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Article

Surface Diffusion with Coverage: The Method of the Characteristic Function

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Abstract

In this work, the so-called characteristic function method is proposed as a new approach to describe and interpret the diffusion process with interacting adsorbates in terms of the surface coverage. In this context, the intermediate scattering function is shown to be a characteristic function of probability theory which is also the generating function of the moments and cumulants of the jump probability distribution. The theoretical analysis carried out here consists of reviewing very briefly firstly the case of non-interacting adsorbates or very low surface coverages and extending secondly this method to low and intermediate surface coverages. As a direct consequence of this analysis, it is shown that the static structure factor is also a characteristic function of the adsorbate separation distances.

Keywords: surface diffusion; helium atom scattering; surface coverage; intermediate scattering function; static structure factor; de Gennes narrowing

1. Introduction

Surface diffusion is a very important elementary and primary step in many processes occurring on surfaces such as chemical reactions, crystal growth, etc. Diffusion is above all a dynamical process which has to be studied and analyzed within the theory of open classical and quantum systems (or stochastic processes), belonging to the more general framework of non-equilibrium statistical mechanics. Two well-known surface techniques can mainly be used for such a goal such as neutron (quasi-elastic neutron scattering, QENS) [1] and helium atom (quasi-elastic helium atom scattering, QHAS) with their respective variants of spin echo (SE) [2,3]. Usually the probe particle (neutron or helium) is interacting weakly with the system of interest (adsorbates) which is coupled to a surface considered as a reservoir (or thermal bath) and measuring its linear response. The original theory dates back to van Hove and Vineyard when dealing with neutron scattering by crystals and liquids. The nature of particles probing the system formed by moving and interacting particles (adsorbates in surface diffusion with a given coverage) is largely irrelevant when the Born approximation is assumed [4–7]. Unlike the neutron scattering where it is coherent or incoherent, atom-surface scattering is fully coherent.

As is well known, two linear response functions are primordial in this context: the dynamic structure factor (DSF), $S(\mathbf{K}, \omega)$, and the intermediate scattering function (ISF), $I(\mathbf{K}, t)$, which are expressed in terms of the energy exchange, $\hbar\omega$, and momentum transfer parallel to the surface, $\mathbf{K}$, undergone by the probing particles in the scattering process. In the QHAS and HeSE surface techniques, the DSF and ISF are the observables (or response functions) measured, respectively. Both of them are related by a Fourier transform as follows

$$\begin{aligned} I(\mathbf{K}, t) &= \int d\omega e^{i\omega t} S(\mathbf{K}, \omega) \\ &= \frac{1}{N} \langle \rho_{\mathbf{K}} \rho_{-\mathbf{K}}(t) \rangle, \end{aligned} \quad (1)$$

where the particle density operator in the reciprocal space is given by

$$\rho_{\mathbf{K}}(t) = \sum_{j=1}^N \exp(-i\mathbf{K} \cdot \mathbf{R}_j(t)), \quad (2)$$

$\mathbf{R}_j(t)$ being the position operators of the $j = 1, \dots, N$ adsorbates on the surface as a function of time. Within the Born approximation, the DSF and ISF can be expressed in terms of the generalized pair-distribution function $G(\mathbf{R}, t)$ (also known as the van Hove space-time correlation function). This function gives us the probability that given a particle at the origin and at time $t = 0$, any particle, including the same one, can be found at the surface position $\mathbf{R}$ and at time t . The ISF is written as (first line of equation) [4]

$$\begin{aligned} I(\mathbf{K}, t) &= \int d\mathbf{R} e^{i\mathbf{K} \cdot \mathbf{R}} G(\mathbf{R}, t), \\ &= \int d\mathbf{R} e^{i\mathbf{K} \cdot \mathbf{R}} \rho(\mathbf{R}, t), \\ &= \langle e^{i\mathbf{K} \cdot \mathbf{R}(t)} \rangle. \end{aligned} \quad (3)$$

In open quantum systems, the probability is given by the diagonal elements of the reduced density matrix after solving the Liouville-von Neumann equation, $\rho(\mathbf{R}, t)$ (second line of equation) [8,9]. And, finally, the third line of this equation can be seen as an average of the exponential function, $\exp i\mathbf{K} \cdot \mathbf{R}(t)$, [10]. In probability theory, this average is known as the *characteristic function* of a probability distribution [11,12]. Thus, one has that the ISF which is a time dependent observable, and therefore real, is the characteristic function (CF) of the probability distribution of the adsorbate positions with time on the surface for the real parameter given by the modulus of the $\mathbf{K}$ -vector (the value of K and its direction of observation is chosen by the experimental technique used). This Fourier transform can be reduced to a Fourier sum when a tight-binding description is used and a jump model is assumed.

There is a vast literature on characteristic functions due to the fact than many times it is easier to evaluate this function for a random variable than its moments and cumulants (at any order) of the corresponding probability distribution function. In this regard, several properties/theorems can be used [11,12] for a better understanding of this approach to surface diffusion:

- A CF characterizes completely a random variable and uniquely determines the corresponding probability distribution function
- If the CF is known, the diagonal elements of the reduced density matrix or probabilities are issued from its inverse Fourier transform determining it unequivocally.
- A CF is real if and only if it is even.
- A distribution function is symmetric if and only if its CF is real and even.
- $I(\mathbf{0}, t) = 1$.
- $I(\mathbf{K}, t)$ is a uniformly continuous function of its argument for all $\mathbf{K}$ values.
- The moments of the probability distribution are obtained by Taylor expansion of the exponential function at any order and, therefore, one can speak of the momentum generating function.
- The natural log of the CF is the corresponding cumulant generating function. A similar Taylor expansion at any order can also be applied
- When time translational invariance is assumed, the CF is an exponential function of time, $\exp(-t\alpha)$, being α the decaying rate which is also known as the characteristic exponent [13].

On the other hand, the diffusive regime is reached at very long times; that is, when time is much greater than the inverse of the friction coefficient. In this dynamical regime, the experimental ISF displays an exponential function of time according to [2]

$$I(\mathbf{K}, t) = B e^{-\alpha(\mathbf{K})t} + C, \quad (4)$$

where B and C are constants and $\alpha(\mathbf{K})$ is the so-called dephasing rate. After Eq. (1), the DSF or the quasi-elastic peak around $\omega = 0$ is a Lorentzian function

$$S(\mathbf{K}, \omega) \propto \frac{\alpha(\mathbf{K})}{\omega^2 + \alpha(\mathbf{K})^2}. \quad (5)$$

This rate also depends implicitly on the friction coefficient, surface structure and temperature.

Thus, the ISF is a CF from probability theory and is the central dynamical measurement which clearly shows the relationship between the surface structure and dynamical process. There are very few theoretical works considering interaction among adsorbates or, in other words, nonzero surface coverages, θ . At very low values, this interaction can be safely neglected, speaking about the tracer diffusion coefficient. At higher values, this interaction is fundamental to better interpret the ISF and the dephasing rate. Due to the fact that the coverage is fixed at the very beginning from experiment, the coverage should be considered as a parameter of the theory, expressing thus the main functions as: $\alpha(\mathbf{K}; \theta)$, $I(\mathbf{K}, t; \theta)$ and $S(\mathbf{K}, \omega; \theta)$. The main purpose of this work is to present the CF method as an alternative theoretical approach of surface diffusion with coverage. As a direct consequence of this analysis it is also shown that the static structure factor (SSF) is again a characteristic function of the adsorbate separation distances.

For this goal, this work is then organized as follows. In Section 2, the CF method is presented for a tight-binding description in a very general way by starting from a master or rate or Pauli equation once the diffusive regime is well established. This master equation is solved for a simple Bravais lattice by assuming adsorbates remain more time inside the surface sites than traveling to another one. The solution provides us the ISF which is a generating function of moments and cumulants of the jump distribution. In particular, we focus on the second moment or cumulant due to the fact it is related to the diffusion coefficient: tracer or collective depending on the value of the surface coverage. As an additional information, the frequency moments or sum rules are also calculated from the ISF. In Section 3, we particularize this method to a simple diffusion process by considering very low and low-intermediate surface coverages. Finally, in Section 4, some conclusions are presented in order to show the convenience of using the CF method to process and interpret experimental data with respect to different alternatives existing in the literature.

2. Diffusion Dynamics in Presence of Surface Coverages. The Characteristic Function Method

Surface coverage is the fraction of a surface which is occupied by adsorbate species such as atoms and molecules. In a tight-binding description, it can be defined as the ratio between adsorbates covering the surface sites and the total number of them. It is usually denoted by θ . This quantity is fixed by the experiment from the very beginning and the diffusion dynamics is studied experimentally and theoretically for a given value of θ . At very low values, adsorbates can be considered as non-interacting. Thus, it is customary to describe the diffusion process by considering θ as a parameter.

Once the diffusive regime is reached for very long times, the ISF is well represented by Eq.(4) but now this function and the dephasing rate depend parametrically on the surface coverage, $I(\mathbf{K}, t; \theta)$ and $\alpha(\mathbf{K}; \theta)$. If the jump diffusion model due to Chudley-Elliott (CE) [14] is assumed (for simplicity, a simple Bravais lattice is considered as well as instantaneous jumps between different surface sites), a Pauli master equation can be written in terms of the diagonal elements of the reduced density matrix as follows

$$\frac{\partial \rho(\mathbf{R}, t; \theta)}{\partial t} = \sum_{\mathbf{L}} \Gamma_{\mathbf{L}} [\rho(\mathbf{R} + \mathbf{L}, t; \theta) - \rho(\mathbf{R}, t; \theta)], \quad (6)$$

where the summation runs over all two-dimensional vectors $\mathbf{L}$ and $\Gamma_{\mathbf{L}}$ are the partial jumping rates and their inverse $\Gamma_{\mathbf{L}}^{-1}$ are interpreted as the average time between successive jumps. In this model, the time for a simple jump is very short compared to the time between successive jumps. The total jump rate is therefore $\Gamma = \sum_{\mathbf{L}} \Gamma_{\mathbf{L}}$, with $\Gamma_{\mathbf{L}} = \Gamma_{-\mathbf{L}}$. Due to the linearity property of the Fourier transform and

considering contributions by pairs coming from $\mathbf{L}$ and $-\mathbf{L}$, the ISF is ruled by the following differential equation

$$\frac{\partial I(\mathbf{K}, t; \theta)}{\partial t} = -4 I(\mathbf{K}, t; \theta) \sum_{\mathbf{L} > 0} \Gamma_{\mathbf{L}}(\theta) \sin^2\left(\frac{\mathbf{K} \cdot \mathbf{L}}{2}\right), \quad (7)$$

with solution given by

$$I(\mathbf{K}, t; \theta) = I(\mathbf{K}, 0; \theta) e^{-2|t| \sum_{\mathbf{L} > 0} \Gamma_{\mathbf{L}}(\theta) (1 - \cos(\mathbf{K} \cdot \mathbf{L}))}, \quad (8)$$

and the dephasing rate by

$$\alpha(\mathbf{K}; \theta) = 2 \Gamma(\theta) \sum_{\mathbf{L} > 0} P_{\mathbf{L}}(\theta) (1 - \cos(\mathbf{K} \cdot \mathbf{L})). \quad (9)$$

The jump probabilities and the total jumping rate are expressed now as $P_{\mathbf{L}}(\theta) = \Gamma_{\mathbf{L}}(\theta) / \Gamma(\theta)$. Experimental dephasing rates have to be fitted to Eq. (9) where the fitting parameters in this model are the partial jumping rates, $\Gamma_{\mathbf{L}}(\theta)$.

Another variable which is also chosen by the experiment is the direction of observation, $\mathbf{K}$. Thus, the scalar product in Eq. (3) can be written, in general, as $\mathbf{K} \cdot \mathbf{R}(t) = K L_{\parallel}(t; \theta)$ where K is the modulus of $\mathbf{K}$ and $L_{\parallel}(t; \theta)$ gives the sum of nonzero projections of the $\mathbf{L}$ -vectors along $\mathbf{K}$ (parallel to the direction of observation) as a function of time. The jumps along the different projections are obviously conditioned by the surface coverage. Usually there are several jump/transition vectors $\mathbf{L}$ contributing to the total diffusion process and one can write $L_{\parallel}(t; \theta) = \sum_m L_{\parallel, m}(t; \theta)$. Thus, Eq.(3) can be expressed now as [10]

$$I(K, t; \theta) = \langle e^{iK L_{\parallel}(t; \theta)} \rangle = \sum_{n=0}^{\infty} \frac{(iK)^n}{n!} \langle L_{\parallel}^n(t; \theta) \rangle. \quad (10)$$

The n^{th} -derivative of the CF or momentum generating function with respect to K , at $K = 0$, provides us the n^{th} -moment of the jump/transition distribution [15,16]

$$\langle L_{\parallel}^n(t; \theta) \rangle = \left(-i \frac{\partial}{\partial K} \right)^n I(K, t; \theta) \Big|_{K=0}, \quad (11)$$

as well as the n^{th} -cumulant of the same distribution given by

$$\langle L_{\parallel}^n(t; \theta) \rangle_c = \left(-i \frac{\partial}{\partial K} \right)^n \ln I(K, t; \theta) \Big|_{K=0}. \quad (12)$$

The second moment plays a fundamental role because one can extract the tracer or collective diffusion coefficient if the surface coverage is very low (non-interacting adsorbates are considered) or low-intermediate coverage values, respectively.

From Eq. (1), the ISF can also be written in terms of the frequency moments of $S(K, \omega; \theta)$ (frequency sum rules) by Taylor expansion with respect to time around $t = 0$ [17]

$$I(\mathbf{K}, t; \theta) = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \langle \omega^n(\mathbf{K}; \theta) \rangle, \quad (13)$$

with

$$\langle \omega^n(\mathbf{K}; \theta) \rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \omega^n S(\mathbf{K}, \omega; \theta), \quad (14)$$

and therefore

$$\langle \omega^n(\mathbf{K}; \theta) \rangle = \left(i \frac{\partial}{\partial t} \right)^n I(\mathbf{K}, t; \theta) \Big|_{t=0}, \quad (15)$$

which only depends on the projectile along the direction of observation thorough Eq. (8). The so-called quasi-elastic peak given by Eq.(5) is an even function of frequency and therefore only even frequency moments will survive.

Interestingly enough, the ISF at $t = 0$ is precisely the SSF which in terms of the coverage is written as

$$I(\mathbf{K}, 0; \theta) = F(\mathbf{K}; \theta), \quad (16)$$

this factor being again a characteristic function of the separation distance distribution among the adsorbates.

3. Results

3.1. Very Low Surface Coverages

In a tight-binding description, we focus on the probability of an adsorbate to stay in a given potential well or surface site n at time t , $P_n(t)$. This description is convenient when the thermal energy is much less than the activation energy, that is, the adsorbates are mainly localized at different surface sites. Furthermore, the time between two consecutive jumps is greater than the duration of a given jump. In the following we are going to consider different jump models in order to illustrate how the characteristic function method is implemented at low surface coverages.

3.1.1. Nearest Neighbors

In order to simplify the discussion, we are going to reduce the diffusion dynamics to only one high symmetry direction on a periodic substrate with projection along $\mathbf{K}$ expressed as $L_{\parallel}$. Within the formalism of the master equation [15], if a simple Bravais lattice is assumed as well as instantaneous jumps between adjacent sites/wells, a Pauli master equation (or rate equation) can be written in terms of such probabilities (this starting point was already used by CE in neutron scattering [14]) [9,18,19]

$$\dot{P}_n(t) = \Gamma_{n-1}^+ P_{n-1}(t) + \Gamma_{n+1}^- P_{n+1}(t) - (\Gamma_n^+ + \Gamma_n^-) P_n(t), \quad (17)$$

where the dot on $\dot{P}_n(t)$ means its time derivative. Here $\Gamma_{n\pm 1}^{\pm}$ is the hopping transition rates from the $(n \mp 1)$ -th well to the n -th well and $\pm$ denotes if diffusion goes to the right or to the left, respectively. Usually, these transition rates are fitting parameters. If the initial condition is such that $P_n(0) = \delta_{n0}$ and $\Gamma = \Gamma^+ + \Gamma^-$ describes the total rate (with $\Gamma_n^+ = \Gamma_n^-$, $\Gamma_n^+ = \Gamma^+$, and $\Gamma_n^- = \Gamma^-$), one obtains

$$P_n(t) = I_n(\Gamma t) e^{-\Gamma t}, \quad (18)$$

where $I_n(x)$ is the modified Bessel function of integer order n .

It is also very instructive to introduce the so-called probability generating function [15] which is very useful to solve a master equation; that is, when a jump model is assumed. In this context, this function is defined as an infinite series

$$G(z, t) = \sum_{n=0}^{\infty} P_n(t) z^n, \quad (19)$$

which converges absolutely for all complex numbers z with $|z| \leq 1$. Eq.(18) could also be reached by using the probability generating function $G(z, t)$.

Thus, the ISF can be rewritten as [9]

$$\begin{aligned} I(K, t) &= \sum_{n=-\infty}^{n=+\infty} P_n(t) e^{in K a \cos \beta} = e^{-\Gamma t} \sum_{n=-\infty}^{+\infty} I_n(\Gamma t) e^{in K a \cos \beta} \\ &= e^{-\Gamma t [1 - \cos(K a \cos \beta)]}, \end{aligned} \quad (20)$$

where a is the unit cell length along the symmetry direction chosen and β the angle formed with the observation direction. Notice that the ISF is an even function of K . Now, after Eqs. (20), one has that the total jumping/transition rate is expressed as

$$\Gamma(K) = \frac{\alpha(K)}{1 - \cos(Ka \cos \beta)}. \quad (21)$$

This rate is a function of the projection along the direction of $\mathbf{K}$ and also implicitly of surface temperature and friction coefficient.

Once the ISF for a given surface diffusion process is known analytically, it is quite straightforward to calculate the moments and cumulants; in particular, the second moment which is related to the tracer diffusion coefficient D (for this case, $\langle L_{\parallel}(t) \rangle = \langle L_{\parallel}(t) \rangle_c = 0$),

$$\langle L_{\parallel}^2(t) \rangle = \langle L_{\parallel}^2(t) \rangle_c = Dt, \quad (22)$$

where

$$D = a^2 \Gamma \cos^2 \beta. \quad (23)$$

The $\cos$ -factor reminds us the projection along the direction of observation and sometimes is disregarded in the literature.

3.1.2. Beyond Nearest Neighbors

When considering jumps beyond nearest neighbors, the probability distribution is given by [20]

$$P_n(t) = e^{-2(\gamma_1 + \gamma_2 + \gamma_3)t} \sum_{k=-\infty}^{+\infty} I_k(2\gamma_3 t) \sum_{j=-\infty}^{+\infty} I_j(2\gamma_2 t) I_{n-2j-3k}(2\gamma_1 t), \quad (24)$$

where γ_1 , γ_2 and γ_3 are the single, double and triple jump rates, respectively. However, one can always generalize this jump process to any number of jumps. The corresponding master equation is expressed now as

$$\dot{P}_n(t) = \sum_{l=1}^{\infty} [\Gamma_l^+ P_{n-l}(t) + \Gamma_l^- P_{n+l}(t) - (\Gamma_l^+ + \Gamma_l^-) P_n(t)]. \quad (25)$$

The ISF can then be written as a product of backward and forward diffusion

$$I(K, t) = \prod_{n=1}^{\infty} I_n^+(K, t) I_n^-(K, t), \quad (26)$$

with

$$I_n^{\pm}(K, t) = e^{t(e^{\pm i n K a \cos \beta} - 1) \Gamma_n^{\pm}}, \quad (27)$$

where again a and β are the unit cell length along the symmetry direction considered and the angle formed by this direction and $\mathbf{K}$, respectively. An alternative expression for the ISF can also be written as (from the CE model)

$$I(K, t) = e^{-2t \Gamma \sum_{n>0} \bar{P}_n [1 - \cos(n K a \cos \beta)]}, \quad (28)$$

where $\sum_n \Gamma_n = \Gamma$ and $\bar{P}_n = \Gamma_n / \Gamma$ and the total jumping rate is now given by

$$\Gamma(K) = \frac{\alpha(K)}{2 \sum_{n>0} \bar{P}_n [1 - \cos(n K a \cos \beta)]}. \quad (29)$$

Eq. (21) clearly shows the relationship between the surface structure and the dynamics through the total jump rate. The moments and cumulants of the probability distribution function can again be straightforward calculated. At second order, one has that

$$\langle L_{\parallel}^2(t) \rangle_c = \langle L_{\parallel}^2(t) \rangle = Dt, \quad (30)$$

where the tracer diffusion coefficient D is expressed as [10]

$$\begin{aligned} D &= 2\Gamma a^2 \cos^2 \beta \sum_{n=1} \bar{P}_n n^2, \\ &= 2\Gamma \frac{b^2 + 2b + 2}{b^3} e^{-b} a^2 \cos^2 \beta. \end{aligned} \quad (31)$$

The first line of this equation indicates us that the second moment of $\bar{P}_n$ is only involved whereas the second one is due to the fact that the jump probabilities usually decrease exponentially with n , $\bar{P}_n = \exp(-bn)$, the summation over n being replaced by an integral from 1 to infinity. Similar expressions have been obtained previously [21].

3.2. Low and Intermediate Surface Coverages

In this Subsection, we are going to consider the effect of the surface coverage in the diffusion. Only one projected jump vector is again assumed here in order to simplify our discussion (the generalization to more contributions is straightforward). The diffusion process has to be seen now as a collective behavior of adsorbates on the surface. If $P_n^c(t)$ is the probability to find an adsorbate or several ones at site n and time t , the conservation of number of adparticles is established as

$$\sum_{n=1}^N P_n^c(t) = N_a, \quad (32)$$

N_a being the number of adsorbates and N the total surface sites and the surface coverage is then expressed as

$$\theta = \frac{N_a}{N}. \quad (33)$$

At this point, we have to distinguish between the diffusion coefficient in previous Subsections, the so-called tracer diffusion coefficient, D , from the collective one, D_c , when the surface coverage begins to be important.

Following the same tight-binding description of the diffusion process, one can start from Eq. (25) but considering now the explicit θ -dependence on the jump/transition rates

$$\dot{P}_n^c(t) = \sum_{l=1}^{\infty} \{ \Gamma_l^+(\theta) P_{n-l}^c(t) + \Gamma_l^-(\theta) P_{n+l}^c(t) - (\Gamma_l^+(\theta) + \Gamma_l^-(\theta)) P_n^c(t) \}. \quad (34)$$

Eq. (8) is expressed now as

$$I(K, t; \theta) = e^{-2t\Gamma(K; \theta) \sum_{n>0} \bar{P}_n(\theta) [1 - \cos(nKa \cos \beta)]}, \quad (35)$$

where $\sum_n \Gamma_n(\theta) = \Gamma(\theta)$ and $\bar{P}_n(\theta) = \Gamma_n(\theta)/\Gamma(\theta)$. After Eq. (35), the total jumping/transition rate is given by

$$\Gamma(K; \theta) = \frac{\alpha(K; \theta)}{2 \sum_{n>0} \bar{P}_n(\theta) [1 - \cos(nKa \cos \beta)]}. \quad (36)$$

Again, Eq. (36) shows the link between the surface structure and the diffusion process through the total jump rate in terms of the surface coverage. Now, following the same procedure as above, at second order, one has that

$$\langle L_{\parallel}^2(t; \theta) \rangle_c = \langle L_{\parallel}^2(t; \theta) \rangle = D_c t, \quad (37)$$

where the collective diffusion coefficient D_c is expressed as

$$D_c(K; \theta) = 2\Gamma(K; \theta) a^2 \cos^2 \beta \sum_{n=1} \bar{P}_n(\theta) n^2, \quad (38)$$

and the second moment of $\bar{P}_n(\theta)$ also depends now on θ . As previously done, we could consider that jump probabilities decrease exponentially with n according to

$$\bar{P}_n(\theta) = \exp[-b(\theta)n], \quad (39)$$

and by integration from 1 to infinity the collective diffusion coefficient D_c is expressed as

$$D_c = 2\Gamma(\theta) \frac{b(\theta)^2 + 2b(\theta) + 2}{b(\theta)^3} e^{-b(\theta)} a^2 \cos^2 \beta, \quad (40)$$

where $b(\theta)$ could be extracted from a fitting procedure.

At this level, several alternative procedures are proposed to be followed. First, due to the fact that the dephasing rate has been assumed to be a parametric function of the surface coverage, this dependence can be extracted from the experimental work since diffusion is usually studied at different surface coverages. One could also assume an analytical function for the dephasing rate in terms of the surface coverage and K in order to obtain an analytical expression for the total jumping rate. This way of proceeding could be seen as the most general case. A third alternative could consist of assuming hard core interactions and different probability distribution functions for $\bar{P}_n(\theta)$. In any case, the method of the characteristic function should be straightforward applied.

3.2.1. Hard Core Interaction

The simplest model one can consider is that the double occupancy is prohibited [22]. The corresponding master or rate equation can be written as

$$\begin{aligned} \dot{P}_n^c(t) &= \sum_{l=1}^{\infty} \{ \Gamma_l^+ P_{n-l}^c(t) [1 - P_n^c(t)] + \Gamma_l^- P_{n+l}^c(t) [1 - P_n^c(t)] \\ &\quad - (\Gamma_l^+ [1 - P_{n-1}^c(t)] + \Gamma_l^- [1 - P_{n+1}^c(t)]) P_n^c(t) \}, \end{aligned} \quad (41)$$

where $[1 - P_n^c(t)]$ gives us the probability as a function of time that the site n is not occupied. Eq.(41) is then reduced to Eq.(25) but for $P_n^c(t)$

$$\dot{P}_n^c(t) = \sum_{l=1}^{\infty} [\Gamma_l^+ P_{n-l}^c(t) + \Gamma_l^- P_{n+l}^c(t) - (\Gamma_l^+ + \Gamma_l^-) P_n^c(t)]. \quad (42)$$

The same expression obtained previously for D (first line of Eq. (31)) it should be valid now for D_c .

If one wants to relate D to D_c , the new master equation in terms of $P_n(t)$ is

$$\begin{aligned} \dot{P}_n(t) &= \sum_{l=1}^{\infty} \{ \Gamma_l^+ P_{n-l}(t) [1 - P_n^c(t)] + \Gamma_l^- P_{n+l}(t) [1 - P_n^c(t)] \\ &\quad - (\Gamma_l^+ [1 - P_{n-1}^c(t)] + \Gamma_l^- [1 - P_{n+1}^c(t)]) P_n(t) \}, \end{aligned} \quad (43)$$

and by assuming a mean field approximation, we replace any $P_n^c(t)$ by the surface coverage θ , Eq.(43) being now written as

$$\dot{P}_n(t) = (1 - \theta) \sum_{l=1}^{\infty} \{ \Gamma_l^+ P_{n-l}(t) + \Gamma_l^- P_{n+l}(t) - (\Gamma_l^+ + \Gamma_l^-) P_n(t) \}, \quad (44)$$

and from Eqs. (31) and (38), we have the so-called Darken equation

$$D = (1 - \theta) D_c, \quad (45)$$

where the factor $(1 - \theta)$ is known as the blocking factor. Both diffusion coefficients become equal when the coverage is going to zero.

3.2.2. Binomial Probability Distribution

When dealing with single adsorbates, $\bar{P}_n$ gives us the jump probabilities. Now, if we consider the surface coverage, we designate $\bar{P}_n^c$ as the new jump probabilities. If we assume a binomial jump distribution function

$$P_n^c = \sum_{k=1}^{\infty} \bar{P}_k \binom{n}{k} \theta^{n-k} (1-\theta)^k \quad (46)$$

the corresponding first two moments are then

$$\begin{aligned} \langle n \rangle_c &= \sum_{n=1}^{\infty} n P_n^c = \frac{\langle n \rangle}{1-\theta} \\ \langle n^2 \rangle_c &= \sum_{n=1}^{\infty} n^2 P_n^c = \frac{\langle n^2 \rangle + \theta \langle n \rangle}{(1-\theta)^2}, \end{aligned} \quad (47)$$

where $\langle n \rangle = \sum_{n=1}^{\infty} n \bar{P}_n$ and $\langle n^2 \rangle = \sum_{n=1}^{\infty} n^2 \bar{P}_n$. Thus, the diffusion coefficient is now expressed as

$$\begin{aligned} D_c &= 2 \Gamma a^2 \cos^2 \beta \sum_{n=1}^{\infty} P_n^c n^2, \\ &= 2 \Gamma a^2 \cos^2 \beta \frac{\langle n^2 \rangle + \theta \langle n \rangle}{(1-\theta)^2}, \end{aligned} \quad (48)$$

which reduces to Eq. (31) when θ is going to zero.

3.3. Sum Frequency Rules

Our next step is to calculate the frequency moments (or frequency rules) when the ISF is given by Eq. (20). Due to the fact that this function is an exponential function of time, the DSF is a Lorentzian function which is an even function of frequency and, therefore, only even frequency moments are allowed. Thus, after Eq. (4), the ISF is expressed now as

$$I(K, t; \theta) = 1 - \frac{t^2}{2} \langle \omega^2(K; \theta) \rangle + \frac{t^4}{4!} \langle \omega^4(K; \theta) \rangle + \dots, \quad (49)$$

with

$$\begin{aligned} \langle \omega^0 \rangle &= 1, \\ \langle \omega^{2n} \rangle &= \Gamma(\theta)^{2n} [1 - \cos(K a \cos \beta)]^{2n}. \end{aligned} \quad (50)$$

Interestingly enough, these frequency moments also depend on the total jump rate (a dynamical property). Similar expressions are easily obtained when the ISF is given by Eq. (35). In this sense, surface diffusion analyzed by He atom scattering differs from other scattering experimental techniques such as neutrons and light. For example, for neutron scattering, the zeroth moment provides the static structure factor and, the second moment, the square of the product of the momentum transfer and thermal velocity [17].

3.4. The Static Structure Factor

According to Frenken and Hinch [23], a simple expression for the SSF of a low density adatom overlayer with a lattice-gas structure can be written as

$$F(\mathbf{K}) = \langle e^{i\mathbf{K} \cdot \mathbf{L}} \rangle = \sum_{\mathbf{L}} P_{\mathbf{L}} e^{i\mathbf{K} \cdot \mathbf{L}}, \quad (51)$$

where again the 2D lattice vector $\mathbf{L}$ runs over the 2D adatom lattice and $P_{\mathbf{L}}$ is the probability of finding an occupied site at $\mathbf{L}$ given that at the origin is occupied. At very low surface coverages, one could assume that $P_{\mathbf{L} \neq 0} = \theta$ and therefore

$$F(\mathbf{K}) = 1 - \theta + \theta \sum_{\mathbf{L}} e^{i\mathbf{K} \cdot \mathbf{L}}, \quad (52)$$

where the sum over location vectors is transformed to a sum over reciprocal lattice vectors with a series of diffraction peaks given by $\delta(\mathbf{K} - \mathbf{G})$.

As discussed above, in Eq. (51) the scalar product in the exponential can again be written as $\mathbf{K} \cdot \mathbf{L} = KL_{\parallel}$, $L_{\parallel}$ being a sum over all the $\mathbf{L}$ -vectors with a nonzero projection along $\mathbf{K}$. Following the same procedure used for the ISF, one has that

$$F(K; \theta) = \langle e^{iKL_{\parallel}(\theta)} \rangle = \sum_{n=0}^{\infty} \frac{(iK)^n}{n!} \langle L_{\parallel}^n(\theta) \rangle. \quad (53)$$

The n^{th} -derivative of the SSF at $K = 0$ provides us the n^{th} -moment of the adsorbate distribution

$$\langle L_{\parallel}^n(\theta) \rangle = \left(-i \frac{\partial}{\partial K} \right)^n F(K; \theta) \Big|_{K=0}, \quad (54)$$

as well as the n^{th} -cumulant

$$\langle L_{\parallel}^n(\theta) \rangle_c = \left(-i \frac{\partial}{\partial K} \right)^n \ln F(K; \theta) \Big|_{K=0}. \quad (55)$$

These moments and cumulants are critical in order to know the adsorbate distribution as well as their separation distance among them on the surface. From the experiment, the SSF is easily extracted as a function of K . Furthermore, as before, some jump distribution as a function of the coverage could be assumed for $P_{\mathbf{L}}$.

4. Conclusions

In general, the ISF decays exponentially with time according to Eq. (4). The dephasing rate, $\alpha(K; \theta)$, is a function of the momentum transfer K for each surface coverage, a periodic function of K and mainly characterizes the diffusion rate in each measurement. Thus, both functions play a fundamental role in any diffusion process. At very low surface coverages, this rate displays maxima and minima leading to faster or lower exponential decays, respectively. The corresponding width of the quasi-elastic peak thus increases or decreases according to Eq. (5). In particular, when a minimum of the rate is reached, the corresponding K value coincides with the first Bragg diffraction peak [2]. This is the condition of the so-called de Gennes narrowing [6] in the quasi-elastic peak. Furthermore, after Eqs. (21) and (36), the total jumping/transition rate follows the same trend that the dephasing rate as well as the tracer diffusion coefficient after Eq. (23) and (31) (in order to simplify the discussion, only one high symmetry direction with nonzero projection along $\mathbf{K}$ is assumed).

The increase of the surface coverage implies higher dephasing rates, faster decays of the ISF and broadening of the width of the quasi-elastic peak as observed, for example, in the systems Na/Cu(001) and CO/Pt(111) [2,3]. Even more, at least for the CO/Pt(111), this is true for the K -values used by the experiment. Following the theoretical aspects here developed, the moments and cumulants at any order as a function of the coverage are easily calculated in an analytical way with the CF method. Concerning the collective diffusion coefficient, this method is simpler than the standard way to calculate it theoretically. When using, for example, Langevin calculations with increasing coverage, one needs to know the position and velocities with time of all adsorbates. From this information, one calculates the corresponding mean square displacements or the velocity/total flux autocorrelation functions. Sometimes, the center of mass displacement is also calculated for such a goal once the so-called thermodynamic factor is known (or even from a Darken equation). Obviously, in order to

carry out such classical calculations several points should be taken into account when increasing the coverage: first, the energy activation and maybe the friction coefficient should be changed; second, the interaction potential as well as the interaction between adsorbates should also change and third longer jumps should be more important. As a straightforward consequence of this analysis is the fact that the SSF is also a characteristic function. The moments and cumulants are important to better understand its dependence with K . When very high surface coverages are involved, some two-dimensional phase transitions could take place. This is not the regime where the CF method could obviously be applied. Finally, the method we propose here could be easily extended to neutron scattering knowing that this scattering is not fully coherent.

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