$$  \hspace{0.5cm} \text{(5.6)}

takes place. The shift (5.6) is quite large, and the T-mode FWHM at this temperature

$$\Delta(T^*) = \sqrt{\frac{5}{4}} \exp \left( -\frac{5}{4} \right) \Omega \approx \frac{1}{5} \Omega$$  \hspace{0.5cm} \text{(5.7)}

approaches the vibrational frequency, leading to a rapid decay of the excitation as it is clearly seen in Fig. 2.

2. Ohmic regime

Analysis of the T-mode temperature dependence at the Ohmic coupling shows that at reasonable values of the vibrational frequency $\Omega$ the T-mode shift

$$\Delta \omega_T(T) = -\frac{(\pi \eta_c T)^2}{2 \Omega}$$  \hspace{0.5cm} \text{(5.8)}

is smaller than in sub- or super-Ohmic systems, since the expansion in (5.8) starts from a quadratic term in the coupling strength. The FWHM is governed by the expression

$$\Delta(T) \sim \eta_c T \Omega^{n-1},$$  \hspace{0.5cm} \text{(5.9)}

which is also valid for the super-Ohmic systems with $1 < n \leq 2$.

It should be stressed that the temperature dependence of the T-mode frequency (5.9) differs from the results presented in Fig. 3. The T-mode is red-shifted in accordance with Eq. (5.8), whereas the blue-shift is observed in Fig. 3. An explanation of this contradiction is quite simple: we used the exponential form (4.6) of the kinetic kernel when calculating (5.8), while at the numerical evaluation we used the exact expression (2.9), which up to 5-10% differs from asymptotic value (4.6) at short times. This deviation can be considered negligible when calculating the temperature dependence of the diffusion coefficients [16, 20]. But it is not true when one evaluates the temperature dependence of one-particle excitation of the adsorbate, that once more shows the exceptional sensitivity of the T-mode behavior to any kind of approximations.

3. Super-Ohmic regime with $n = 2$

At the super-Ohmic regime with $n = 2$, weak coupling limit $\eta_c \ll 1$, and moderate vibrational frequencies $\Omega \ll \omega_{max}$, the temperature dependence of the T-mode localization can be presented as

$$\omega_T(T) = \Omega + \eta_c T \Omega \ln(2\Omega).$$  \hspace{0.5cm} \text{(5.10)}

It is seen from the last expression that the T-mode is red-shifted with temperature up to the vibrational frequencies $\Omega/\omega_{max} = 1/2$, being at the same time a strongly nonlinear function of $\Omega$. Exact numerical evaluations show that the $\omega_T(T)$-curve at first reaches a plateau as the vibrational frequency increases and then becomes a decreasing function of temperature at $\Omega \sim \omega_{max}/2$.

On the other hand, the T-mode FWHM is very small even at the Debye temperature

$$\Delta(k_B T/\hbar \omega_{max} = 1) \sim \eta_c \sim \Omega \ll \hbar \omega_{max}$$  \hspace{0.5cm} \text{(5.11)}

Thus, the T-mode is not broadened too much and should be well defined. It is also to be pointed out that
in the super-Ohmic regime the T-mode shift is much smaller than that in the sub-Ohmic case, since $\Omega |\ln \Omega| \ll |\ln \omega_0|/\Omega$.

Summarizing, the analytic investigation of the T-mode behavior confirms completely the main tendencies observed in Figs. 2-4. Namely: i) a linear increase of the T-mode FWHM with temperature in the Ohmic and super-Ohmic regimes and a non-linear increase of $\Delta(T)$ in the sub-Ohmic regime; ii) the corresponding red- or blue-shifts of the T-mode location; iii) a considerable T-mode broadening in the sub-Ohmic regime even at weak “adsorbate–substrate” coupling and a small broadening at $1 \leq n \leq 2$.

Since there is a one-to-one correspondence between the system ohmicity and the kind of the coupling, one can deduce about a nature of the “adsorbate–substrate” interaction from the temperature induced shift of the T-mode. When several kinds of the “adsorbate–substrate” interaction act simultaneously, the data obtained could be more complicated than those reported in this Section. However, such a situation is rather infrequent since usually the typical relaxation times of different interactions are separated by several orders of magnitude [2, 5], and it is possible to talk about a single effective interaction.

VI. T-MODE AND MULTIPLE ADSORBATE HOPPING

Investigation of the adparticle diffusion on the basis of the Klein-Kramers equation [1, 15, 17] allows us to look at the problem of T-mode from another viewpoint, considering this one-particle excitation as a precursor of multiple or long jumps of the adsorbate. Such a jumping regime should not be confused with the situation, when at very low barriers the particle performs a quasi-continuous hopping at several sites [1, 17], and a diffusive stage of evolution is not reached. One rather has to talk about the situation when the velocity of the particle, which has localized at a certain adsorption site $s$, is not thermalized yet, and the adparticle jumps to the next nearest neighboring site $s'$ very soon. Thus, we will use the term “multiple” rather than “long” hopping of the adsorbate.

In Ref. [17] two conditions for the multiple jumps of the adsorbate at the thermal activated diffusion have been established, formulated as strong inequalities

$$\tau_{th} \ll \tau_v, \quad \tau_{osc} \ll \tau_v$$

(6.1)

for three typical times of the system dynamics

$$\tau_{osc} = a \sqrt{\frac{m}{U}}, \quad \tau_v \sim \frac{1}{\eta_c}, \quad \tau_{th} = a \sqrt{\frac{m}{k_BT}}$$

(6.2)

where $\tau_{osc}$ means the period of oscillation of the adparticle with mass $m$ at the bottom of the potential well of the depth $U$; $\tau_v$ is a relaxation time of the velocity autocorrelation function, and $\tau_{th}$ denotes the time taken by the particle to cross over a lattice spacing $a$ with a mean thermal velocity $v_{th}$.

It is seen from the presented above analysis that the T-mode is defined by the second inequality of (6.1). If the system parameters allow the typical times to obey the first inequality too, then the multiple jumps can be observed in the system.

Let us suppose that conditions (6.1) are fulfilled. Then during both the jump to the nearest neighboring site (left inequality) and oscillation within a certain adsorption site (right inequality) the particle does not have enough time to be thermalized, and the multiple hopping scenario of the diffusion can be realized. In such a case, the Einstein-Smoluchowski equation is found to be insufficient [1, 17] for the description of the adparticle diffusion, and one has to use the Klein-Kramers equation for the distribution function, which depends both on the velocity and on the coordinate of the adsorbate.

In the case of quantum diffusion the multiple hopping conditions (6.1) remain valid too, but the values $\tau_{osc}$ and $\tau_{th}$ from Eq. (6.2) should be substituted by the typical times

$$\tau_{osc} = \frac{2\pi}{\Omega}, \quad \tau_{th} = \frac{2\pi h}{\ell_{inter}}$$

(6.3)

where $\tau_{osc}$ denotes the inverse vibrational frequency, and $\tau_{th}$ is a time taken by the particle to perform an under-barrier hopping to the nearest neighboring site.

It should be pointed out that Refs. [1, 17] were directed mainly to the investigation of inelastic peak of the dynamic structure factor (or, alternatively, the side peak of velocity autocorrelation function) at various coupling constants and barrier heights, and no study of the temperature dependence of the inelastic peak was performed to attribute it to the T-mode features.

On the other hand, a generalization of the Klein-Kramers equation to description of the quantum diffusion (especially in the weak coupling limit, when there is the energy-diffusion-controlled regime from the viewpoint of transition state theory [15]) is an intricate problem, which, up to our knowledge, has not been solved yet. In Ref. [20] we followed an alternative way, having studied a behavior of the “velocity–velocity” time correlation functions, defined on the adjacent sites, with taking into account the memory effects. It has been shown that at given parameters of the model the multiple jumps are absent (the relation $\tau_{inter} \sim \tau_v$ was found to be valid), but they should appear when the tunnelling amplitude increases or the coupling strength decreases. The most interesting question – about the influence of temperature on the multiple hopping of adsorbate – can be answered only after an additional analysis of the T-mode behavior.

VII. CONCLUDING REMARKS

In this paper, we carry out numerical and analytical investigation of the temperature dependence of the T-mode of adsorbate which diffuses from one adsorption site to
another by a tunnelling mechanism. The T-mode characteristics (its localization frequency and width) are known to depend on temperature \[4, 5, 20\]. Having adopted a concept that the T-mode appearance is dealt with memory effects of the adsorbate motion, we propose an explanation of either (red or blue) temperature induced shifts of the above mentioned one-particle excitation on the basis of comparative analysis of two typical timescales: the correlation time \(\tau_{\text{cor}}\) of the thermal bath random forces and the relaxation time \(\tau_v\) of the velocity autocorrelation functions.

We show that in the strong sub-Ohmic regime with \(n < 1\) the relation \(\tau_v \ll \tau_{\text{cor}}\) is valid, leading to a blue-shift of the T-mode with temperature, since the excess energy of the lattice is being delivered to the adparticle, thereby increasing its effective vibrational energy. On the contrary, in the strong super-Ohmic regime with \(n \approx 2\) the inequality \(\tau_v \gg \tau_{\text{cor}}\) becomes valid. At the timescales of about \(\tau_{\text{cor}}\) the adparticle does not have enough time to be thermalized and starts to transfer its energy to the lattice, yielding the observed red-shift of the T-mode.

We have also analyzed in detail the temperature behavior of the T-mode width, which changes from a strongly nonlinear function of \(T\) (in the case of strong sub-Ohmic regime with \(n \approx 1\)) to the linear dependence in temperature (for Ohmic and super-Ohmic systems).

The ohmicity type is closely related to the nature of the “adsorbate–substrate” interaction: the case with \(n = 0\) corresponds to the flicker noise, the Ohmic regime is being realized in the systems with “electronic” friction or at the coupling with nonlinear phonons, while the super-Ohmic case with \(n = 2\) corresponds to the linear Debye phonon coupling. Therefore, one can draw a conclusion about the interaction mechanism from analysis of the temperature induced shift of the T-mode. On the other hand, extrapolating the obtained data to the zero temperature limit, it is possible to evaluate the microscopic parameters (vibrational frequency \(\Omega\) and coupling strength \(\eta\)), which govern behavior of the “adsorbate–substrate” system.

We consider a slow underbarrier site-to-site hopping of the adparticle to be a “driving force” of the surface motion of the adsorbate. Unlike the impulsive collision approximation \[3\], a “driving term” \[2,2\] of the Hamiltonian is treated on equal footing with other interaction mechanisms and defines a time evolution of the system. Since there is a lack of data about the T-mode behavior for the case, when the diffusion is mediated by tunnelling, and the non-Markovian effects play an important role \[30\] (or, what is almost the same, when different regimes of the ohmicity manifest themselves), we believe that our investigations have a good perspective from a viewpoint of the study of transition regimes of the adsorbate.

It has to be emphasized that a similar approach should be quite promising in the case of thermally activated diffusion as well. It was shown in Ref. \[31\] that in non-Ohmic systems with \(0 < n < 2\), \(n \neq 1\), the thermal bath random forces were correlated as \(\langle F_v(t)F_v(0) \rangle \sim \frac{-k_B T}{m \tau_{\text{cor}}}\), whereas the long time asymptotics of the velocity autocorrelation functions was scaled as \(\langle v(t)v(0) \rangle \sim \frac{k_B T}{m \tau_{\text{cor}}}\). Thus, the relations \(\tau_v \ll \tau_{\text{cor}}\) or \(\tau_v \gg \tau_{\text{cor}}\) remain valid also at thermally activated diffusion, allowing one to perform a similar comparative analysis of the typical timescales and to study the temperature behavior of the T-mode.

Finally, we relate the T-mode to the onset of the multihops of the adsorbate. If an eventual temperature induced shift of the T-mode toward lower frequencies and its broadening are not too 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 \[32\] and direct evaluation of the “flux–flux” time correlation functions \[33, 34\] support this suggestion. Thus, investigation of the T-mode behavior along with a study of the “velocity–velocity” cross correlation functions can shed more light upon the nature of such an interesting phenomenon of the adsorbate motion as a diffusion by the multi-hopping scenario.

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