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Abstract
Surface diffusion of small adsorbates is analyzed in terms of the so-called intermediate scattering function and dynamic structure factor, observables in experiments using the well-known quasielastic Helium atom scattering and Helium spin echo techniques. The linear theory applied is an extension of the neutron scattering due to van Hove and considers the time evolution of the position of the adsorbates in the surface. This approach allows us to use a stochastic trajectory description following the classical, quantum and Bohmian frameworks. Three different regimes of motion are clearly identified in the diffusion process: ballistic, Brownian and intermediate which are well characterized, for the first two regimes, through the mean square displacements and Einstein relation for the diffusion constant. The Langevin formalism is used by considering Ohmic friction, moderate surface temperatures and small coverages. In the Bohmian framework, analyzed here, the starting point is the so-called Schrödinger-Langevin equation which is a nonlinear, logarithmic differential equation. By assuming a Gaussian function for the probability density, the corresponding quantum stochastic trajectories are given by a dressing scheme consisting of a classical stochastic trajectory followed by the center of the Gaussian wave packet, and issued from solving the Langevin equation (particle property), plus the time evolution of its width governed by the damped Pinney differential equation (wave property). The Bohmian velocity autocorrelation function is the same as the classical one when the initial spread rate is assumed to be zero. If not, in the diffusion regime, the Brownian-Bohmian motion shows a weak anomalous diffusion.

1. Introduction
Surface diffusion is one of the most elementary dynamical process occurring on surfaces and a preliminary step to more complex surface phenomena. It is a very active field of surface science from fundamental as well as technological (catalysis, crystal growth, energy storage, etc.) points of view. Typically, this diffusion process is analyzed as in spectroscopic experiments where a probe particle is interacting perturbatively with a given system at thermal equilibrium with a reservoir (or thermal bath) and measuring its response. According to van Hove’s theory for neutron scattering by crystal and liquids [1–3], the nature of particles (photons, neutrons, electrons or atoms) probing systems of moving and interacting particles (adsorbates) is largely irrelevant when the Born approximation is assumed, reducing this scattering event to a typical statistical mechanics problem. The corresponding linear response is then determined by the spectrum of the spontaneous fluctuations of the reservoir as established by the very well-known fluctuation-dissipation theorem [4]. Information provided by the experiment together with a theoretical support or theory behind can allow us to better understand the dynamics as well as extract valuable information for molecular interactions (adsorbate-substrate and adsorbate-adsorbate interactions) within the general framework of stochastic processes. A very large amount of information about the diffusion process in surfaces has been gathered along the last twenty eight years from the well-known review paper by Gomer [5]. For fast diffusion motions, we are going to focus on He atoms as nondestructive probe particles used in two types of experiments, quasielastic He atom scattering (QHAS) [6] and He spin echo spectroscopy (HeSE) [7]. These time of flight techniques are sensitive to surface processes on the length and time scales on which single atoms diffusion occurs (length scales between around $10^{-10}$ up to $10^{-8}$
meters and time scales going from around $10^{-12}$ up to $10^{-8}$ seconds). Time of flight spectra are usually converted to energy transfer scale allowing a frequency analysis of the surface phonons as well as slow motions of the adsorbates. Angular (around $0.3^\circ$) as well as velocity (around 1%) resolutions are very small covering a large dynamical range in intensity; much better for the HeSE technique. Typical He velocities are less than $3 \times 10^5$ m/sec. The practical limit of these techniques lies in the velocity spread in the beam but, with the spin-echo method, one measures velocity changes of individual atoms rather than the velocity change with respect to the mean incident velocity. The major challenges facing these techniques are to analyze and extract valuable information from the observed line shapes as well as time behavior.

Van Hove’s theory of neutrons was generalized to atom surface scattering within the transition matrix formalism [8] and the Chudley-Elliott approximation [9, 10]. In surface diffusion problems, most of work is based on the Langevin equation formalism which is widely used when dealing with stochastic processes, as the diffusion one. Thanks to Caldeira and Leggett, this formalism can be derived from a Hamiltonian which is split into three parts describing the dynamics of the system, the thermal bath or reservoir and their mutual interaction [11, 12]. The surface is usually considered to be corrugated and, at a given temperature, is replaced by an infinite number of harmonic oscillators, mimicking the phonon dynamics as well as the mechanism of dissipation. An Ohmic friction is typically assumed and the damping mechanism is mainly due to acoustic phonons. For barriers greater than $3k_B T$ ($k_B$ is the Boltzmann factor and $T$ the surface temperature), the diffusion process is activated and the instantaneous jump picture works quite well. Activation barrier heights are extracted from an Arrhenius plot of the diffusion coefficient. Large discrepancies are obtained when comparing the experimental or theoretical results to the classical transition state theory [13] due to the existence of long jumps at high surface temperatures, multiple jumps where the Chudley-Elliott model does not apply. A quantum and classical Kramer’s theory was developed to overcome such discrepancies [14–18], leading to analytic expressions for diffusion coefficients, escape rates and hopping distributions within the Langevin formalism.

Whenever the diffusing atoms are light such as hydrogen or deuterium, quantum effects are present. It is known that quantum diffusion coefficients can be smaller or greater than the classical ones [15]. For example, if the substrate is Pt(111), Arrhenius plots of the diffusion constant and overall hoping rate show clearly a region where deviations from the linearity are observed, which is characteristic of the classical transition state theory (TST) [19]. This deviation starts occurring at low temperatures (below 90 K) and the theory of dissipative tunneling [20], based on the quantum TST, is sufficient to be applied. The flattening of the Arrhenius plot at the crossover temperature is however not observed which is a feature of deep tunneling [12]. In this regime, Grabert and Weiss accounted for quantum diffusion in periodic potentials [21, 22] by using the so-called bounce technique together with the Chudley-Elliott model, leading to analytic expressions for transition rates and diffusion constants in an incoherent tunneling regime. This theoretical framework was successfully applied to this diffusion problem [23] for low coverages. In any case, as far as we know, this interesting and particular quantum dynamics has not been analyzed in the Langevin formalism, that is, by using quantum stochastic trajectories.

In this work, a natural theoretical approach considering quantum trajectories is analyzed within Bohmian mechanics which is being more and more applied to conservative and open problems [24–27]. Recently, an extension to open quantum systems (see, stochastic processes), within the nonlinear, logarithmic Schrödinger-Langevin (SL) equation framework derived by Kostin [28], has been proposed under the presence or not of a continuous measurement [27, 29] and for nonlinear dissipation [30]. The resulting quantum stochastic trajectories have been applied to simple systems such as the damped free particle, linear potential, and harmonic oscillator[31] and dissipative quantum tunnelling through an inverted parabolic barrier under the presence of an electric field [32] when analysing the classical-quantum transition of trajectories in the gradual decoherence process. These works introduced the so-called scaled trajectories having as a particular case the Bohmian ones. By assuming a time-dependent Gaussian ansatz for the probability density, theses scaled trajectories are written as a sum of a classical trajectory followed by the center of the Gaussian wave packet (a particle property) plus a term containing the time evolution of its width (a wave property) within of what has been called dressing scheme [27].

The organization of this work is as follows. In section 2, the general theory for neutron scattering due to van Hove is briefly reviewed to better understand the extension to atom scattering. Two main observable functions the so-called dynamic structure factor and intermediate scattering function are introduced and written in terms of adsorbate trajectories. These trajectories are briefly presented and discussed within the general Langevin formalism starting from the so-called Caldeira-Leggett Hamiltonian in the classical and quantum frameworks, being the adsorbate coverage introduced by a collisional friction. In this way, the Bohmian framework developed afterwards in terms of the Schrödinger-Langevin equation is easier to follow. In section 3, three main different regimes in the diffusion process are well characterized and analyzed in the classical and quantum domains: the ballistic, Brownian (or diffusion) and intermediate regimes. For each case, the corresponding trajectories are analyzed in terms of the mean square displacements and velocity autocorrelation functions leading to analytical
expressions for the observable lines shapes. In the second regime, the Brownian–Bohmian motion shows a weak anomalous diffusive behavior.

2. General theory

2.1. Observables

In 1954, van Hove [1] established the differential cross section of the scattering of slow neutrons by a system of interacting particles in terms of the generalized pair distribution function, the so-called \( G(\mathbf{r}, t) \) function of van Hove (with \( \mathbf{r} \) being a position vector and \( t \) a time interval). This \( G \) function is a natural extension of the standard pair distribution function \( g(\mathbf{r}) \) well known, for example, in liquids with \( G(\mathbf{r}, 0) = g(\mathbf{r}) \). Moreover, \( G \) describes the correlation between a particle in position \( \mathbf{r} + \mathbf{r}' \) at \( t + t' \) and a particle in position \( \mathbf{r}' \) at time \( t' \). In the Born approximation or first order perturbation theory, the scattering problem is reduced essentially to a problem in statistical mechanics [1–3] where the nature of the scattered particles (neutrons, light, atoms, etc.) and details of the interaction potential are irrelevant. In this formalism, the linear response of the system implies that it is determined entirely by the properties exhibited by the system in the absence of probe particles. This differential cross section can also be written in terms of the independent variables associated with the momentum transfer, \( \hbar \mathbf{k} \), and energy transfer \( \hbar \omega \) as

\[
\frac{d^2 \mathcal{R}(\mathbf{k}, \omega)}{d\Omega d\omega} \propto S(\mathbf{k}, \omega) = (2\pi)^{-1}N \int e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} G(\mathbf{r}, t) d\mathbf{r} dt
\]

(1)

providing the probability that the probe particles scattered from the diffusing system reach a certain solid angle \( \Omega \) in an interval of outgoing energy \( \hbar \omega \). The response function or line shape \( S(\mathbf{k}, \omega) \) is also termed the scattering law or dynamic structure factor (DSF) where \( N \) is introduced for convenience and represents the number of interacting particles in the system under study. The spatial Fourier transform of the \( G \)-function

\[
I(\mathbf{k}, t) = \int e^{i\mathbf{k} \cdot \mathbf{r}} G(\mathbf{r}, t) d\mathbf{r}
\]

(2)

is called intermediate scattering function (ISF) and therefore \( S \) and \( I \) are related by the inverse Fourier transform in time. These functions are easily showed to be expressed in terms of the density–density correlation function where the particle density operator is defined as

\[
\rho(\mathbf{k}, t) = \sum_j \hat{b}(\mathbf{r} - \mathbf{r}_j(t))
\]

(3)

In this work, we are going to describe on the QHAS technique probing the dynamics of adsorbates or adparticles on surfaces [1,3]. With this technique, at thermal energies, time–of–flight measurements of the probe particles are converted to energy transfer spectra given by the dynamics structure factor. In this scattering, He atoms present an energy exchange \( \hbar \omega = E_{\text{final}} - E_{\text{initial}} \) and a parallel (to the surface) momentum transfer \( \mathbf{K} = \mathbf{K}_{\text{final}} - \mathbf{K}_{\text{initial}} \) (it is standard to express variables projected on the surface as capital letters for position \( \mathbf{R} = (x, y) \) and parallel momentum \( \mathbf{K} \)). The prominent peak around the zero energy transfer, the so-called quasi–elastic peak (Q–peak), provides direct information of adsorbate diffusion. Additional weaker peaks at low energy transfers around the Q–peak are also observed and attributed to the parallel frustrated translational motion of some adsorbates (the so-called T–mode) and to surface phonons excitations. Long distance and time correlations are extracted from the scattering law when considering small values of \( \mathbf{K} \) and \( \hbar \omega \), respectively. The nature of the adsorbate–substrate and adsorbate–adsorbate interactions can also be known from the scattering law. In this context, the dynamic structure factor is usually expressed as

\[
S(\mathbf{K}, \omega) = (2\pi)^{-1}N \int e^{-i\mathbf{K} \cdot \mathbf{R}} I(\mathbf{K}, t) dt,
\]

(4)

with

\[
I(\mathbf{K}, t) \equiv \frac{1}{N} \left\langle \sum_j e^{-i\mathbf{K} \cdot \mathbf{R}_j(0)} e^{i\mathbf{K} \cdot \mathbf{R}_j(t)} \right\rangle
\]

(5)

where the brackets denote an ensemble average and \( \mathbf{R}_j(t) \) the position vector of the \( j \) adparticle at time \( t \) on the surface. This intermediate scattering function is precisely what is directly measured from the HeSE technique [7] which is quite similar to the well known neutron spin echo one.

At this point, it is important to stress the main difference between neutron and Helium scattering. The \( G \)-function can naturally be split into a part describing the correlations between the same particle, \( G_o \) and distinct particles, \( G_{ij} \), where the crossing terms are taken into account. Thus, the full pair correlation function can then be expressed as
According to its definition, \( G_i(\mathbf{R}, 0) = \delta(\mathbf{R}) \) which the Dirac delta function gives the presence of the particle at that position and \( G_d(\mathbf{R}, 0) = g(R) \). At low adparticle concentrations (coverage, \( \theta \ll 1 \)), when interactions among adsorbates can be neglected because they are far apart from each other, the main contribution to (6) is \( G_i \) (particle–particle correlations are negligible and \( G_d \approx 0 \)). On the contrary, at high coverages, \( G_d \) is expected to have a significant contribution to (6). As a result of this splitting, the intermediate scattering function can also be expressed as a sum of distinct \( (I_d) \) and self \( (I) \) functions. Following neutron scattering language, the corresponding Fourier transforms of \( f \) and \( I \) give the so-called coherent scattering law, \( S(\mathbf{K}, \omega) \) and incoherent scattering law \( S_i(\mathbf{K}, \omega) \), respectively. In QHAS and HeSE experiments, only coherent scattering is observed.

After equation (5), the ISF contains information about the dynamics of the adsorbates through \( \mathbf{R}_i(t) \). This dynamics is open since the surface can be seen as a reservoir or thermal bath at a given temperature, leading to dissipation and stochasticity within a classical or quantum framework. In the following, we are going to focus on the nature of the adsorbate-adsorbate and adsorbate-substrate interactions. In any case, a proper comparison between the experimental and theoretical observables (issued from any theoretical method) has to be carried out through a convolution integral which takes into account the response of the apparatus which is usually assumed a Gaussian function.

### 2.2. Classical stochastic trajectories

For heavy adsorbates, the time-dependent position vectors can be obtained from classical stochastic trajectories. As mentioned above, if the coverage is very small, the adsorbate-adsorbate interaction is negligible and the dynamics can be well described only by the self part of the \( G \)-function, \( G_i \). The main interaction is then the adsorbate-substrate interaction as well as the thermal fluctuations of the surface through a random force or noise. In the literature, the standard Hamiltonian used is that proposed by Magalinskij [33] and Caldeira and Leggett [11] written in this context as [18, 34]

\[
H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + V(x, y) + \frac{1}{2} \sum_{j=1}^{N} \left[ \frac{p_{x_j}^2}{m_j} + m_j \omega_j^2 \left( x_j - \frac{c_{x_j}}{m_j \omega_j^2} x \right)^2 \right] + \frac{1}{2} \sum_{j=1}^{N} \left[ \frac{p_{y_j}^2}{m_j} + m_j \omega_j^2 \left( y_j - \frac{c_{y_j}}{m_j \omega_j^2} y \right)^2 \right],
\]

where \((p_x, p_y)\) and \((x, y)\) are the adparticle momenta and positions with mass \( m \) and \((p_{x_j}, x_j)\) and \((p_{y_j}, y_j)\) with \( i = 1, \ldots, N \) are the momenta and positions of the bath oscillators (phonons) for each degree of freedom, with mass and frequency given by \( m_i \) and \( \omega_i \), respectively. Phonons with polarization along the \( z \)-direction are not considered. The adsorbate-substrate interaction \( V(x, y) \) is a periodic function describing the surface corrugation at zero temperature. The Hamiltonian (7) is not translational invariance since the term coupling the parallel motions to the phonon bath in both directions is not periodic but linear [35]. However, this Hamiltonian is still used because it leads to the correct generalized Langevin equation once the bath degrees of freedom are eliminated

\[
\begin{align}
mx(t) + m \int_0^t \gamma_x(t - t')\dot{x}(t') \, dt' + \frac{\partial V(x, y)}{\partial x} &= \xi_x(t), \\
m\dddot{y}(t) + m \int_0^t \gamma_y(t - t')\dddot{y}(t') \, dt' + \frac{\partial V(x, y)}{\partial y} &= \xi_y(t),
\end{align}
\]

where the friction coefficients are defined through the cosine Fourier transform of the spectral densities,

\[
\gamma_i(t) = \frac{2}{\pi m} \int_0^\infty \frac{J_i(\omega)}{\omega} \cos \omega t \, d\omega,
\]

with \( i = x, y \) and

\[
J_i(\omega) = \frac{\pi}{2} \sum_{j=1}^{N} \frac{c_j^2}{m_j \omega_j^3} [\delta(\omega - \omega_i)].
\]

The nonhomogeneity of (8) represents a fluctuating or random force \( \xi \) for each degree of freedom which depends on the initial position of the system and initial positions and momenta of the oscillators of each bath according to [12].

\[ G(\mathbf{R}, t) = G_i(\mathbf{R}, t) + G_d(\mathbf{R}, t). \]
\[ \xi_x(t) = -\sum_j \gamma_j \left\{ x_j(0) + \frac{c_{ij}(0)}{m_j \omega_{ij}} x(0) \right\} \cos(\omega_{ij} t) + \frac{\eta_j(0)}{m_j \omega_{ij}} \sin(\omega_{ij} t) \right\}, \]  

and

\[ \xi_y(t) = -\sum_j \gamma_j \left\{ y_j(0) + \frac{c_{ij}(0)}{m_j \omega_{ij}} y(0) \right\} \cos(\omega_{ij} t) + \frac{\eta_j(0)}{m_j \omega_{ij}} \sin(\omega_{ij} t) \right\}. \]

If Ohmic friction is assumed, \( \gamma_i(t) = 2 \gamma_i \delta(t) \), where \( \gamma_i \) is a constant and \( \delta(t) \) is Dirac’s \( \delta \)-function. Equations (8) then reduce to two coupled standard Langevin equations (the \( \delta \)-function counts only one half when the integration is carried out from zero to infinity)

\[ m \ddot{x}(t) + m \gamma_x \dot{x}(t) + \frac{\partial V(x, y)}{\partial x} = \xi_x(t), \]  

\[ m \ddot{y}(t) + m \gamma_y \dot{y}(t) + \frac{\partial V(x, y)}{\partial y} = \xi_y(t). \]

within the Markov approximation. The properties of noise are: (i) \( \langle \xi_i(t) \rangle = 0 \) (zero mean) and (ii) \( \langle \xi_i(0) \xi_j(\tau) \rangle = m k_B T \delta_{ij} \), with \( i = x, y \). The corresponding classical stochastic trajectories are given by \( R(t) = (x(t), y(t)) \). When a flat surface is considered, \( V(x, y) = 0 \) and the standard Brownian motion takes place.

At higher coverages, adsorbate–adsorbate interactions can no longer be neglected and typically pairwise interaction potentials are usually introduced in Langevin molecular dynamics simulations [36]. These simulations always result in a relatively high computational cost due to the time spent by the codes in the evaluation of the forces among particles. This problem is even worse when working with long–range interactions, since a priori they imply that one should consider a relatively large number of particles to numerical convergency. An alternative approach is to consider a purely stochastic description for these interactions [37–39] through what is called the interacting single adsorbate (ISA) approximation in a two-bath model. The motion of a single adsorbate is then modelled by a series of random pulses within a Markovian regime (i.e., pulses of relatively short duration in comparison with the system relaxation and acting during a long period of time). These pulses simulate the collisions among adsorbates and are described by means of a white shot noise. In this way, a typical molecular dynamical simulation problem involving \( N \) adsorbates is substituted by the dynamics of a single adsorbate where the action of the remaining \( N - 1 \) adparticles is replaced by a random force given by the white shot noise. The surface coverage is related to a collisional friction providing the average number of collisions per unit time, \( \gamma_0 \). The probability of observing a given number of collisions, after an elapsed time, follows closely a Poisson distribution. The adsorbate is then subject to two uncorrelated white noises, one for each degree of freedom of the surface.

In this way, differences between self and distinct time–dependent pair correlation function do not exist but equations (1) and (2) still hold. The ISF can now be rewritten as

\[ I(K, t) \equiv \langle e^{-iK[R(t) - R(0)]} \rangle = \langle e^{-iK \int_0^t \dot{r}(t') \, dt'} \rangle. \]

Within the so–called Gaussian approximation [40], which is exact when the velocity correlations at more than two different times are negligible, equation (14) is expressed again as a second order cumulant expansion in \( K \)

\[ I(K, t) \approx e^{-K^2 \int_0^t \dot{r}(t') \, dt'} \]

with

\[ C_K(\tau) \equiv \langle v_K(0) v_K(\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T v_K(t) v_K(t + \tau) \, dt \]

being the velocity autocorrelation function (VAF) projected onto the direction of the parallel momentum transfer. The velocity is considered to be a stationary stochastic process. This autocorrelation function decays with time, allowing us to define a characteristic time, the so–called correlation time, as

\[ \tau \equiv \frac{1}{\langle \dot{v}^2 \rangle} \int_0^\infty C_K(\tau) \, d\tau, \]

where \( \sqrt{\langle \dot{v}^2 \rangle} = \sqrt{k_B T/m} \) is the average thermal velocity in one dimension, along the direction given by \( K \), \( m \), \( T \) and \( k_B \) being the adsorbate mass, surface temperature and Boltzmann constant, respectively.

The advantage of this approximation consists in providing a direct expression for the coherent scattering which is observed when He atoms are used as probe particles. The dynamical structure factor depends on the
VAF through the intermediate scattering function if the Gaussian approximation is also assumed. Two extreme regimes are well characterized in this context, the ballistic diffusion, at very small times ($\eta t \ll 1$), which is a frictionless motion and the diffusion regime, at very long times ($\eta t \gg 1$), when the thermal equilibrium is already reached and details of the surface such as its corrugation is no longer important. Analytical expressions for line shapes in these two extreme regimes are easily derived due to have simple velocity autocorrelations functions [34].

2.3. Quantum Langevin equation

When considering light adsorbates, quantum mechanics in the Heisenberg picture should be applied. Quantum vector positions in equations (5) and (14) are then seen as operators. At two different times, they do not commute. However, it is possible to factorize the ISF in two factors due to the disentangling theorem according to $e^{A}e^{B} = e^{A+B}g^{A, B}/2$ which holds when the corresponding commutator is a c-number. Thus, if $A = iK \cdot R(0)$ and $B = -iK \cdot R(t)$ then [34]

$$I_1(K, t) = I_2(K, t)I_1(K, t)$$

with the $I_2$-factor is given by equation (15). The $I_1$ factor can be readily obtained from the formal solution of the corresponding Langevin equation (if the Ohmic friction is assumed) given by equation (13)

$$R(t) = R(0) + P(0)\Phi(\eta t) + \frac{1}{m\eta^2} \int_0^t \Phi(\eta t - \eta t') [F(R(t')) + \delta E_i(t')] dt'$$

where $\Phi(x) = 1 - e^{-x}$, $F(R) = -\nabla_{R} V_{r} \delta F_i(t)$ is the random force including the Gaussian and shot noises and $R(0)$ and $P(0)$ are the initial conditions for the position and momentum, respectively. The commutator involved in $I_1$ is $i\hbar$ since $[R(0), P(0)] = i\hbar$, $[R(0), F] = i\hbar \partial F / \partial P(0) = 0$ and $[R(0), \delta F_i] = 0$ if the noise is assumed to be classical (moderate surface temperatures). Thus,

$$I_1(K, t) = e^{iE_i\Phi(\eta t)/\hbar}$$

where $E_i = \hbar^2K^2/2m$ is the adsorbate recoil energy, $I_1$ is a time dependent phase factor which is less and less important when the adsorbate mass and the friction coefficient increase.

2.4. Bohmian stochastic trajectories

Once the classical and quantum Langevin approach have been briefly reviewed, the Bohmian formalism is easier implemented and understood. An alternative way to describe the quantum diffusion motion is through Bohmian (or quantum) stochastic trajectories. For this goal, we start from the so-called SL o Kostin equation [28]. In 1972, Kostin derived heuristically this equation from the standard one-dimensional Langevin equation. In this context, from equation (13), the corresponding nonlinear two-dimensional Schrödinger equation is written as

$$i\hbar \frac{\partial \Psi(R, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(R, t) + [V(R) + V_r(R, t) + V_D(R, t) + G(t)]\Psi(R, t),$$

where the random potential is given by

$$V_r(R, t) = -R \cdot F_i(t),$$

the damping potential by

$$V_D(R, t) = -i\eta \ln \left( \frac{\Psi(R, t)}{\Psi^*(R, t)} \right)$$

and

$$G(t) = \frac{i\hbar}{2} \int \Psi^*(R, t) \ln \left( \frac{\Psi(R, t)}{\Psi^*(R, t)} \right) \Psi(R, t) dR$$

is a time dependent function resulting from the average value of $V_D$ by integration with respect to the position variable. The norm of the wave function is conserved and the expectation value of the corresponding nonlinear Hamiltonian is, as usual, the sum of the kinetic and potential energies at any time. The SL equation does not fulfill the superposition principle. If the wave function is written in polar form as

$$\Psi(R, t) = \phi(R, t)e^{iS(R, t)/\hbar}$$

where $\phi(R, t)$ and $S(R, t)$ are real valued functions and then is substituted into equation (21), the resulting Schrödinger-Langevin-Bohm (SLB) equation reads as [27]
Now, by writing the real and imaginary parts separately, we readily reach the continuity equation
\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0
\] 
with \( \rho = \phi^2 \) and the velocity field defined by \( \mathbf{v} = \nabla S/m \), and the quantum dissipative Hamilton-Jacobi equation given by
\[
\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} + \eta \mathbf{v} = -\frac{1}{m} \nabla (V + V_t + Q),
\] 
\( Q \) being the quantum potential defined in terms of \( \rho \) as follows
\[
Q \equiv -\frac{\hbar^2}{2m} \frac{\nabla^2 \rho^{1/2}}{\rho^{3/2}} = \frac{\hbar^2}{4m} \left[ \frac{1}{2} \left( \frac{\nabla \rho}{\rho} \right)^2 - \frac{\nabla^2 \rho}{\rho} \right].
\]
If a Gaussian ansatz is assumed for the probability density
\[
\rho(\mathbf{R}, t) = \frac{1}{\sqrt{2\pi \delta(t)^2}} e^{-(\mathbf{R} - \mathbf{q}(t))^2/2\delta(t)^2},
\]
where \( \delta(t) \) and \( \mathbf{q}(t) \) are the width and the center of the wave packet, respectively. From equation (27), the velocity field turns out to be
\[
\mathbf{v}(\mathbf{R}, t) = \frac{\dot{\delta}(t)}{\delta(t)} (\mathbf{R} - \mathbf{q}(t)) + \dot{\mathbf{q}}(t)
\]
where the dot on the variable means time derivation. The time integration of this velocity field is straightforward leading to the equation for the Bohmian stochastic trajectories
\[
\mathbf{R}(t) = \mathbf{q}(t) + (\mathbf{R}(0) - \mathbf{q}(0)) \frac{\delta(t)}{\delta(0)}.
\]
Equation (32) is given by a sum of a particle property through a classical trajectory followed by the center of the wave packet plus a wave property involving the time evolution of its width. This scheme is known as dressing scheme [27] which is issued only from the continuity equation (27). Now, substitution of equation (31) into equation (28) and after lengthy but straightforward calculations, we reach
\[
\left[ \frac{\delta(t) + \eta \dot{\delta}(t) + \omega^2 - \frac{\hbar^2}{4m \delta^2(t)} (\mathbf{R} - \mathbf{q}(t))^4}{\delta(t)} \right] \mathbf{R} - \mathbf{q}(t) + \frac{1}{m} \nabla (V + V_t)_{\mathbf{q}} = 0,
\]
leading to the standard Langevin equation for the center of the Gaussian wave packet when a Taylor expansion of the interaction potential around \( \mathbf{q} \) up to second order is developed
\[
\dot{\mathbf{q}}(t) + \eta \mathbf{q}(t) + \frac{1}{m} \nabla (V + V_t)_{\mathbf{q}} = 0
\]
and the so-called dissipative or damped Pinney equation for its width
\[
\ddot{\delta}(t) + \eta \dot{\delta}(t) - \frac{\hbar^2}{4m \delta^3(t)} = 0.
\]
The solution of this nonlinear differential equation was given by Pinney for the conservative case [41] \( \eta = 0 \) when \( \hbar \) is replaced by an arbitrary constant.

Zander et al [42] have also used the same ansatz to solve the Kostin equation under the presence of a continuous measurement. This procedure can also be seen as the ‘wave packet approximation’ due to Gutzwiller [43] where it is supposed that within the spatial range where the wave function is appreciably different from zero, the interaction potential \( V \) changes slowly enough so that it can be approximated to second order.

The commutation rule for the positions at different times does not work in this context. Moreover, the ISF given by equation (5) can be replaced by equation (14) within the ISA approximation and equation (15) when assuming the Gaussian approximation. Within this approximation, the VAF is the key function to be known or evaluated. The velocity of the quantum stochastic trajectories (32) is readily obtained to be
\[ v(R, t) = \frac{\delta(t)}{\delta(0)}(R(0) - q(0)) + \dot{q}(t) \]  

(36)

and the VAF along the \( K \) direction is then

\[ C_K(\tau) \equiv \langle v_K(0) v_K(\tau) \rangle = \langle \dot{q}(0) \dot{q}(\tau) \rangle_K + \langle (R(0) - q(0))^2 \rangle_K \frac{\delta(0)}{\delta^2(0)} \delta(t) \]  

(37)

where cross correlations are zero due to the statistical independence. It should be noticed that if the initial spread rate is assumed to be zero, \( \delta(0) = 0 \), the VAF behaves as in the classical regime. The quantum stochastic dynamics involved in the surface diffusion process within the Bohmian framework and with the Gaussian ansatz is thus reduced to solve equations (34) and (35).

3. Applications

In surface diffusion, three different regimes of motion can be clearly distinguished. First, at very short times, \( \eta t \ll 1 \), the motion is frictionless giving place to the so-called ballistic regime. Second, at very long times, \( \eta t \gg 1 \), the thermodynamical equilibrium has already been reached and we speak about the Brownian or diffusion regime and where the interaction with the surface is no longer relevant. And, finally, we have the intermediate regime where the thermodynamical equilibrium is still far to be reached. We pass now to analyze these three regimes within the classical, quantum and Bohmian frameworks for comparison and provide analytical expressions (if possible) of the lines shapes within the Gaussian and ISA approximations.

3.1. The ballistic regime

Due to the frictionless motion taking place at very short times (less than the mean free time), the corrugation of the surface plays no role in the surface dynamics. In the classical framework, the VAF is expected to be constant with time and given by the thermal velocity along the \( K \) direction according to

\[ C_K(\tau) = \langle v_K^2(0) \rangle = \frac{k_B T}{m} \]  

(38)

From equation (15), we have

\[ I(K, t) \propto e^{-K^2/\langle v_K^2(0) \rangle t^2/2} \]  

(39)

and from equation (4)

\[ S(K, \omega) \propto \frac{1}{|K| \sqrt{\langle v_K^2(0) \rangle}} e^{-\omega^2/2K^2\langle v_K^2(0) \rangle}, \]  

(40)

which are the Gaussian behaviors predicted for both observables, the ISF and DSF or line shape. This regime has been observed for a two dimensional free gas of Xe atoms on Pt(111) [44, 45]. Thus, for times much shorter than the mean collision time, the adsorbate displays a free motion showing a dynamical coherence since no memory lost of its velocity takes place. Furthermore, the full width at half maximum (FWHM) of the line shape is linearly dependent on the wave vector transfer, \( \Gamma' \propto \sqrt{\langle v_K^2(0) \rangle} |K| \). In this ballistic regime, the mean square displacement (MSD) of the classical stochastic trajectories is known to be characterized by

\[ \langle (q(t) - q(0))^2 \rangle \simeq \frac{k_B T}{m} t^2 \]  

(41)

showing a quadratic behavior with time.

In the quantum Langevin framework, the ISF is given by equation (18) together with equations (15) and (20). As mentioned above, \( I_1 \) is a time dependent phase factor. In the limit of small times, \( \Phi(\eta t) \sim \eta t \) and

\[ I_1(K, t) = e^{iE_h t / h}. \]  

(42)

The second factor \( I_2 \) is similar to the classical case and therefore

\[ I(K, t) \propto e^{iE_h t / h} e^{-K^2/\langle v_K^2(0) \rangle t^2/2}, \]  

(43)

and

\[ S(K, \omega) \propto \frac{1}{|K| \sqrt{\langle v_K^2(0) \rangle}} e^{-\omega^2/2K^2\langle v_K^2(0) \rangle}. \]  

(44)

The Gaussian lineshape is thus shifted by the recoil energy whereas the FWHM is the same as before.

In the Bohmian framework, the starting point is equation (37). At very short times, the adsorbate represented by a Gaussian function follows a free motion whose center is ruled by the simple differential equation
and its width is governed by the nondissipative Pinney equation
\[\dot{\delta}(t) - \frac{\hbar^2}{4m^2\delta^3(t)} = 0.\]

The solution of this nonlinear differential equation is \[\delta(t) = \delta(0) \left(1 + \frac{\hbar^2 t^2}{8m^2\delta^3(0)}\right)^{1/2}.\]

In order to have the width contribution in equation (37), we can assume, for example, that \(\dot{\delta}(0) < \delta(0)\) (that is, the initial spreading rate is smaller than its initial width) leading, in the so-called Fresnel or short time regime [26], to
\[\delta(t) \approx \delta(0) + \frac{\hbar^2 t^2}{8m^2\delta^3(0)}\]

where the spreading increases quadratically with time. Thus, in the ballistic regime, and after equation (32), the Bohmian stochastic trajectories projected on \(K\) have the expression
\[R(t) \approx vt - (R(0) - q(0))\left(1 + \frac{\hbar^2 t^2}{8m^2\delta^3(0)}\right)\]

where \(v\) is the constant velocity of the adsorbate, \(q(0)\) gives the initial condition for the center of the Gaussian wave packet and \(R(0)\) is generated from the assumed initial Gaussian wave function.

On the other hand, the VAF along the \(K\) direction is expressed according to equation (37) as
\[C_K(\tau) = \langle v_K^2(0) \rangle + \langle (R(0) - q(0))^2 \rangle_K \delta(0) + \frac{\hbar^2}{8m^2\delta^3(0)}\]

and from equation (15), we have
\[I(K, t) \propto e^{-K^2f(K, \delta(0))}t^2/2\]

and from equation (4)
\[S(K, \omega) \propto \frac{1}{|K|\sqrt{f(K, \delta(0))}} e^{-\omega^2/2K^2f(K, \delta(0))},\]

where
\[f(K, \delta(0)) = \langle v_K^2(0) \rangle + \langle (R(0) - q(0))^2 \rangle_K \delta(0)\]

where only the first term in equation (49) has been considered in order to keep constant the velocity autocorrelation function which is the key point in the ballistic regime. The Gaussian functions thus obtained are different from those of the classical case except, as mentioned before, for the case where \(\delta(0) = 0\). The commutation rule for the positions at different times is replaced, in this formalism, by the statistical choice of \(K(0)\).

Finally, in this regime, the MSD of the Bohmian or quantum stochastic trajectories is characterized by
\[\langle |R(t)|^2 \rangle \simeq \frac{k_B T}{m} t^2 + \langle (R(0) - q(0))^2 \rangle \delta(0) + \frac{\hbar^2 t^2}{4m^2\delta^3(0)}\]

showing as expected a quadratic behavior with time.

3.2. The Brownian or diffusion regime

In this regime, as mentioned above, the thermodynamical equilibrium is already reached playing no role the details of the surface such as the corrugation and the interaction potential. This takes place at long times, that is, when \(\eta \Gamma \gg 1\), dynamics. After Doob's theorem [47], the classical VAF is now given by
\[C_K(\tau) = \langle v_K^2(0) \rangle e^{-\eta} = \frac{k_B T}{m} e^{-\eta}\]

which tell us that the corresponding correlation is decreasing exponentially with time. The ISF and DSF in this classical framework are well known and given by [34]
\[ I(K, t) = e^{-\chi \left( e^{-\eta t} + \eta - 1 \right)} \]  

and

\[ S(K, \omega) = \frac{e^{\chi^2}}{\pi} \sum_{n=0}^{\infty} (-1)^n \frac{\chi^{2n}}{n!} \frac{(\chi^2 + n)\eta}{\omega^2 + \eta^2(\chi^2 + n)^2} \]  

respectively, where the so-called shape parameter \( \chi \) is defined by

\[ \chi = \frac{K}{\eta} \sqrt{\langle \chi^2(0) \rangle} = K \tilde{I} \]  

which governs the dynamical coherence of the diffusion process. In this expression, \( \tilde{I} \) is the mean free path. It is well known that the time asymptotic behavior of the MSD gives the diffusion coefficient through Einstein’s relation

\[ D = \lim_{t \to \infty} \frac{1}{4t} \langle |q(t) - q(0)|^2 \rangle = \lim_{t \to \infty} \int_0^t dt' \langle v_K(0)v_K(t') \rangle = \frac{k_B T}{m \eta}. \]  

The information about \( D \) can also be extracted from the observable ISF and DSF. In this diffusion regime, we have that \( \chi \ll 1 \) and the ISF is given by a time exponential function

\[ I(K, t) = e^{-K^2 \Delta t} \]  

and the DSF by a single Lorentzian function

\[ S(K, \omega) \propto \frac{K^2 \Delta}{\omega^2 + K^2 \Delta^2} \]  

which its FWHM is \( \Gamma = 2D K^2 \). Interestingly enough, in the extreme opposite case, \( \chi \gg 1 \), we approach the ballistic regime already discussed previously. In general, the continuous variation of the \( \chi \)-parameter can also be seen as a simple way to define the surface dynamical regime. When decreasing \( \chi \), the corresponding DSF or line shape becomes narrower and narrower. This gradual change of line shape is known as the motional narrowing effect \cite{4}, going from a Gaussian to a Lorentzian line shape for the two extreme cases studied so far.

In the quantum Langevin framework, it has been shown \cite{34} that the VAF is given by

\[ C_K(t) = \left( 1 \frac{m \beta}{\hbar} e^{-\eta} \right) - \frac{2}{m \beta} \sum_{n=1}^{\infty} \frac{\nu_n e^{-\nu_n t} - \eta e^{-\eta t} - \nu_n e^{-\nu_n t}}{\eta^2 - \nu_n^2} \]  

with \( \nu_n = 2\pi n / \hbar \beta \) (with \( \beta = (k_B T)^{-1} \)) being the so-called Matsubara frequencies. Quantum effects are important at low temperatures, the long time behavior being mainly determined by the first term of the Matsubara series. Thus, relaxation is no longer governed only by the damping constant. The ISF in this quantum framework is then given by \cite{34}

\[ I(K, t) = e^{-\chi^2(\theta(t) - \phi(t)) - \kappa t \cdot K^2 g(t)} \]  

which

\[ g(t) = \frac{2}{m \beta} \sum_{n=1}^{\infty} \frac{\nu_n e^{-\nu_n t} - \eta e^{-\eta t} - \nu_n e^{-\nu_n t}}{\eta^2 - \nu_n^2} \]  

and where it is clearly seen that the extra term \( K^2 g(t) \) in the argument of the ISF exponential is the difference with respect to the classical result. The DSF is now much more involved and can not be reduced to a simple analytical function. The diffusion coefficient is a complex number given by

\[ D = \frac{k_B T}{m \eta} - \frac{\hbar}{2m} \]  

whose real part is Einstein’s law. The same result can be obtained from the MSD by considering only the symmetric part of the autocorrealtion function. In any case, the limit to very small temperatures is questionable since we are not taking into account the quantum noise correlation.

In the Bohmian framework, from equations \((37)\) and \((56)\), the VAF along the \( K \) direction is expressed as

\[ C_K(\tau) \equiv \langle v_K(0) v_K(\tau) \rangle = \frac{k_B T}{m} e^{-\eta \tau} + \langle (R(0) - q(0))^2 \rangle \kappa \frac{\delta(0)}{\delta(0)^2} \delta(t) \]  

and the dynamical equations governing this regime are given by equations \((34)\) and \((35)\). As mentioned before, the damped Pinney equation has not an analytical solution but it is possible to look for an approximate one \cite{46}. Equation \((35)\) can be rewritten as
\[
\frac{d}{dt} \left( \frac{\delta^2}{2} + \frac{\hbar^2}{8m_0^2} \right) = -\eta \delta^2 \leq 0. \tag{68}
\]

The expression inside brackets is essentially a positive definite quantity; the first term could be seen as the kinetic energy of the spreading and the second one as a potential function. At long times, due to the negative derivative (decreasing function with time), both terms tend to be negligible at different rates. In this regime, the spreading acceleration is expected to be much smaller than the damping term \( \eta \delta \), leading to a simple solution for equation (35) to be

\[
\delta \sim \sqrt{\frac{\hbar}{m}} \eta^{-1/4} t^{1/4}. \tag{69}
\]

It is then straightforward to have that

\[
\frac{\delta}{\eta \delta} \sim \frac{3}{4\eta t}, \tag{70}
\]

justifying the assumption made when \( \eta t \gg 1 \). Thus, equation (67) becomes

\[
\mathcal{C}_\mathbf{K}(\tau) \equiv \langle v_\mathbf{K}(0) v_\mathbf{K}(\tau) \rangle \simeq \frac{k_B T}{m} e^{-\eta \tau} + g_{\mathbf{K},0} \eta^{-1/4} t^{-3/4} \tag{71}
\]

with

\[
S_{\mathbf{K},0} = \frac{1}{4} \sqrt{\frac{\hbar}{m}} \langle (R(0) - q(0))^2 \rangle_\mathbf{K} \frac{\delta(0)}{\delta^2(0)} \tag{72}
\]

showing the time dependence of the Bohmian VAF. The time dependent extra contribution goes with \( t^{-3/4} \), typical from a dissipative behavior for the spreading of the Gaussian distribution function [46]. The Bohmian stochastic trajectories, after equation (32), are then expressed as

\[
R(t) = q(t) + (R(0) - q(0)) - \frac{1}{\delta(0)} \sqrt{\frac{\hbar}{m}} \eta^{-1/4} t^{1/4}. \tag{73}
\]

The ISF in this framework is then given by

\[
I(\mathbf{K}, t) = e^{-\chi^2(\tau - \eta \tau^{-1})} e^{-\mathbf{K}^2 \tau g_{\mathbf{K},0} \eta^{-1/4} t^{3/4}}. \tag{74}
\]

Now, at very long times, the argument of the first and second factors contributes linearly with \( t \) and then

\[
I(\mathbf{K}, t) \simeq e^{-\mathbf{K}^2(D + \alpha) t}. \tag{75}
\]

with

\[
\alpha = \frac{16}{5} g_{\mathbf{K},0} \eta^{-1/4} \hat{a} \tag{76}
\]

where \( \hat{a} \) is an average time value of the extremely slow varying function \( t^{1/4} \). The DSF or line shape is now expressed as

\[
S(\mathbf{K}, \omega) \propto \frac{\mathbf{K}^2(D + \alpha)}{\omega^2 + \mathbf{K}^2(D + \alpha)^2} \tag{77}
\]

which again a single Lorentzian function is obtained but with a higher FWHM given by \( \Gamma = 2(D + \alpha) \mathbf{K}^2 \). The parameter \( \alpha \) is zero at least when \( \delta(0) = 0 \).

In the diffusion regime, the corresponding MSD is no longer linear with time

\[
\langle R^2(t) \rangle \simeq 2D \tau + \langle (R(0) - q(0))^2 \rangle \frac{1}{\delta^2(0)} \frac{\hbar}{m} \eta^{-1/2} t^{1/2}. \tag{78}
\]

since the crossing term goes to zero at long times. This MSD also keeps the same dressing scheme of the stochastic trajectories, the first contribution is a particle contribution given in terms of the diffusion coefficient \( D \) (behaving as in the classical case) and the second one comes from the wave spreading but with different time dependent behaviors. This dressing scheme for the MSD and its time dependence characterize the so-called Bohmian-Brownian motion [27]. This slight deviation from the linearity could be seen as a weak anomalous diffusion process [48].

### 3.3. The intermediate regime

In this intermediate regime, analytical results for ISF and DSF are only obtained if the classical VAF is assumed to follow simple functional forms; in any case, numerical simulations of the Langevin equations have to be carried out to extract the parameters involving the particular functional form assumed.
In the classical framework, it is acceptable [34] to assume that the VAF is well described by

$$C_K(\tau) = \langle v_K^2(0) \rangle = \frac{k_B T}{m} e^{-\nu \tau} \cos(\omega \tau + \delta). \quad (79)$$

where a temporary trapping of the adsorbate is expected to occur inside the wells of the corrugated surface interaction potential. The $\omega$-parameter gives the frequency of these intrawell oscillations with a certain dephase $\delta$. Physically, this expression has the correct time behavior corresponding to the ballistic and Brownian regimes analyzed previously. As has been shown elsewhere, the ISF issue from equation (79) has a more or less simple analytical expression leading to a DSF taking into account the intrawall motions which are of low energy quite close to the main quasiequilibrating peak due to zero energy transfer.

For massive particles, the mean interparticle distance is most of the time greater than the thermal de Broglie wavelength $\lambda_B = h/\sqrt{2 mk_B T}$ and quantum effects are only considered to be a correction [49]. The $I_2$ factor could be replaced by the classical equation (15) but this approximation is not good at small times. However, due to the fact the diffusion regime is reached at long times, the only quantum correction comes from the $I_1$ factor. Obviously, for light particles, where tunnelling can be present, the approach is radically different.

The nice thing about the Bohmian framework with respect to the quantum one is that information of the classical motion can still be used. Thus, the Bohmian VAF can now expressed as

$$C_K(\tau) \equiv \langle v_K(0) v_K(\tau) \rangle = \frac{k_B T}{m} e^{-\nu \tau} \cos(\omega \tau + \delta) + \langle (R(0) - q(0))^2 \rangle_K \frac{\delta(0)}{\delta^2(0)} \delta'(t). \quad (80)$$

The adiabatic approximation could be still used in order to calculate the Bohmian stochastic trajectories. When the corrugation of the surface is strong enough this approximation is no longer valid and alternative solutions should be found. As mentioned before, the Pinney equation governing the width of the Gaussian density can not be solved analytically. A numerical solution has been obtained by Tsekov [50] and a first-order perturbation solution by Haas et al [46] where the acceleration term is assumed to be small, reproducing very well the asymptotic behavior. For initially rapidly expanding wave packets, the damping term becomes dominant after a long period of time. With this in mind, the ISF and DSF are only known by numerical calculations. Again, for an initial spreading velocity zero, the standard classical stochastic trajectories and VAF are recovered as well as the ISF and DSF.

As a word of conclusion, in this work we have put in evidence that Bohmian stochastic trajectories are also able to describe surface diffusion processes when Ohmic friction, moderate surface temperatures and small coverages are assumed. An important difference can be seen when the initial spreading rate of the Gaussian wave packet is considered zero or not. In particular, when this initial rate is not zero, the diffusion process described in terms of Bohmian stochastic trajectories displays a weak anomalous diffusive behavior. Within this approach, the incoherent tunnelling regime could be carried out with success after our experience of applying it to the dissipative tunneling by a parabolic barrier [32]. It is true that the corresponding formalism should be extended to include the surface periodicity. At the same time, this diffusion process could also be extended and described by scaled trajectories, recently proposed to study dissipative dynamics [31, 32] providing a smooth classical-quantum transition. When the Ohmic friction is not a good assumption then the generalized Langevin equation formalism is the appropriate dynamical equation together with colored noise [31]. These interesting topics as well as to analyse the diffusion process in terms of continuous measurement [27] are hopefully to be considered in the near future.

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