

Generalized Chudley-Elliott vibration-jump model in activated atom surface diffusion

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Here the authors provide a generalized Chudley-Elliott expression for the activated atom surface diffusion which takes into account the coupling between both low-frequency vibrational motion (namely, the frustrated translational modes) and diffusion. This expression is derived within the Gaussian approximation framework for the intermediate scattering function at low coverage. Moreover, inelastic contributions (arising from creation and annihilation processes) to the full width at half maximum of the quasielastic peak are also obtained. © 2007 American Institute of Physics. [DOI: 10.1063/1.2735586]

I. INTRODUCTION

In 1960 Chudley and Elliott¹ proposed a jump diffusion model for the neutron scattering from a liquid, where the latter was assumed to be locally a quasicrystalline structure. Within this model, the diffusive motion undergone by the (liquid) atoms is described in terms of large discrete jumps; otherwise, the atoms remain oscillating around their fixed (lattice) point between jumps. Because of the very different time scales ruling each type of motion (diffusive and oscillatory), they are considered as completely uncorrelated. This jump model has also been extensively used to interpret the full width at half maximum (FWHM) of the so-called *quasielastic peak* (Q peak) observed in quasielastic helium atom (surface) scattering (QHAS) experiments.²⁻⁶ This peak, obtained from time-of-flight measurements converted to energy transfers, accounts for the adatom surface diffusion process. Apart from the Q peak, in this type of experiments one also observes oscillatory motions associated with the temporary trapping of the adatom inside surface potential wells. This is the so-called *frustrated translational mode* (or T mode), the lowest frequency mode of the adsorbate, whose line shape is located very close to the Q peak which is centered at zero energy transfer.

Following the Chudley-Elliott model, the coupling between the diffusive and vibrational motions is very often neglected in theoretical descriptions. Of course, for short parallel momentum transfers of the scattered particles (He atoms), the coupling between both motions can be naturally disregarded, since no overlapping between the corresponding

peaks will be observed. However, the same does not hold for large momentum transfers. This is important because the experimental deconvolution of the Q and T -mode peaks is often carried out independently.^{2,3} In this paper, we propose a working formula for the whole line shape based on the Gaussian approximation and that takes into account a generalized Chudley-Elliott expression dealing with the coupling between the diffusive peak and the low-frequency vibrational modes. In this way, the experimental deconvolution procedure can be carried out in a more appropriate manner, and the typical information extracted (jump distributions, and diffusion and friction coefficients) from both motions at the same time would lead to more realistic values.

II. THEORY

In real diffusion experiments performed by means of the QHAS technique, the observable magnitude is the *differential reflection probability*,⁷

$$\frac{d^2\mathcal{R}(\Delta\mathbf{K}, \omega)}{d\Omega d\omega} = n_d F S(\Delta\mathbf{K}, \omega). \quad (1)$$

This magnitude gives the probability that the probe (He) atoms scattered from the diffusing collective (chattered on the surface) reach a certain solid angle Ω with an energy exchange $\hbar\omega = E_f - E_i$ and a parallel momentum transfer $\Delta\mathbf{K} = \mathbf{K}_f - \mathbf{K}_i$. In Eq. (1), n_d is the (diffusing) particle concentration, and F is the *atomic form factor*, which depends on the interaction potential between the probe atoms in the beam and the adparticles. The function $S(\Delta\mathbf{K}, \omega)$ is the so-called *dynamic structure factor*, which provides a complete information about the dynamics and structure of the adsorbed particle ensemble, and therefore also about the surface diffusion process and vibrational spectroscopy of their low-frequency modes. Information about long distance correlations is obtained when using small values of $\Delta\mathbf{K}$, while long

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time scale correlation information is available at small energy transfers, $\hbar\omega$.

In a series of previous works,⁴⁻⁶ we have analyzed in detail the line shape structure of both the Q and T -mode peaks in terms of the standard jump Chudley-Elliott model. This model can be improved in order to provide a better analysis of the experimental line shapes. For this goal, we start expressing the dynamic structure factor that appears in Eq. (1) as

$$S(\Delta\mathbf{K}, \omega) = \frac{1}{2\pi} \int e^{-i\omega t} I(\Delta\mathbf{K}, t) dt, \quad (2)$$

where

$$I(\Delta\mathbf{K}, t) \equiv \langle e^{-i\Delta\mathbf{K} \cdot [\mathbf{R}(t) - \mathbf{R}(0)]} \rangle = \langle e^{-i\Delta\mathbf{K} \int_0^t v_{\Delta\mathbf{K}}(t') dt'} \rangle \quad (3)$$

is the so-called *intermediate scattering function* (the brackets denote ensemble averaging), with $\mathbf{R}(t)$ the trajectory of the adparticles and $v_{\Delta\mathbf{K}}$ the corresponding velocity projected onto the direction of the parallel momentum transfer $\Delta\mathbf{K}$ (with length $\Delta K = \|\Delta\mathbf{K}\|$). Both the dynamic structure factor and the intermediate scattering function can be readily obtained from standard Langevin numerical simulations.⁸ Note that this type of simulation is valid as long as no collective, clustering, or self-organizing behaviors are present; in such cases one should make use of more detailed numerical techniques (e.g., molecular dynamics), which allow us to follow the processes that happen during short time scales (as the aforementioned ones).

After a second order cumulant expansion in $\Delta\mathbf{K}$ in the right-hand side of the second equality of Eq. (3), $I(\Delta\mathbf{K}, t)$ can be expressed as

$$I(\Delta\mathbf{K}, t) \approx e^{-\Delta K^2 \int_0^t (t-t') C(t') dt'}, \quad (4)$$

where $C(t) = \langle v_{\Delta\mathbf{K}}(0) v_{\Delta\mathbf{K}}(t) \rangle$ is the *velocity autocorrelation function*. This is the so-called *Gaussian approximation*,⁹⁻¹¹ which is exact provided that velocity correlations at more than two different times are negligible.⁹ If non-Gaussian corrections are considered the theory cannot be expressed in a simple analytical manner; deviations from the Gaussian approximation are a clear indicator of the importance of such corrections.

At low coverage, adsorbate-adsorbate interactions can be neglected; diffusion is then fully characterized by only studying the dynamics of an isolated adsorbate on the surface. This is the so-called *single adsorbate approximation* in self-diffusion. Within the Langevin framework, the adsorbate-substrate interaction is described in terms of two contributions: (i) a deterministic, fitted adiabatic potential V , which models the adsorbate-surface interaction at zero surface temperature $T_s = 0$ K, and leading therefore to a deterministic force, $F = -\nabla V$; and (ii) a stochastic force (Gaussian white noise) accounting for the vibrational effects induced by the temperature on the (surface) lattice atoms that act on the adsorbate.

For an almost flat surface ($V \approx 0$), any direction is equivalent and therefore the dimensionality of the numerical Langevin simulation reduces to one. The corresponding nu-

merical velocity autocorrelation function (in self-diffusion) then follows an exponential decreasing behavior,

$$C(t) = \frac{k_B T_s}{m} e^{-\gamma t}, \quad (5)$$

where m is the adparticle mass, k_B the Boltzmann constant, and γ the friction coefficient, which is related to the Gaussian white noise source through the fluctuation-dissipation theorem. Introducing Eq. (5) into Eq. (4), one obtains¹⁰

$$I(\Delta\mathbf{K}, t) = \exp[-\chi^2 (e^{-\gamma t} + \gamma t - 1)], \quad (6)$$

where χ is the *shape parameter*, defined as¹²

$$\chi \equiv \sqrt{\langle v^2 \rangle} \Delta K / \gamma = \bar{l} \Delta K. \quad (7)$$

Here, $\sqrt{\langle v^2 \rangle} = \sqrt{k_B T_s / m}$ is the thermal velocity in one dimension, and $\bar{l} \equiv \sqrt{\langle v^2 \rangle} / \gamma$ is the mean free path. The diffusion coefficient is related to the friction as $D \equiv \langle v^2 \rangle / \gamma$. The only information about the structure of the lattice is found in the shape parameter [Eq. (7)] through ΔK . When large parallel momentum transfers are under consideration, both the periodicity and structure of the surface have to be taken into account. Consequently, the shape parameter should be changed for different lattices.

The simplest model including the periodicity of the surface is that developed by Chudley and Elliott,¹ who proposed a master equation for the pair-distribution function in space and time⁷ assuming instantaneous discrete jumps on a two-dimensional Bravais lattice. The Fourier transform of this master equation gives rise to an exponential function for the intermediate scattering function

$$I(\Delta\mathbf{K}, t) = I(\Delta\mathbf{K}, 0) e^{-\Gamma_{\nu}(\Delta\mathbf{K}) t}. \quad (8)$$

The inverse of the correlation time $\Gamma_{\nu}(\Delta\mathbf{K})$ has a periodic dependence on $\Delta\mathbf{K}$ of the form

$$\Gamma_{\nu}(\Delta\mathbf{K}) = \nu \sum_{\mathbf{j}} P_{\mathbf{j}} [1 - \cos(\mathbf{j} \cdot \Delta\mathbf{K})], \quad (9)$$

where ν is the total jump rate out of an adsorption site, and $P_{\mathbf{j}}$ is the relative probability that a jump with a displacement vector \mathbf{j} occurs. The time Fourier transform of Eq. (8) is a Lorentzian function with FWHM equal to $\Gamma_{\nu}(\Delta\mathbf{K})$. At sufficiently small values of the parallel momentum transfer, $\Gamma_{\nu}(\Delta\mathbf{K})$ displays a quadratic dependence on χ according to Eq. (7),

$$\Gamma_{\nu}(\Delta\mathbf{K}) \approx 2D\Delta\mathbf{K}^2 = 2\gamma\chi^2. \quad (10)$$

From Eqs. (9) and (10) the shape parameter can now be generalized in terms of the jump distribution on the surface Bravais lattice, defining

$$\chi_l(\Delta\mathbf{K}) \equiv \sqrt{\frac{\Gamma_{\nu}(\Delta\mathbf{K})}{2\gamma}}, \quad (11)$$

which is valid for any value of the parallel momentum transfer, and where the subscript l denotes the importance of the lattice. Note that, as a consequence of the effects induced by the periodicity and structure of the surface Bravais lattice, the shape parameter χ for free diffusion is replaced by χ_l . This is related to the exponential dependence on time dis-

played by the intermediate scattering function. Equation (11) can then be seen as a definition for the new shape parameter χ_l , which takes into account the surface structure.

Numerical Langevin simulations for corrugated surface potentials have shown⁴ that the Gaussian approximation is quite often appropriate. In such cases, the velocity autocorrelation function can be fitted to a general function described by

$$C(t) = \langle v_{\Delta\mathbf{K}}^2 \rangle e^{-\gamma t} \cos(\omega_T t + \delta), \quad (12)$$

where ω_T gives the T -mode frequency (including the shift due to the surface temperature) and δ is a phase which is added to better fit numerical results. The ω_T frequency is related to the harmonic one ω_0 according to the relation

$$\omega_T = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}. \quad (13)$$

Analogously, in the case of a harmonic oscillator, δ can also be expressed¹³ in terms of a relationship between γ and ω_T [in particular, $\delta = (\tan)^{-1}(\gamma/2\omega_T)$]. However, this constraint is lost when we apply Eq. (12) to cases of interest due to anharmonicity; as seen below, in such cases, γ , ω_T , and δ are considered as fitting parameters.

Introducing Eq. (12) into Eq. (4) the intermediate scattering function can be expressed in terms of a double infinite sum of exponential functions, each contribution coming from the different quantum states of the T -mode oscillator. This allows us to use χ_l instead of χ , and, in analogy to the result obtained in Ref. 4, the intermediate scattering function of the full process can be generalized as

$$\begin{aligned} I(\mathbf{K}, t) &= \exp[-\chi_l^2 f(\omega_T, \delta, t)] \\ &= e^{-\chi_l^2 A_1 - \chi_l^2 A_2 t} \sum_{n,m} \frac{(-1)^n (-1)^m}{n! m!} \chi_l^{2(n+m)} A_3^n A_4^m \\ &\quad \times e^{-i(m-n)\delta} e^{-(m+n)\gamma t} e^{-i(m-n)\omega_T t}, \end{aligned} \quad (14)$$

where

$$A_1 = \frac{\gamma^2 [2\gamma\omega_T \sin \delta + (\omega_T^2 - \gamma^2) \cos \delta]}{(\gamma^2 + \omega_T^2)^2}, \quad (15a)$$

$$A_2 = \frac{\gamma^2 (\gamma \cos \delta - \omega_T \sin \delta)}{\gamma^2 + \omega_T^2}, \quad (15b)$$

$$A_3 = \frac{\gamma^2}{2(\gamma - i\omega_T)^2}, \quad (15c)$$

$$A_4 = \frac{\gamma^2}{2(\gamma + i\omega_T)^2}. \quad (15d)$$

Now, Fourier transforming Eq. (14), an analytical expression for the dynamic structure factor is also readily obtained,

$$\begin{aligned} S(\Delta\mathbf{K}, \omega) &= \frac{e^{-\chi_l^2 A_1}}{\pi} \sum_{n,m=0}^{\infty} \frac{(-1)^{n+m} \chi_l^{2(n+m)} A_3^n A_4^m}{n! m!} e^{-i(m-n)\delta} \\ &\quad \times \frac{[\chi_l^2 A_2 + (n+m)\gamma]}{[\omega - (n-m)\omega_T]^2 + [\chi_l^2 A_2 + (n+m)\gamma]^2}, \end{aligned} \quad (16)$$

where the n and m indices represent different excitations of T -mode creation and annihilation events.

The double sum over Lorentzian shapes in Eq. (16) clearly shows that both motions (diffusion and oscillations) cannot be separated at all. Only the terms with $m=n$ (events with a zero energy balance) contribute to the Q peak, while those with $n \neq m$ will contribute to the T -mode peaks. As discussed in Refs. 4 and 12, the shape parameter also governs the shape of the peaks. Depending on the new shape parameter (the dependence on $\Delta\mathbf{K}$ is only through χ_l), the sums will contribute globally to different intermediate shapes ranging from a Gaussian function (high values of χ_l) to a Lorentzian one ($\chi_l \ll 1$). This smooth shape transition is the so-called *motional narrowing effect*, well-known in the theory of nuclear magnetic resonance line shapes.¹⁴ For a given system, this effect could be observable by changing the $\Delta\mathbf{K}$ value, as shown below. In Ref. 4 we proposed a similar functional form to Eq. (16) as a working formula but using instead the shape parameter for a flat surface [χ , as given by Eq. (7)]. With the new expression provided here, where χ has been replaced by χ_l , one can now determine the line shapes displayed by the Q and T -mode peaks in numerical calculations or in experiments after deconvolution for the whole first Brillouin zone. This is an important issue because the experimental deconvolution procedure is generally carried out for each peak separately (i.e., there is no overlapping), preassuming a given shape (an effective Lorentzian function) with no theoretical justification. This assumption leads to a proportionality between the effective width and the diffusion coefficient, which is not correct in general. In this sense, to perform the whole deconvolution procedure a generalization of such an equation is convenient, which will allow us to extract, at the same time, good diffusion coefficients, information about jump mechanisms, friction coefficients, and low T -mode frequencies. When more than one Lorentzian function contribute to Eq. (16), diffusion coefficients should be then obtained from the calculated jump distributions, and therefore not directly extracted from the experimental Q peak.

From the generalized expression for the line shape of the full process, given by Eq. (16), the width of each sum contributing to the Q peak reads now as

$$\Gamma_n^Q(\Delta\mathbf{K}) = \frac{\Gamma_\nu(\Delta\mathbf{K})}{2\gamma} A_2 + 2n\gamma. \quad (17)$$

Note that A_2 provides information about the dynamical process through the frequency associated with the T mode, the friction coefficient, and the phase of the velocity autocorrelation function [see Eqs. (12) and (15b)]. The surface temperature dependence appears implicitly in the shift of the position of the T -mode frequency and the jump distribution

P_j through $\Gamma_\nu(\Delta\mathbf{K})$ according to Eq. (9). Typically, the most important contribution to the Q peak at low temperatures is $\Gamma_{n=0}^Q$. Within this model, if $\delta=0$, $\omega_T=0$, and the regime of very small values of the parallel momentum transfer is studied, Eq. (10) is then satisfied and $\Gamma_0^Q(\Delta\mathbf{K})=D\Delta\mathbf{K}^2$, as obtained when a pure (or effective) Lorentzian function is assumed. Inelastic contributions (with zero energy balance) $\Gamma_{n\neq 0}^Q$ to the total width due to creation and annihilation processes of the T mode are important with the surface temperature and increase by integer numbers of γ . Mixed Lorentzian-Gaussian line shapes are very often obtained, the FWHM being calculated from the general expression of the dynamic structure factor.

In a similar fashion, the width of each sum contributing to the T peaks, according to Eq. (16), is given by

$$\Gamma_{n+m}^T(\Delta\mathbf{K}) = \frac{\Gamma_\nu(\Delta\mathbf{K})}{2\gamma} A_2 + (n+m)\gamma, \quad (18)$$

where the jump distribution P_j is also involved in the vibrational relaxation process through $\Gamma_\nu(\Delta\mathbf{K})$. It is generally assumed that the corresponding width is γ , which (within this model) is obtained when $n=1$, $m=0$, $\delta=0$, and $\gamma \ll \omega_0$; note that the first term in Eq. (18) behaves as γ^2/ω_0^2 , which is much smaller than the second term (which is equal to γ). In this case, the line shape is a pure Lorentzian function.

III. RESULTS

As an illustration of the theoretical approach proposed and described in Sec. II, we have carried out numerical Langevin simulations for the Na/Cu(001) system, which has been largely analyzed both experimentally and theoretically. The adiabatic nonseparable adsorbate-substrate interaction is taken from Ref. 3, with a coverage of 2.8% and for a surface temperature $T_s=150$ K. In Fig. 1(a), the shape parameter χ_l is plotted as a function of the parallel momentum transfer covering the first Brillouin zone. The solid curve has been obtained from Eqs. (9) and (11) after jump distributions were calculated. The circles give the fittings of the different Langevin simulations to the dynamic structure factor given by Eq. (16). In panels (b) and (c) of Fig. 1, the quality of the fitting for $\Delta K=1.23 \text{ \AA}^{-1}$ [black circle in panel (a)] for the Q and the two T -modes peaks, respectively, are shown; dotted lines correspond to the application of Eq. (16) with no adjustable parameters (nominal values: $\gamma=0.6$ meV, $\omega_T=5.99$ meV, and $\delta=0.05$), and dashed lines to the case where Eq. (16) has been used as a working formula with three different adjustable parameters ($\gamma=0.53$ meV, $\omega_T=5.82$ meV, and $\delta=0.032$). The whole spectrum is better reproduced in the last case; in the first fitting the right positions of the T -mode peaks are obtained but with very small intensities compared to the numerical simulations. Note, however, that for the Q peak, both fittings are approximately the same. The small deviations from the nominal values of the three parameters are a clear indicator of the non-Gaussian behavior of the dynamical system. Concerning the shape of the Q peak, when χ_l is greater than one (central region of the Brillouin zone), a mixed Gaussian-Lorentzian function is expected.

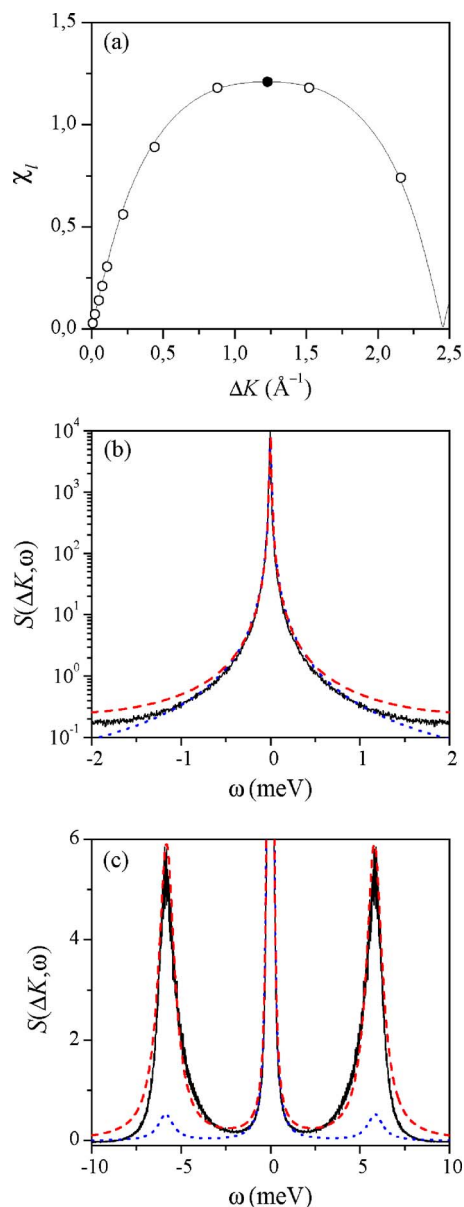


FIG. 1. (Color online) (a) Shape parameter χ_l as a function of the parallel momentum transfer covering the first Brillouin zone for the Na/Cu(001) system at $T_s=150$ K. Open circles correspond to the fitting of the numerical simulation, while the solid line is the result obtained from Eq. (11). The dynamic structure factor for the maximum momentum transfer, $\Delta K=1.23 \text{ \AA}^{-1}$ (solid circle), is plotted in panels for the Q peak (b) and for the two T -mode peaks (c). Solid (black) lines correspond to the numerical simulation; dotted (blue) lines represent the result obtained from using the working formula with no fitting parameters; and dashed (red) lines are the result when three fitting parameters (γ , ω_T , and δ) are employed.

In Fig. 2, the convolution of the dynamic structure factor (denoted by C_S) obtained from the Langevin numerical simulation for $\Delta K=1.23 \text{ \AA}^{-1}$ [see Fig. 1(c)] is plotted (solid line). Moreover, the convolutions of separate Lorentzian functions for the Q and T -mode peaks are also shown (dashed line for the Q peak and dotted lines for the T -mode peaks). The two panels correspond to two different surface temperatures: (a) 150 K and (b) 250 K. The response function of the experimental setup is known and given in Ref. 3. Discrepancies between the standard procedure and the one proposed here are apparent, as indicated by their different backgrounds, widths, and peak intensities.

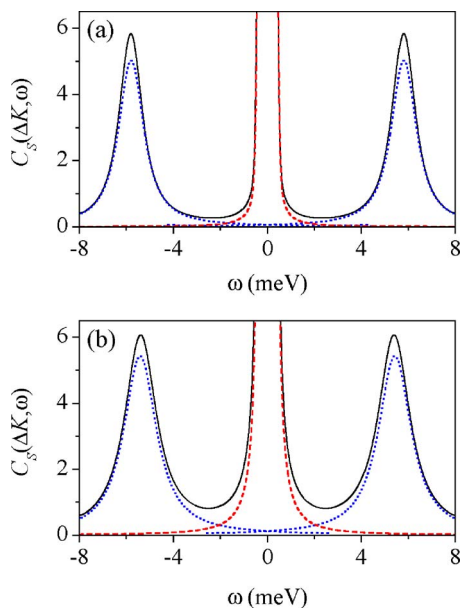


FIG. 2. (Color online) Numerical convolutions (solid line) of the Q and T -mode peaks for the Na/Cu(001) system with parallel momentum transfer $\Delta K=1.23 \text{ \AA}^{-1}$ at two different surface temperatures: (a) 150 K and (b) 250 K. Dashed (red) lines correspond to the convolution of a pure Lorentzian function for the Q peak; dotted (blue) lines denote the same but for the T -mode peaks.

As a word of conclusion, we consider that a convolution of the whole spectrum should be carried out in order to properly take into account the contributions of the events with zero energy balance in the Q peak, as well as the existing overlapping between both Q and T -mode peaks at larger momentum transfers and high surface temperatures.

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