Quantum Zeno and anti-Zeno effects in surface diffusion of interacting adsorbates

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Abstract. Surface diffusion of interacting adsorbates is here analyzed within
the context of two fundamental phenomena of quantum dynamics, namely the
quantum Zeno effect and the anti-Zeno effect. The physical implications of
these effects are introduced here in a rather simple and general manner within
the framework of non-selective measurements and for two (surface) temperature
regimes: high and very low (including zero temperature). The quantum
intermediate scattering function describing the adsorbate diffusion process is then
evaluated for flat surfaces, since it is fully analytical in this case. Finally, a
generalization to corrugated surfaces is also discussed. In this regard, it is found
that, considering a Markovian framework and high surface temperatures, the anti-
Zeno effect has already been observed, though not recognized as such.

1. Introduction

Traditionally, one finds in the literature that activated surface diffusion and related
phenomena, such as the frustrated translational motion (the so-called T-mode), are
well described by classical models whenever heavy particles and long time scales (of
the order of tens and hundreds of picoseconds) are considered. In such cases, which
are the typical ones, any trace of quantumness is essentially swept out; one only finds
clues of the lost quantumness through "reminders", for example, in recoil energies.
However, below these time scales also explored through collisions between the probe
particle and the diffusive one, quantum effects should be stronger. In this domain, the
commutation rule for position operators at different times should play an important
role in the corresponding dynamics, for example. In principle, this time domain would
be ruled by a coherence time $t_c \sim \hbar\beta(\beta = 1/k_BT$ and k_B is the Boltzmann constant),
determined essentially by the surface (substrate) temperature T. Thus, in general,
for times smaller than t_c, quantum effects should be dominant over thermal effects.
Hence, a question that arises in a natural way is how and why this transition takes
place or, in other words, why the diffusing, interacting adsorbates lose their quantum
behavior. Within the scenario depicted by this quantum-to-classical transition, one
can understand surface diffusion processes as decaying processes, with their evolution
being monitored along time through the so-called intermediate scattering function.

Transitions like the aforementioned one are strongly connected with measure processes in the sense that, regardless of how a measure is defined, in general such processes can be understood as a system coupled to an external agent acting on it continuously or at certain times. With each interaction between the system and the measuring device, the former would lose part of its quantumness, thus leading to typical classical behaviors (*decoherence*). This brings us to the scenario of the quantum Zeno effect (QZE) and its complementary, the anti-Zeno effect (AZE), which consist of precisely inhibiting or enhancing, respectively, the system natural (quantum) decay by carrying out a series of measures on it. These effects appear and are analyzed commonly within the context of unstable quantum systems. However, here we would like to introduce them within a very different context, namely surface diffusion of interacting adsorbates. In this regard, a novel analysis and (to some extent) new interpretation of quantum surface diffusion in terms of QZE and AZE (excluding tunneling mediated diffusion) is presented. The primary motivation of this work arises from the possibility at present to carry out surface diffusion experiments finely resolved in time by means of neutron [1] and ^{3}He spin-echo techniques [2,3]. From these experiments, one obtains the time-evolution of a quantity (namely the so-called polarization function) proportional to the intermediate scattering function,

$$I(\Delta\mathbf{K}, t) = \langle e^{-i\Delta\mathbf{K}\cdot\mathbf{R}(0)} e^{i\Delta\mathbf{K}\cdot\mathbf{R}(t)} \rangle. \tag{1}$$

This time-dependent (correlation) function is the space Fourier transform of the time-dependent pair correlation function or G-van Hove function, $G(\mathbf{R}, t)$, a generalization of the pair-distribution function from the theory of liquids [4,5]. Given an adparticle is at some position $\mathbf{R}(0)$ on the surface at time $t = 0$, $G(\mathbf{R}, t)$ accounts for the averaged probability of finding the same or another adparticle at $\mathbf{R}$ at a time t (here, $\mathbf{R}$ denotes the adparticle position operators given in the Heisenberg picture). To some extent, one could therefore interpret this function as a *time decay law*, describing the loss of correlation between a system initial configuration, represented by $e^{i\Delta\mathbf{K}\cdot\mathbf{R}(0)}$, and its configuration at time t, $e^{i\Delta\mathbf{K}\cdot\mathbf{R}(t)}$, measured along the $\Delta\mathbf{K}$-direction ($\Delta\mathbf{K}$ is the wave-vector transfer parallel to the surface of the probe particles, i.e., neutrons or ^{3}He atoms).

Experimentally, it is observed that $I(\Delta\mathbf{K}, t)$ decays smoothly with time, quadratically at short times and like $e^{-\eta_{\text{eff}}t}$ at longer times, with η_{eff} depending on the reciprocal lattice associated with the surface, the momentum transfer and the friction coefficient η ruling the diffusion time scale. In activated surface diffusion, the quantum Langevin equation formalism has been considered to evaluate the intermediate scattering function (1). The Caldeira-Leggett Hamiltonian model has also been used to describe the diffusion dynamics, representing the surface as an infinite collection of harmonic oscillators at a given surface temperature T (reservoir) and with an Ohmic (constant) friction (one-bath model [6]). If interacting adsorbates are considered, the total friction splits up into two contributions, $\eta = \gamma + \lambda$, as shown by means of the so-called interacting single adsorbate (ISA) approximation, which has been applied with success at low and intermediate coverages (two-bath model [7,8]). Within this model, γ is associated with the substrate or reservoir, while λ represents a collisional friction due to the collisions among adsorbates, thus being connected with the surface coverage. By invoking the elementary kinetic theory of transport of gases, a simple relation can be found between the collisional friction and the coverage θ at a

temperature T

$$\lambda = \frac{6\rho\theta}{a^2}\sqrt{\frac{k_B T}{m}}, \tag{2}$$

where a is the unit cell length of an assumed square surface lattice and ρ is the effective radius of an adparticle of mass m. From a quantum-mechanical viewpoint, when the adsorbate interacts with the surface the entanglement with the degrees of freedom of the latter leads to the loss of coherence (or decoherence) of the former, i.e., its ability to display quantum behaviors in the corresponding dynamics (e.g., quantum interference) [9]. In the context of quantum Brownian motion [10], this phenomenon where a highly delocalized state in position and/or momentum transforms into a localized classical state is called *environment induced decoherence*. In the particular case of the adsorbate surface diffusion, the role of the measurement process on the adsorbates would be associated with the surface and the other surrounding adsorbates. This process thus belongs to the class of non-selective, continuous and indirect measurements, which are different to the more common projective (von Neumann) measurements. As a consequence, the adsorbate position would be describable by a Langevin equation, where the apparatus would be included through an interaction Hamiltonian [11]. More specifically, the apparatus would be a reservoir [12, 13], where the effect of indirect, non-selective measurements (e.g., collisions) would contribute to the dephasing of the system quantum state, making the phase of the adparticle completely random [14]. Within the two-bath model, the surrounding adsorbates form a reservoir, such that their collisions with the tagged adsorbate (and therefore their frequency, measured through λ) can be controlled through the coverage after Eq. (2).

Finally, we would like to mention that in the context of atom-surface scattering, Levi has recently introduced and discussed decoherence [15] and the QZE [16].

The organization of this work is as follows. To be self-contained, in Section 2 the physics behind the QZE and AZE is introduced in a brief manner. In Section 3 an overview of the wave packet diffusion dynamics through flat surfaces is presented in order to introduce some concepts and notions on QZE and AZE within the context of surface diffusion. We would like to stress here that the appearance of QZE and AZE is very much related to the type of measurement carried out, leading to conclusions which can be quite different. In Section 4, the intermediate scattering function for flat and corrugated surfaces is analyzed, seeing it as a decay rate in the Heisenberg picture, and provides a new interpretation of the experimental and theoretical results previously reported. Finally, in Section 5, some conclusions are present together with possible extensions of this type of analysis to the frustrated translational mode.

2. Elementary grounds of QZE and AZE

In the standard fashion, the QZE and AZE are usually introduced within the context of a series of ideal, repeated measurements (or projections) on a system during its time-evolution [13, 14, 17–26]. Thus, let us first focus on the short-time decay dynamics of an unstable system described by the total Hamiltonian

$$H = H_0 + V, \tag{3}$$

where H_0 accounts for the system free dynamics and V describes some interaction that ultimately leads to the system decay. At $t = 0$, the system is supposed to be in a pure state $|\psi_0\rangle$, which is a normalized vector in Hilbert's space. The *survival*

probability or probability to find the system in the same state at a certain subsequent time t is given by

$$P(t) = |\langle\psi_0|\psi(t)\rangle|^2 = |\langle\psi_0|e^{-iHt/\hbar}|\psi_0\rangle|^2. \tag{4}$$

At very short times, $P(t)$ can be expressed by Taylor expansion of the evolution operator up to second order as

$$P(t) \approx 1 - \left(\langle\psi_0|H^2|\psi_0\rangle - \langle\psi_0|H|\psi_0\rangle^2\right)\frac{t^2}{\hbar^2} = 1 - \left(\frac{t}{\tau_Z}\right)^2. \tag{5}$$

That is, at very short times the survival probability decays quadratically with time. If initially the system is in an eigenstate of H_0, then we find the characteristic Zeno time τ_Z depends essentially on the variance of the interaction potential, i.e.,

$$\tau_Z = \frac{\hbar}{\sqrt{\langle\psi_0|V^2|\psi_0\rangle - \langle\psi_0|V|\psi_0\rangle^2}}. \tag{6}$$

Now, consider a number N of instantaneous ideal measurements (projections) are performed at very small intervals of time τ, such that $t = N\tau$, in order to ascertain whether the system still remains in its initial state or not. Each time a measurement is performed, the system wave function is "collapsed" and its subsequent evolution starts again from the state $|\psi_0\rangle$. Therefore, the probability to find the system in this state after a time t and after performing N measurements will be

$$P^{(N)}(t) = [P(\tau)]^N = \left[1 - \left(\frac{t}{N\tau_Z}\right)^2\right]^N. \tag{7}$$

In the limit $N \to \infty$, this quantity becomes

$$P^{(\infty)} \approx e^{-t^2/N\tau_Z^2} \longrightarrow 1. \tag{8}$$

That is, in the ideal limit where the system can be monitored indefinitely, its quantum state will remain the same, without evolving, because the interaction is not enough to remove its quantum coherence. In this way, by means of consecutive measurements, the system decay is slowed down. This is the QZE, predicted by Misra and Sudarshan in 1977 for an unstable particle [17]. Later on, in 1989, Itano *et al.* [22] observed how Be atoms were inhibited to evolve into the excited state by means of ultraviolet pulses. More recently, Fischer *et al.* [24] observed QZE with cold Na atoms in an experiment trying to mimic the proposal of Misra and Sudarshan.

In the experiments conducted by Fischer *et al.* [24], AZE was also found, which was predicted by Kofman and Kurizki [14, 23] within the density matrix formalism. This phenomenon occurs when the decay process is accelerated due to continuous measurements (ideal and sufficiently frequent). Notice that the survival probability (7) can also be expressed as a general function of the measurement time, τ, as [25, 26]

$$P^{(N)}(t) = e^{-\gamma_{\text{eff}}(\tau)t}, \tag{9}$$

If τ is small compared to τ_Z (although not always this constitutes an appropriate time scale [26]), then $\gamma_{\text{eff}} \to \tau/\tau_Z^2$, as in (8). However, for τ large enough (but still small), the system should display a typical decay at a constant rate γ_{free}, as it is found in unstable systems according to Fermi's golden rule, i.e., $\gamma_{\text{eff}} \to \gamma_{\text{free}}$. The accelerated decay with respect to the exponential decaying behavior is the AZE. The general decay law ruling the behavior of unstable quantum systems has been discussed in detail by Peres [27]. The physical conditions for leading to the observation of QZE and AZE

have been established in a very illuminating way by Kofman and Kurizki [14]. If the spectral density of states coupled to the initial state is a dense band or continuum (acting as a reservoir), the measurement-modified decay rate can be expressed as a simple overlap between the spectral density of final states or reservoir coupling spectrum, $G(\omega)$, and the measurement-induced initial state level width, $F(\omega; \tau)$, according to

$$\gamma_{\text{eff}}(\tau) = 2\pi \int_0^\infty G(\omega)F(\omega; \tau)d\omega, \tag{10}$$

where the measurement frequency $\bar{\lambda} = \tau^{-1}$ (we use the bar over λ in order to avoid confusions with the collisional frequency from surface diffusion), is related to the initial state energy uncertainty, ΔE, as $\Delta E/\bar{\lambda} \sim \hbar$. Hence the decay rate is essentially determined by the spectral density profile within a bandwidth around its energy level. According to the same authors [14], (10) constitutes a universal result: frequent measurements on a given initial state generally lead to its dephasing through randomization of the corresponding phase. The broadening of the initial state is of the order of the measurement frequency and it can be seen as an analog of the collisional broadening leading to a phase randomization of the state. Two extreme cases are then envisaged. On the one hand, when the measurement frequency $\bar{\lambda}$ is much greater than the spectral density width and the detuning between the reservoir center of gravity and the initial state frequency position, the QZE holds (the decay rate goes like $\bar{\lambda}^{-1}$). A reduction of the decay rate is then obtained when compared to the measurement-free (or Fermi's golden rule) decay. Mathematically, the spectral density is assumed to be a Dirac δ peak. In other words, when an Ohmic friction or white noise, characterized by a linear spectral density, is assumed, the QZE will not be observable. Non-Ohmic reservoirs should be then considered with a cut-off frequency. On the other hand, if the measurement frequency is much smaller than the corresponding detuning, the decay rate is shown to grow with $\bar{\lambda}$, which leads to AZE. Actually, the AZE seems to be much more ubiquitous than the QZE [14]. More recently, Maniscalco *et al* [28], within the density matrix formalism, have established the conditions for the occurrence of such effects within the quantum Brownian motion; in particular, they have studied a quantum harmonic oscillator linearly coupled to a quantum reservoir modeled as a collection of non-interacting harmonic oscillators at thermal equilibrium. During the time-evolution, the system was subject to a series of non-selective measurements, i.e., measurements which do not select the different outcomes [11]. The factorization displayed in (7) follows from the fact that at second order in the coupling, the density matrices of the system and environment factorize at any time [29].

Within the scenario of the surface diffusion of interacting adsorbates, and according to (10), the collisional friction λ would govern the F function, and the surface friction γ, the G function. Furthermore, it is interesting to note the following comparison. Within the standard projective-measurement scenario described above, a series of N measurements is carried out at regular intervals of time; within the non-selective-measurement scenario, λ provides an average number of collisions per time unit [30] and, therefore, an average number of measures per time unit, although such measures are carried out at random (according to a Poissonian distribution).

3. Surface diffusion of a wave packet by a flat surface

Consider the diffusion of a wave packet through a flat surface. It is the simplest integrable dissipative quantum system we may devise. This simple example is quite illustrative to show the different conclusions about the appearance of the QZE and AZE when carrying out ideal (or projections) and indirect measurements.

3.1. High surface temperatures

Within the ISA model, the quantum Langevin equations for the Heisenberg position operators read (for Ohmic friction or linear spectral density) as

$$\ddot{x}(t) = -\eta \dot{x}(t) + \delta F_x(t),$$
$$\ddot{y}(t) = -\eta \dot{y}(t) + \delta F_y(t), \tag{11}$$

where $\mathbf{R} = (x, y)$ denotes the position operators of a single adsorbate moving on a flat surface and the "dots" over the position operators denote time-derivatives. In this model, two non-correlated noises (per mass unit) are assumed to simulate the two baths: a Gaussian white noise, accounting for the lattice vibrational effects due to the surface temperature and leading to the interaction with the adsorbates, and a white shot noise, which simulates the adsorbate-adsorbate collisions. Then, for each degree of freedom, we have $\delta F_i(t) = \delta F_{i,G}(t) + \delta F_{i,S}(t)$ where $i = x, y$, the noise fluctuation is given by $\delta F = F - \langle F \rangle$, and G and S stand for the Gaussian and shot noise, respectively. At high surface temperatures, $\beta^{-1} \gg \hbar\eta$ (or $\eta^{-1} \gg t_c \sim \hbar\beta$), noise is considered to be classical and its autocorrelation function at two different times is well described by a Dirac δ-function, as assumed in (11). In other words, the time interval between these two times has to be greater than t_c.

Consider an adparticle of mass m initially placed on a given position of a flat surface and represented by a Gaussian state

$$\psi(x, y, 0) = \frac{1}{\sqrt{2\pi\sigma_0^2}} \, e^{-x^2/4\sigma_0^2 - y^2/4\sigma_0^2}, \tag{12}$$

where the initial width along each direction is the same and equal to σ_0. The adparticle is assumed to be initially in equilibrium with the reservoir or heat bath (surface) at a temperature T, but weakly coupled to the environment that dissipation can be neglected. The role of the initial conditions has been very often discussed in the literature (see, for example, [12, 31]). After a time t, the probability to find the particle at a given position (x, y) is given by averaging the survival probability over a thermal (Maxwell-Boltzmann) distribution of velocities [12, 31–35]

$$P(x, y, t) = \frac{1}{2\pi w_x(t) w_y(t)} \, e^{-x^2/2w_x^2(t) - y^2/2w_y^2(t)}. \tag{13}$$

Note here that the interaction with the environment makes the quantum state describing the system to pass from pure to a statistical mixture. Therefore, the probability (13) has to be interpreted as a conditional probability, rather than the probability density associated with a pure state. According to Ford *et al.* [33,34], this normal distribution is associated with two measurements at two different times. For each degree of freedom, the overall time-dependent spreading of the wave packet can be written as

$$w_i^2(t) = \sigma_0^2 + \sigma_i^2(t) + s_i(t), \tag{14}$$

with $i = x, y$. Here the quantum contribution to the spreading is given by

$$\sigma_x^2(t) = -\frac{[x(0), x(t)]^2}{4\sigma_0^2},$$
$$\sigma_y^2(t) = -\frac{[y(0), y(t)]^2}{4\sigma_0^2}, \qquad (15)$$

and $s_i(t)$ is the mean-square displacement (MSD) along each direction,

$$s_x(t) = \langle \{x(t) - x(0)\}^2 \rangle,$$
$$s_y(t) = \langle \{y(t) - y(0)\}^2 \rangle. \qquad (16)$$

In order to understand the effects of the measurements on the quantum system, apart from the survival probability seen in (2), one can also analyze the decay rate of its initial state by monitoring the ratio between the probabilities at t and $t = 0$, and evaluated at $(x, y) = (0, 0)$ [35]. Thus, in the case of the initial Gaussian state (12), we find

$$R(t) = \frac{\sigma_0^2}{w_x(t) \ w_y(t)}, \qquad (17)$$

which, taking into account (14), can be explicitly written as

$$R(t) = \frac{\sigma_0^2}{w^2(t)} = \frac{\sigma_0^2}{\sigma_0^2 + s(t) + \sigma^2(t)}, \qquad (18)$$

since the spreading along each direction is obviously the same. Accordingly, this calculation reduces to the simple evaluation of the quantum spreading $\sigma_i(t)$ and the MSD $s_i(t)$ along each direction ($i = x, y$). The same time-dependence is obtained if Gaussian integrations are carried out in the corresponding ratio instead of evaluating it at $(x, y) = (0, 0)$. The quantum spreading depends on the commutator of the position operators at two different times, from which

$$\sigma_i^2(t) = \frac{\hbar^2}{4m^2\sigma_0^2\eta^2} \ \Phi^2(\eta t), \qquad (19)$$

with $\Phi(\eta t) = 1 - \exp(-\eta t)$. For each degree of freedom, one obtains the same spreading because the Gaussian initial with is assumed to be the same for both directions. Analogously, the MSD along each direction takes the form

$$s_i(t) = \frac{2\hbar\eta}{\pi m} \ t^2 H(\eta t; T). \qquad (20)$$

Here, the function

$$H(\eta t; T) = \int_0^\infty \frac{1 - \cos z}{z(z^2 + \eta^2 t^2)} \ \coth\left(\frac{\hbar z}{2t k_B T}\right) dz \qquad (21)$$

has an analytical solution, which allows us to express (20) as

$$s_i(t) = \frac{2k_B T}{m\eta} \left[t - \frac{1}{\eta}\Phi(\eta t) \right]. \qquad (22)$$

In order to analyze (18) now for high surface temperatures, we will consider two time regimes: $\eta t \ll 1$ (short time) and $\eta t \gg 1$ (long time). In the short-time regime, $\eta t \ll 1$, the quantum spreading (19) goes like t^2, according to

$$\sigma^2(t) \approx \frac{\hbar^2}{4m^2\sigma_0^2} \ t^2, \qquad (23)$$

which corresponds to the wave packet spreading in the absence of dissipation. Analogously, the MSD also goes like t^2 according to

$$s(t) \approx \frac{k_B T}{m} \, t^2, \tag{24}$$

where the prefactor is the thermal velocity in two dimensions. Thus, the overall time-dependent spreading can be expressed in a more compact form as

$$w^2(t) \approx \sigma_0^2 + \langle v^2 \rangle t^2, \tag{25}$$

with

$$\langle v^2 \rangle = \frac{k_B T}{m} + \frac{\hbar^2}{4m^2 \sigma_0^2}. \tag{26}$$

In this short-time regime (friction-free motion or ballistic regime), we have usually that $\langle v^2 \rangle t^2 \ll \sigma_0^2$ (the wave packet has not spread too much compared to its initial spreading which can be assumed to be arbitrary large) and therefore (18) becomes

$$R(t) \approx 1 - \frac{\langle v^2 \rangle}{\sigma_0^2} t^2 + \ldots \approx e^{-\langle v^2 \rangle t^2 / \sigma_0^2}, \tag{27}$$

which is the standard short-time, t^2-behavior usually associated with QZE. Notice that the effective decay rate ($\eta_{\mathrm{eff}}(\tau) = \tau \sqrt{\langle v^2 \rangle}/\sigma_0$) is independent of the total friction η and, in particular, of λ. Hence the dynamical system displays a friction-free motion with a quadratic time behavior of the decay rate. By replacing τ by t/N (with $N \to \infty$), some authors [35] show that the factorization given in (7) also applies for $R(t)$ and claim that in the absence of friction, the QZE always holds. However, after Kofman and Kurizki, for Ohmic friction or linear spectral density, the QZE is not expected to occur (see Section 2). In the indirect measurement scheme used here, the dynamical system and the reservoir are entangled at all times except for such a regime, since $\eta = \gamma + \lambda$ is not playing any role yet. Thus, the QZE does not hold because any indirect measurement through λ has been carried out. Moreover, decoherence is absent in this short-time regime since it is a free-motion regime.

In the long-time (or diffusion) regime, $\eta t \gg 1$, the quantum spreading in both directions is time-independent, with

$$\sigma^2(t \to \infty) \approx \frac{\hbar^2}{4m^2 \sigma_0^2 \eta^2}. \tag{28}$$

On the contrary, the corresponding MSD is linear with time, according to

$$s(t) \approx \frac{2k_B T}{m\eta} \, t, \tag{29}$$

and Einstein's law is fulfilled, with the diffusion constant given by

$$D = \frac{k_B T}{m\eta} \tag{30}$$

in both directions for an isotropic surface. Thus, the full time-dependent spreading can be expressed as

$$w^2(t) \approx \sigma_0^2 + \frac{\hbar^2}{4m^2 \sigma_0^2 \eta^2} + \frac{2k_B T}{m\eta} \, t. \tag{31}$$

Assuming $\sigma_0^2 \gg s(t) \gg \sigma^2(t)$ for a certain time within the long-time regime, $R(t)$ can be approximated by

$$R(t) \approx 1 - \frac{2k_B T}{m\sigma_0^2 \eta} \, t. \tag{32}$$

Therefore, by increasing the coverage or collisional frequency, λ, according to (32), the decay rate decreases, but obviously one cannot speak about the QZE, because the system has already relaxed dynamically and decoherence is already manifested.

3.2. Low and zero surface temperatures

At low surface temperatures ($\eta^{-1} \ll t_c \sim \hbar\beta$), the noise autocorrelation function is complex [36] and depends on the ratio between the interval of the two times and t_c (colored noise). In general, the noise function acts like a driving force and the surface dynamics is better described within the generalized Langevin framework as

$$
\begin{aligned}
\ddot{x}(t) + \int_{-\infty}^{t} dt' \eta_x(t-t')\dot{x}(t') &= \delta F_x(t), \\
\ddot{y}(t) + \int_{-\infty}^{t} dt' \eta_y(t-t')\dot{y}(t) &= \delta F_y(t),
\end{aligned}
\tag{33}
$$

where $\eta_x(t)$ and $\eta_y(t)$ represent the time-dependent frictions or memory functions along each direction. The one-dimensional expression for the noise function can be found in the literature [32]. If we assume the surface is isotropic and both frictions are Ohmic, (33) reduces to (11). Thus, the corresponding quantum mechanical process is not a Markovian process in the customary sense of the term [32]. The quantum spreading is the same as before, i.e., given by (19), since it is independent of the surface temperature. However, the MSD along each direction, given by (20), now reads as

$$
s_i(t) = \frac{2k_B T}{m\eta}\left[t - \frac{1}{\eta}\Phi(\eta t)\right] + \frac{4}{\beta m}\sum_{n=1}^{\infty}\frac{\eta - \nu_n - \eta e^{-\nu_n t} + \nu_n e^{-\eta t}}{\nu_n(\eta^2 - \nu_n^2)},
\tag{34}
$$

with

$$
\nu_n = \frac{2\pi n}{\hbar\beta}
\tag{35}
$$

being the so-called *Matsubara frequencies*, which come from the Taylor series expansion of the coth-function in the integral of (21). At high surface temperatures, (34) reduces to (22). The sum over n plays an important role only at very low surface temperatures. Nevertheless, at zero surface temperature, the sum disappears, since the coth-function becomes unity and $H(\eta t; 0)$ acquires a different dependence on time. In this case ($T = 0$), the corresponding MSD expression reads as

$$
s_i(t) = \frac{2\hbar}{\pi m\eta}\left\{\gamma_E + \ln\eta t - \frac{1}{2}\left[e^{\eta t}\bar{E}i(-\eta t) + e^{-\eta t}Ei(\eta t)\right]\right\},
\tag{36}
$$

where $\gamma_E = 0.577$ is Euler's constant, and $\bar{E}i(-\eta t)$ and $Ei(\eta t)$ are the exponential integrals [37]. The environment no longer transfers energy to the adparticle due to the zero-point motion of the surface oscillators.

A similar dynamical analysis can also be carried out in terms of the short- and long-time regimes. The quantum spreading in both dimensions remains the same and is given by (23) and (28), respectively. However, the MSD is different due to its temperature dependence. Thus, in the short-time regime, $\eta t \ll 1$, we find

$$
s(t) \approx \frac{k_B T}{m}t^2 + \frac{\hbar\eta}{\pi m}t^2
\tag{37}
$$

which depends linearly on η. Analogously, at zero surface temperature, we have

$$
s(t) \approx \frac{\hbar\eta}{\pi m}t^2\left(\frac{3}{2} - \gamma_E - \ln\eta t\right),
\tag{38}
$$

where we observe essentially the same friction and time dependence, since the presence of the friction in the log-function is much weaker. On the other hand, in the long-time regime, it can be shown that

$$s(t) \approx \frac{2k_B T}{m\eta} \, t + \frac{2\hbar}{\pi m} \frac{1}{\eta + \nu_1}, \tag{39}$$

which, at zero surface temperature, becomes

$$s(t) \approx \frac{2\hbar}{\pi m\eta} \left(\gamma_E + \ln \eta t\right). \tag{40}$$

Taking into account these behaviors, the following conclusions are drawn at low and zero surface temperatures:

- Short-time regimes. The same formal expression as that given by (27) is obtained for $R(t)$, except for now $\langle v^2 \rangle$ depends linearly on η, i.e. on λ, even at zero temperature. Thus, by increasing the coverage or λ, $R(t)$ decreases (contrary to the manifestation of the QZE).

- Long-time regime. The $R(t)$ function can be expressed as

$$R(t) \approx 1 - \frac{s(t)}{\sigma_0^2}, \tag{41}$$

  where the MSD goes with λ^{-1} according to (39) and (40). Thus, by increasing λ, the decay rate decreases. However, as before, this manifestation cannot be attributed to the QZE, because the relaxation process has already been established and decoherence dominates the diffusion process. The AZE is not found either.

For ideal measurements, at zero surface temperatures, Dorlas and O'Connell [35] showed that the QZE is characterized by small ηt values, whereas the AZE by large values of ηt. According to the previous analysis, though, we conclude again differently due to the non-selectiveness or indirectness of the measurements we have considered on the time evolution of the adparticle.

4. The quantum intermediate scattering function

4.1. Flat surfaces

For flat or weakly corrugated surfaces where the thermal energy, $k_B T$, is greater than the diffusion barrier, the quantum motion of the adparticles can be exactly described within the Heisenberg picture and the scenario of the ISA model [8,38]. As mentioned before, this study can be carried out by means of the so-called intermediate scattering function. This function provides us information about the time decay associated with the position of the adparticle, which is initially located at $\mathbf{R}(0)$ and, after a time t, it will be in a position $\mathbf{R}(t)$, as it can be inferred from the autocorrelation function (1). In spin-echo experimental techniques, this function is proportional to the polarization, with the real and imaginary parts of the latter being observable magnitudes [1–3].

In general, an exact, direct calculation of $I(\Delta\mathbf{K}, t)$ results difficult to carry out due to the non-commutativity of the adparticle position operators at different times. The product of the two exponential operators in (1) can be evaluated according to a special case of the Baker-Hausdorff theorem (*disentangling theorem*), namely $e^{\hat{A}} e^{\hat{B}} = e^{[\hat{A}, \hat{B}]/2} e^{\hat{A} + \hat{B}}$, with $\hat{A} = -i\Delta\mathbf{K} \cdot \mathbf{R}(0)$ and $\hat{B} = i\Delta\mathbf{K} \cdot \mathbf{R}(t)$, which holds

whenever the corresponding commutator is a c-number. When no adsorbate-substrate interaction potential is assumed, the formal solution of (11) can be written as [5,8,38]

$$\mathbf{R}(t) = \mathbf{R}(0) + \frac{\mathbf{P}(0)}{m\eta}\Phi(\eta t) + \frac{1}{m\eta}\int_0^t \Phi(\eta t - \eta t')\delta\mathbf{F}(t')dt', \qquad (42)$$

where $\mathbf{P}(0)$ is the initial adparticle momentum operator. The commutator of the position operators at two different times is a c-number, since the commutator $[\mathbf{R}(0), \delta\mathbf{F}]$ is zero. This can be justified considering the Caldeira-Leggett model, where the two noise functions depend on time, on the initial positions and momenta of the harmonic oscillators associated with the two baths, and therefore only on the adparticle initial position [6–8]. Thus, $I(\Delta\mathbf{K}, t)$ can be expressed as

$$I(\Delta\mathbf{K}, t) = I_q(\Delta\mathbf{K}, t)I_c(\Delta\mathbf{K}, t), \qquad (43)$$

i.e., as the product of a quantum-mechanical intermediate scattering function, I_q, and a classical-like one, I_c.

Assuming a Markovian scenario, I_q reads as [8,38]

$$I_q(\Delta\mathbf{K}, t) = \exp\left[\frac{iE_r}{\hbar\eta}\Phi(\eta t)\right], \qquad (44)$$

where $E_r = \hbar^2\Delta\mathbf{K}^2/2m$ is the *adsorbate recoil energy*, which becomes less important as the adparticle mass increases. The I_q-factor is a time-dependent phase with its argument decreasing with the total friction and therefore with the coverage; its time-dependence only comes through the $\Phi(\eta t)$ function. At short-times ($\eta t \ll 1$ or $\hbar\beta \ll \eta^{-1}$), $\Phi(\eta t) \approx \eta t$ and the argument of I_q becomes independent of the total friction, thus increasing linearly with time. On the contrary, in the asymptotic time limit ($\eta t \gg 1$ or $\hbar\beta \gg \eta^{-1}$), this argument approaches a constant phase. Regarding the classical-like factor, I_c, in the Gaussian approximation, it takes the form [8]

$$I_c(\Delta\mathbf{K}, t) \simeq e^{-\Delta\mathbf{K}^2\int_0^t (t-t')C_v(t')dt'} = e^{-\Delta\mathbf{K}^2[f(t)+g(t)]}, \qquad (45)$$

where $C_v(t)$ is the velocity autocorrelation function, which can be expressed in terms of the time-dependent functions $f(t)$ and $g(t)$, given by

$$f(t) = \left(\frac{1}{m\beta\eta^2} - i\frac{\hbar}{2m\eta}\right)[e^{-\eta t} + \eta t - 1] \qquad (46)$$

and

$$g(t) = \frac{2}{m\beta}\sum_{n=1}^{\infty}\frac{\nu_n e^{-\eta t} - \eta e^{-\nu_n t} + \eta - \nu_n}{\nu_n(\eta^2 - \nu_n^2)}. \qquad (47)$$

The total intermediate scattering function (43) can then be expressed as

$$I(\Delta\mathbf{K}, t) = e^{-\chi^2[\alpha^*\eta t - \Phi(\eta t)]}e^{-\Delta\mathbf{K}^2 g(t)}, \qquad (48)$$

with $\chi^2 = \Delta\mathbf{K}^2\langle v^2\rangle/\eta^2$ and $\alpha = 1 + i\hbar\beta\eta/2$, $\langle v^2\rangle = 1/m\beta$ being the thermal square velocity. The recoil energy is included in the imaginary part of the product $\chi^2\alpha^*$, which disappears when $\hbar \to 0$. Equation (48) is the generalization of the intermediate scattering function for the quantum motion of interacting adsorbates in a flat surface. The dependence of this function on $\Delta\mathbf{K}^2$ through the so-called shape parameter, χ, is the same as in the classical theory [38]. From now on, we will just focus on (48), which will be analyzed in terms of the QZE and AZE considering the same two time regimes as before (short- and long-times).

In the short-time (ballistic or free-diffusion) regime ($\eta t \ll 1$), (48) becomes

$$I(\Delta \mathbf{K}, t) \approx e^{iE_r t/\hbar}, \tag{49}$$

where the real part has also the typical t^2-behavior characteristic of the QZE,

$$\mathrm{Re}\{I(\Delta \mathbf{K}, t)\} \approx 1 - \frac{1}{2}\frac{E_r^2}{\hbar^2}t^2, \tag{50}$$

which is friction free. As before, not always one has a quadratic time dependence, the QZE holds. Indeed, with Ohmic environments, as in our case, the QZE does not take place. The imaginary part, in turn, is linear with time, according to

$$\mathrm{Im}\{I(\Delta \mathbf{K}, t)\} \approx \frac{E_r}{\hbar}t. \tag{51}$$

The short-time regime is related to a Gaussian behavior of the real part of the intermediate scattering function, which has been observed in real experiments [2, 3]. The time Fourier transform of this function is the so-called dynamic structure factor (which is also observable), leading to Gaussian wings in the corresponding quasi-elastic peak. This frictionless motion (no collisions among adsorbates and no interaction with the substrate) is the regime where dynamical coherence prevails, i.e., adparticles keep their memory of velocity.

In the long-time (diffusive) regime ($\eta t \gg 1$), (48) can be written as

$$I(\Delta \mathbf{K}, t) \approx e^{-\chi^2 \eta t}e^{iE_r t/\hbar}, \tag{52}$$

where it is clear that the real part exponentially annihilates any trace of the oscillations associated with the phase depending on the recoil energy. Here, the Markovian character of the evolution is very noticeable and the regime of coherent dynamics is completely lost, which is a typical trait of diffusion regimes. The corresponding dynamic structure factor displays a Lorentzian shape around zero energy transfers of the quasi-elastic peak. This gradual change of shape in the dynamic structure factor is known as the *motional narrowing* effect [39–41]. Actually, strictly speaking, the quasi-elastic peak is a mixture of both shapes: Lorentzian-like at very small frequencies and Gaussian-like at very large frequencies. According to (52), the real part of the intermediate scattering function decays slower with the coverage and therefore the dynamic structure factor becomes narrower (Gaussian wings) [30, 42]. At this time regime, decoherence is already manifested (or relaxation process). In other words, the loss of coherence (or loss of quantum features) begins at times greater than the coherence time t_c. Quantum motion only plays an important role around this time and when $t \gg t_c$, the classical intermediate scattering function dominates, since the commutator in I_q plays no role and I_c approaches the classical result. The lowest surface temperature reached in a typical ^{3}He spin echo experiment is around 100 K, which means $t_c = 0.074$ ps. For neutron spin echo measurements, the surface temperature can be slowed down up to a few Kelvin, leading to a better analysis for quantum coherence.

Quasi-elastic He-atom scattering measurements [43] constitute an interesting example worth mentioning, since they provide a clear evidence for a two-dimensional free gas of Xe atoms on Pt(111) at low coverages ($\theta = 0.017$), low incident atom energy ($E_i = 10.15$ meV) and surface temperature of 105 K along the (100) direction. The corrugation of the surface is assumed to be negligible at that surface temperature, which manifests in a dynamic structure factor displaying a Gaussian-like line shape. Apart from quite different mean free paths extracted from the experiment [43] and

from our own analysis [41], one would be tempted to consider this system an ideal candidate to observe QZE, since the intermediate scattering function is quadratic in time for a quite long time interval. However, due to the heavy adsorbate mass, the recoil energy is expected to be really small and a classical diffusion motion should be good enough to describe this two-dimensional free gas. The classical intermediate scattering function for a flat surface is

$$I_{\text{classical}}(\Delta K, t) = \exp\left[-\chi^2\left(e^{-\eta t} + \eta t - 1\right)\right], \tag{53}$$

which comes from considering $\hbar = 0$ in the complex number α and $g(t) = 0$ in (48). When $\eta t \ll 1$, the t^2-behavior is again obtained

$$I_{\text{classical}}(\Delta K, t) \approx \exp(-\delta^2 t^2), \tag{54}$$

with $\delta = \Delta \mathbf{K}^2 k_B T / 2m$. This behavior with time remains until the adparticle has travelled a distance of the order of the mean free path and it starts to lose its coherence. But again, for Ohmic friction, the QZE does not hold.

4.2. Corrugated surfaces

Surface diffusion of adsorbates on corrugated surfaces can be very often described in the Markovian approximation and ISA model by the standard Langevin equation [8]

$$m\ddot{\mathbf{R}} = -m\eta\dot{\mathbf{R}} + \nabla V(\mathbf{R}) + \delta\mathbf{F}, \tag{55}$$

where $V(\mathbf{R})$ is the adiabatic interaction potential between the adsorbate and the surface. Again the formal solution of (55) is given by

$$\mathbf{R}(t) = \mathbf{R}(0) + \frac{\mathbf{P}(0)}{m\eta}\,\Phi(\eta t) + \frac{1}{m\eta}\int_0^t \Phi(\eta t - \eta t')[\nabla V(\mathbf{R}(t')) + \delta\mathbf{F}(t')]dt'. \tag{56}$$

The presence of the adiabatic force introduces an additional commutator, $[\mathbf{R}_0, \nabla V(\mathbf{R}(t))] = (i\hbar)\partial\nabla V(\mathbf{R}(t))/\partial\mathbf{P}_0$, where the dependence of this force on the initial state $(\mathbf{R}(0), \mathbf{P}(0))$ is through $\mathbf{R}(t)$. Within a quantum Markovian framework [38], this commutator is very small or negligible. Thus, in the quantum intermediate scattering function (43), the I_q factor is the same as in the case of a flat surface, given by (44), determining again the very short time, friction free behavior of the real part of the total intermediate scattering function. The classical-like factor, I_c, deserves special attention, since exact quantum Langevin calculations for corrugated surfaces are in general, prohibitive. Only the long time regime can be analyzed in simple terms. Quantum corrections at different coverages and temperatures in the activated surface diffusion of Na atoms on Cu(001) have been analyzed [38]. We have shown that within the Gaussian approximation, Eq. (45), and by assuming a velocity autocorrelation function given by

$$C_v(t) = \frac{k_B T}{m}\,e^{-\tilde{\eta}t}\cos(\tilde{\omega}t + \tilde{\delta}), \tag{57}$$

I_c becomes

$$\begin{aligned}
I_c(\Delta K, t) &= e^{-\chi_l^2 \tilde{f}(\tilde{\omega}, t)} \\
&= e^{-\chi_l^2 \tilde{A}_1 - \chi_l^2 \tilde{A}_2 t} \\
&\quad \times \sum_{m,n=0}^{\infty} \frac{(-1)^{m+n}}{m!\,n!}\, \chi_l^{2(m+n)} \tilde{A}_3^m \tilde{A}_4^n e^{-(m+n)\tilde{\eta}t + i(m-n)(\tilde{\omega}t + \tilde{\delta})},
\end{aligned} \tag{58}$$

where

$$\tilde{f}(\tilde{\omega}, t) \equiv \tilde{A}_1 + \tilde{A}_2 t + \tilde{A}_3 e^{i\tilde{\delta}} e^{-(\tilde{\eta} - i\tilde{\omega})t} + \tilde{A}_4 e^{-i\tilde{\delta}} e^{-(\tilde{\eta} + i\tilde{\omega})t}, \qquad (59)$$

and

$$\tilde{A}_1 = \frac{\tilde{\eta}^2 [2\tilde{\eta}\tilde{\omega}\sin\tilde{\delta} + (\tilde{\omega}^2 - \tilde{\eta}^2)\cos\tilde{\delta}]}{(\tilde{\eta}^2 + \tilde{\omega}^2)^2}, \qquad (60)$$

$$\tilde{A}_2 = \frac{\tilde{\eta}^2 (\tilde{\eta}\cos\tilde{\delta} - \tilde{\omega}\sin\tilde{\delta})}{\tilde{\eta}^2 + \tilde{\omega}^2}, \qquad (61)$$

$$\tilde{A}_3 = \frac{\tilde{\eta}^2}{2(\tilde{\eta} - i\tilde{\omega})^2}, \qquad (62)$$

$$\tilde{A}_4 = \frac{\tilde{\eta}^2}{2(\tilde{\eta} + i\tilde{\omega})^2}. \qquad (63)$$

Usually, the values of the parameters $\tilde{\eta}$, $\tilde{\omega}$ and $\tilde{\delta}$ are obtained from a fitting of the numerical results issued from solving the standard Langevin equation with periodic boundary conditions to (57). Moreover, $\chi_l(\Delta\mathbf{K})$ is a generalized shape parameter proposed by the authors to be [44]

$$\chi_l(\Delta\mathbf{K}) \equiv \sqrt{\frac{\Gamma_\nu(\Delta\mathbf{K})}{2\eta}}, \qquad (64)$$

where $\Gamma_\nu(\Delta\mathbf{K})$ represents the inverse of the correlation time and is expressed as

$$\Gamma_\nu(\Delta\mathbf{K}) = \nu \sum_{\mathbf{j}} P_{\mathbf{j}} \left[1 - \cos(\mathbf{j} \cdot \Delta\mathbf{K})\right], \qquad (65)$$

with ν being the total jump rate out of an adsorption site and $P_{\mathbf{j}}$ the relative probability that a jump with a displacement vector $\mathbf{j}$ occurs.

Notice the linear dependence on time in $\tilde{f}$ because of the parameters $\tilde{\eta}$, $\tilde{\omega}$ and $\tilde{\delta}$ are time-independent. This leads to an effective decay rate in (58) given by $\chi_l^2 \tilde{A}_2$, which accounts for the diffusion and causes the intermediate scattering function to vanish at asymptotic times. This scattering function also provides information on the low vibrational motion or T-mode. This fact is better appreciated in the dynamic structure factor which is the time Fourier transform of the intermediate scattering function,

$$S(\Delta\mathbf{K}, \omega) = \frac{e^{-\chi_l^2 \tilde{A}_1}}{\pi} \sum_{m,n=0}^{\infty} \frac{(-1)^{m+n}}{m!\, n!} \chi_l^{2(m+n)} \tilde{A}_3^m \tilde{A}_4^n e^{i(m-n)\delta}$$

$$\times \frac{\chi_l^2 \tilde{A}_2 + (m+n)\tilde{\eta}}{[\omega - (m-n)\tilde{\omega}]^2 + [\chi^2 \tilde{A}_2 + (m+n)\tilde{\eta}]^2}. \qquad (66)$$

This general expression clearly shows that both motions (diffusion and T-mode) cannot be separated at all. The quasielastic or Q-peak is formed by contributions where $m = n$. Analogously, the contributions to the T-mode or T-peaks come from the sums with $n \neq m$. If the Gaussian approximation is good enough, the value of $\tilde{\eta}$ will not be too different from the nominal value of η and, therefore, both peaks will display broadening as η (or λ) increases. As an illustration, in Fig. 1 the widths of the Q-peak for the diffusion of Na atoms on Cu(001) at two different coverages and two different surface temperatures are plotted. As clearly seen, the experimental [45] and theoretical [30, 42] values of the Q-peak width display broadening. Taking into
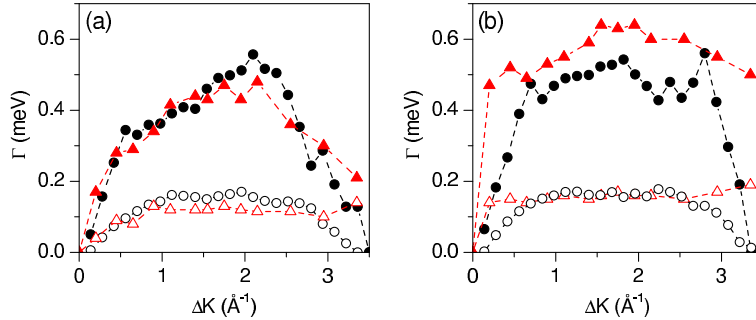
Figure 1. Diffusion of Na atoms on Cu(001). Numerical (triangles) and experimental (circles) dependence of the broadening of the Q-peak on ΔK, at 200 K (open circles and triangles) and 300 K (full circles and triangles) along the azimuth [100] for two different values of the surface coverage: (a) $\theta = 0.064$ and (b) $\theta = 0.106$.

account the preceding discussion, this implies a faster decay rate of the intermediate scattering function with the coverage which should be attributed to a manifestation of the AZE.

5. Conclusions

The characteristic quantum short-time behavior of the observable magnitude (t^2-law) is always present and, contrary to what is widely accepted, this behavior is not always a clear-cut characteristic of the QZE. In general, it depends on the type of measurements carried out during the time evolution of the system. This is true, at least, within this context (activated surface diffusion of interacting adsorbates), where the evolution of the intermediate scattering function in this time regime is governed by friction-free (ballistic) motion. Moreover, within a Markovian framework, the AZE in surface diffusion by corrugated surfaces has been reported by experimental and theoretical works, but it has not been recognized as such.

In this work, we have left on purpose for a future investigation several important points in the surface diffusion and how they are related to the QZE and AZE. First, the diffusion mediated by tunneling. Second, the non-Markovian character of the environment and therefore the role played by the sub-Ohmic and supra-Ohmic regimes. Third, at very short times, the adparticle is mainly inside any of the potential wells of the corrugated surface and the corresponding quantum motion is mainly intra-well within a harmonic potential. This simple model allows us to understand the physics associated with the so-called T-mode (or frustrated translational mode). Recently, QZE and AZE have been shown to occur for the undamped harmonic oscillator in terms of the survival probability [28]. A similar analysis could be carried out in terms of the intermediate scattering function. Fourth, and finally, a true quantum mechanical calculation of the surface diffusion by using the so-called stochastic Schrödinger equation of the quantum theory of open systems [11] could also be carried out. Work in these directions is currently in progress.

Acknowledgments

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