Phonon contribution in grazing-incidence fast atom diffraction from insulator surfaces

L. Frisco\textsuperscript{1} and M.S. Gravielle\textsuperscript{1}

\textsuperscript{1}Instituto de Astronomía y Física del Espacio (UBA-CONICET). Casilla de Correo 67, Sucursal 28, (C1428EGA) Buenos Aires, Argentina.

(Dated: February 5, 2022)

We study the effect of crystal lattice vibrations on grazing-incidence fast atom diffraction (GIFAD) from insulator surfaces. To describe the phonon contribution to GIFAD we introduce a semi-quantum method, named Phonon-Surface Initial Value Representation (P-SIVR), which represents the surface with a harmonic crystal model, while the scattering process is described by means of the Surface Initial Value Representation approach, including phonon excitations. Expressions for the partial scattering probabilities involving zero- and one-phonon exchange are derived. In particular, the P-SIVR approach for zero-phonon scattering is applied to study the influence of thermal lattice vibrations on GIFAD patterns for Ne/LiF(001) at room temperature. It is found that the thermal lattice fluctuations introduce a polar-angle spread into the projectile distributions, which can affect the relative intensities of the interference maxima, even giving rise to interference sub-patterns depending on the incidence conditions. Present results are in agreement with the available experiments.

PACS numbers:

I. INTRODUCTION

Like in any interference phenomenon, in grazing-incidence fast atom diffraction (GIFAD or FAD) from ordered surfaces, the observation of interference patterns depends on the coherence conditions\cite{1,2}. In this regard, since the early reports of GIFAD\cite{1,2}, thermal lattice vibrations were suspected of deteriorating the coherence, making the observation of interference structures completely unexpected\cite{3,4}. This was based on the fact that in typical GIFAD experiments the de Broglie wavelengths of the projectiles are much smaller than the mean thermal fluctuations of the surface atoms, which would suggest a strong coherence loss. However, over the last decade GIFAD was observed for a wide variety of materials at room temperature\cite{5,6,7}, indicating that the quantum interference prevails over the decoherence mechanisms. Moreover, GIFAD patterns were found to be extremely sensitive to the projectile-surface interaction, allowing the determination of surface parameters smaller than the thermal vibration amplitudes, like rumpling\cite{8} or corrugation\cite{9} distances.

From the theoretical point of view, in spite of the above mentioned features, most of the GIFAD models\cite{10,11,12,13,14} consider an ideal and static crystal surface, with atoms or ions at rest at their equilibrium positions. On the other hand, few articles deal with the decoherence introduced in GIFAD by lattice vibrations\cite{15,16,17,18,19}, so this issue represents a problem not fully understood yet.

In this paper we study the effect of lattice vibrations, i.e., phonons, on GIFAD distributions from insulator surfaces. This kind of surfaces is a good candidate to investigate the partial decoherence introduced by phonons because the presence of a wide band-gap strongly suppresses the electronic excitations of the target, causing the main source of decoherence to come from the vibrational movements of the surface atoms\cite{20,21}.

With a view to describe the collision with a realistic crystal that enables phonon transitions, we develop a semi-quantum method, named Phonon-Surface Initial Value Representation (P-SIVR) approximation. It is based on the previous SIVR approach for elastic scattering from a rigid surface\cite{22}, which was successfully employed to describe experimental GIFAD patterns for different collision systems\cite{5,11,12}. The basic idea of the P-SIVR method is to incorporate a quantum representation of the surface, given by the harmonic crystal model\cite{23}, making possible the description of the phonon effects involved in the GIFAD process.

Within the P-SIVR approximation, the scattering probability can be expressed as a series on the number $n$ of phonons emitted or absorbed during the collision. Each term of the series, named here as $P_n$-SIVR probability, is associated with the grazing scattering involving the exchange of $n$ phonons. Mathematical formulas for the $P_n$-SIVR probabilities corresponding to $n = 0$ and $n = 1$ exchanged phonons are presented.

In this work the $P_0$-SIVR approach for zero-phonon scattering is applied to study the influence of thermal lattice vibrations on GIFAD patterns for Ne/LiF(001) at room temperature. With the aim of examining the thermal contribution, $P_0$-SIVR results for different incidence conditions are compared with values derived from the SIVR approach for the static surface. In all the considered cases, it is found that the thermal lattice vibrations contribute to the polar-angle spread of the projectile distributions, in accord with previous predictions\cite{3}. Furthermore, depending on the incidence conditions, such thermal fluctuations can affect the relative intensity of the interference peaks, even introducing an interference sub-pattern, as it is observed at a high normal energy. We show that present $P_0$-SIVR results are in very good agreement with the available experimental data\cite{24}. In addition, results from an incoherent model to include
The article is organized as follows. The P-SIVR approach is summarized in Sec. II, while details about its derivation are given in the Appendix. Results are presented and discussed in Sec. III and in Sec. IV we outline our conclusions. Atomic units (a.u.) are used unless otherwise stated.

II. THEORETICAL MODEL

The P-SIVR approximation can be considered as a natural extension of the SIVR approach to incorporate phonon effects into the GIFAD description. Summarizing, within the P-SIVR approximation the atom-surface scattering probability corresponding to the transition \( K_i \rightarrow K_f \), with \( K_i (K_f) \) being the initial (final) projectile momentum, is evaluated by adding the partial contributions coming from the different initial and final crystal states, which are derived from a quantum harmonic-crystal model. The result is then expanded in terms of the number \( n \) of phonons that are exchanged with the crystal, giving rise to a series of \( n \)-SIVR probabilities associated with \( n \)-phonon scattering. In this Section we present mathematical expressions of the \( n \)-SIVR probability for a given value of \( n \), as well as the steps involved in its derivation, are given in the Appendix.

The P0-SIVR probability for the transition \( K_i \rightarrow K_f \) without phonon exchange, which corresponds to the elastic scattering with \( K_f = K_i \), can be expressed as

\[
\frac{dP_0}{dK_f} = |A_{n_{ph}=0}|^2, \tag{1}
\]

while the P1-SIVR probability for one-phonon scattering reads

\[
\frac{dP_1}{dK_f} = \sum_{k,l} \left[ \frac{N_{l}(k)}{\omega_l(k)} |A_{n_{ph}=-1}(k,l)|^2 + \frac{N_{l}(k) - 1}{\omega_l(k)} |A_{n_{ph}=+1}(k,l)|^2 \right], \tag{2}
\]

where \( A_{n_{ph}} \) is the effective transition amplitude for scattering involving \( n_{ph} = \pm n \) phonons emitted (\( n_{ph} = -n \)) or absorbed (\( n_{ph} = +n \)) by the crystal. In Eq. \((2)\) the sum runs over all the normal modes of the crystal, with \( \omega_l(k) \) being the phonon frequency in the branch \( l \), with the wave vector \( k \). The factor \( N_l(k) = \frac{\exp[\omega_l(k)/k_BT] - 1}{\omega_l(k)/k_BT} \) is the Bose-Einstein occupation function for \( k,l \) phonons in a crystal target at temperature \( T \), with \( k_B \) being the Boltzmann constant.

In Eqs. \((1)\) and \((2)\), the effective transition amplitude \( A_{n_{ph}}(k,l) \) reads

\[
A_{n_{ph}}(k,l) = \int dR_o\ f(R_o) \int dK_o\ g(K_o) \times \int d\nu_o\ \alpha_{n_{ph}}^{(k,l)}(R_o, K_o, \nu_o), \tag{3}
\]

where the function \( f (g) \) describes the position (momentum) profile of the incident wave packet and

\[
\alpha_{n_{ph}}^{(k,l)}(R_o, K_o, \nu_o) = \int_0^{+\infty} dt \ |J_P(t)|^{1/2} e^{i\nu_o t/2} \mathcal{V}_n^{(k,l)}(R_t) \times \exp[i(\varphi_t - Q \cdot R_o + n_{ph}\omega_l(k)t)] \tag{4}
\]

represents the partial amplitude associated with the classical projectile trajectory \( R_t = R_i + k_f t \), which starts at the position \( R_i \) with momentum \( K_f \) and is determined by the spatial configuration \( \nu_o \) of the crystal at the initial time \( t = 0 \). That is, the underlined vector \( \nu_o \) denotes the \( 3N \)-dimensional vector associated with the spatial deviations of the \( N \) ions contained in the crystal sample, with respect to their equilibrium positions, at \( t = 0 \).

In Eq. \((2)\), \( J_P(t) = |J_P(t)| \exp(\nu_o t) \) is the Jacobian factor given by Eq. \((A.16)\), \( \varphi_t \) is the SIVR phase at the time \( t \) [Eq. \((A.14)\)], and \( Q = K_f - K_i \) is the projectile momentum transfer. The function \( \mathcal{V}_n^{(k,l)}(R_t) \) is a crystal factor that depends on the number \( n \) of exchanged phonons. For zero-phonon scattering, \( \mathcal{V}_0^{(k,l)}(R_t) \) is independent on \( (k,l) \) and can be expressed as

\[
\mathcal{V}_0(R_t) = \int dq \sum_{R_B} \tilde{\nu}_{R_B}(q) \exp[-W_{R_B}(q)] \times \exp[i(q \cdot R_t - R_B)], \tag{5}
\]

where \( \tilde{\nu}_{R_B}(q) \) denotes the Fourier transform of the binary interaction between the projectile and the crystal placed at the Bravais position \( R_B \), with \( R_B \) coming from Eq. \((A.16)\). The summation on \( R_B \) covers all the occupied lattice sites and \( W_{R_B}(q) \) is the usual momentum-dependent Debye-Waller function, defined by Eq. \((A.21)\).

For one-phonon scattering, instead, \( \mathcal{V}_1^{(k,l)}(R_t) \) depends on \( (k,l) \), reading

\[
\mathcal{V}_1^{(k,l)}(R_t) = \int dq \ [q \cdot \alpha_t(k)] \sum_{R_B} \tilde{\nu}_{R_B}(q) \exp[-W_{R_B}(q)] \times \exp[i(q \cdot R_t + i(k - q) \cdot R_B)], \tag{6}
\]

where \( \alpha_t(k) \) is the polarization vector corresponding to the \( (k,l) \) phonon.

From Eq. \((6)\) it can be noted that in absence of the Debye-Waller factor, \( \exp[-W_{R_B}(q)] \), \( \mathcal{V}_0(R_t) \) coincides with the projectile-surface potential for an ideal crystal, given by Eq. \((A.16)\) with \( \nu = 0 \). Therefore, within the

thermal lattice vibrations are analyzed.
P0-SIVR approach the contribution of the thermal lattice vibrations can be seen as an effective screening of the projectile-surface interaction, given by the Debye-Waller factor, in addition to the thermal effect on the projectile trajectories that is produced by the different crystal configurations $u_o$.

III. RESULTS

In this article we investigate the influence of the thermal lattice vibrations on GIFAD patterns produced by $^{20}$Ne atoms grazingly colliding with a LiF(001) surface at room temperature. Incidence along the (110) direction, for which experimental spectra were reported [30], is analyzed. Concerning the atomic projectile, the relatively large mass of neon is expected to play some role in inelastic processes, like phonon excitations [23, 24]. However, we confine our study to the P0-SIVR approach, corresponding to zero-phonon scattering, leaving the investigation of one-phonon excitations, as given by Eq. [2], for a future work.

The P0-SIVR probability for scattering in the direction of the solid angle $\Omega_f = (\theta_f, \phi_f)$ was derived from Eq. [1] as

$$dP_f/d\Omega_f = K_f^2 |A_{ph}=0|^2,$$

(7)

where $\theta_f$ is the final polar angle, measured with respect to the surface, and $\phi_f$ is the azimuthal angle, measured with respect to the axial channel. The transition amplitude $A_{ph}=0$ was calculated from Eq. [3], where the integration on $R_o$ was reduced to the plane parallel to the surface, $R_o||$, by considering that at $t = 0$ all the classical trajectories start at a fixed distance $Z_o$ from the surface, chosen as equal to the latent constant, for which the projectile is hardly affected by the surface interaction [3, 20]. In turn, the integral on $K_o$ was solved in terms of the solid angle $\Omega_o = (\theta_o, \phi_o)$ that determines the $K_o$-orientation, with $K_o = K_i$ accounting for the negligible energy dispersion of the incident beam [24, 24]. In Eq. [3], the wave-packet profiles $f(R_o||)$ and $g(\Omega_o)$ were represented by products of Gaussian functions, as respectively given by Eqs. (12) and (14) of Ref. [3]. The widths of these profiles depend on the collimating setup and the incidence conditions [3, 31]. However, in this work we have used fixed values for such dispersion widths in order to control their influence on the GIFAD patterns. Specifically, in the Subsections III. A and III. B the angular widths were chosen as $\Delta \theta_o = \Delta \phi_o = 0.03$ deg, values that are in the range of the experimental conditions [30].

The projectile-surface interaction was described with the pairwise additive model of Ref. [22]. In addition, the integral on $u_o$ involved in Eq. [3] was evaluated by considering that each crystal ion is randomly displaced from its equilibrium position following an independent Gaussian distribution, with a mean-square vibrational amplitude $(u_o(r_b)^2)$. For the LiF(001) target at temperature $T = 300$ K, the $(u_o(r_b)^2)$ values were extracted from Ref. [16] by taking into account the differences between Li and F ions and between bulk and surface (topmost layer) sites.

For the calculation of $V_0(R_t)$ [Eq. [5]], the Debye-Waller function was approximated as $W_{D}(q) \approx q^2(u_o(r_b)^2)/2$ [22, 29]. This assumption allowed us to transform the $q^2$ integral involved in Eq. [5] into a space integral, which was solved together with the $R_o||$, $\Omega_o$ and $u_o$ integrals of Eq. [3] by employing the Monte Carlo technique, with more than $6 \times 10^6$ points for each incidence condition. Furthermore, for each integration point the time integral involved in Eq. [4] was numerically solved by using an adaptive-stepsize method, with an error lower than 1%. In this respect, the incorporation of $u_o$ into the evaluation of the projectile trajectories leads to increase strongly the numerical effort necessary to reach the convergence of the Monte Carlo integration, in relation to that required within the SIVR approach [20].

A. Thermal influence on GIFAD patterns

In Fig. 1 we show SIVR and P0-SIVR two-dimensional (2D) distributions, as a function of the final angles $\theta_f$ and $\phi_f$, for Ne atoms impinging on LiF(001) along the (110) channel, with $E = 3.0$ keV and $\theta_i = 0.47$ deg. Results derived within a) the SIVR approximation, for a static crystal, and b) the P0-SIVR approach, including thermal vibrations, are displayed.

FIG. 1: (Color online) Two-dimensional projectile distributions, as a function of $\theta_f$ and $\phi_f$, for Ne atoms impinging on LiF(001) along the (110) channel, with $E = 3.0$ keV and $\theta_i = 0.47$ deg. Results derived within a) the SIVR approximation, for a static crystal, and b) the P0-SIVR approach, including thermal vibrations, are displayed.
Probability (arb. units) based on the comparison of the relative intensities of the Bragg order, as shown in the inset of Fig. 2. Hence, which can increase or reduce the SIVR intensity of a given maxima are strongly modified by the contribution of the thermal fluctuations included in the P0-SIVR approach, as it is usually done to derive the experimental projected angular positions of the Bragg peaks (indicated with vertical lines in the inset) are not affected by the thermal vibrations, coinciding for the P0-SIVR and SIVR approximations. Instead, the relative intensities of the Bragg vibrations, coinciding for the P0-SIVR and SIVR approximations. From Fig. 2 we observe that the angular positions of the Bragg peaks (indicated with vertical lines in the inset) are not affected by the thermal vibrations, coinciding for the P0-SIVR and SIVR approximations. Instead, the relative intensities of the Bragg maxima are strongly modified by the contribution of the thermal fluctuations included in the P0-SIVR approach, which can increase or reduce the SIVR intensity of a given Bragg order, as shown in the inset of Fig. 2. Hence, since the use of GIFAD for surface analysis is commonly expected to be more affected by thermal fluctuations than the rainbow, which is confirmed in Fig. 3.

The P0-SIVR spectrum of Fig. 3 presents a small angular shift in the positions of the central supernumerary rainbow maxima with theoretical models, these results suggest that the thermal vibrations might play an important role in the GIFAD technique. At this point, it is important to take into account that the Bragg-peak intensities are determined by an intra-channel factor due to the interference inside a single channel, which acts as an enveloped function of the inter-channel interference [20]. Therefore, for the purpose of analyzing the influence of lattice vibrations on the Bragg intensities under different incidence conditions, hereinafter we restrict our study to pure intra-channel spectra, which are produced by initial wave-packet profiles covering a transverse distance equal to the channel width [31].

B. Thermal effects in the intra-channel interference

GIFAD distributions due to a single coherently illuminated channel are governed by the normal incidence energy, \( E_\perp = E \sin^2 \theta_i \), which is associated with the projectile motion perpendicular to the surface plane [33, 35]. In Fig. 3 we display P0-SIVR and SIVR intra-channel spectra, as a function of the azimuthal angle \( \varphi_f \), for \( E = 1.3 \) keV and \( E_\perp = 0.30 \) eV. Notice that this normal energy is barely lower than the upper \( E_\perp \)-limit of available GIFAD experiments for Ne/LiF(001) [30]. Both curves of Fig. 3 display equivalent interference patterns, with rainbow and supernumerary rainbow maxima. While the rainbow peaks, corresponding to the high-intensity outermost maxima, have a classical origin, the supernumerary peaks are produced by quantum interference, being expected to be more affected by thermal fluctuations than the rainbow, which is confirmed in Fig. 3.

In Figs. 1a) and 1b) the Bragg maxima look like vertical stripes placed inside an annulus with mean radius \( \theta_i \), due to the energy conservation. Even though the SIVR and P0-SIVR distributions of Fig. 1 display qualitatively similar interference patterns, with almost the same \( \varphi_f \)-extension of the spectrum, the relative intensities of the interference maxima, as well as the \( \theta_f \)-angular spreads, predicted by the two approximations differ each other, these discrepancies being indicative of the effect of the thermal lattice vibrations.

To look with more detail into the projectile distributions of Fig. 1 in Fig. 2 we plot the corresponding \( dR/\theta_f \) probabilities, as a function of the deflection angle \( \Theta_f = \arctan(\varphi_f/\theta_f) \). These differential probabilities were obtained by integrating Eq. 7 over a reduced annulus of mean radius \( \theta_i \) and central thickness 0.03 deg, as it is usually done to derive the experimental projected intensities [33, 34]. From Fig. 2 we observe that the angular positions of the Bragg peaks (indicated with vertical lines in the inset) are not affected by the thermal vibrations, coinciding for the P0-SIVR and SIVR approximations. Instead, the relative intensities of the Bragg maxima are strongly modified by the contribution of the thermal fluctuations included in the P0-SIVR approach, which can increase or reduce the SIVR intensity of a given Bragg order, as shown in the inset of Fig. 2.
angular distributions, as a function of the deflection angle $\Theta_f$, for the incidence energy $E = 1.3$ keV and angle $\theta_f = 0.55 \text{ deg}$ [i.e., $E_\perp = 0.12$ eV]. Lines, analogous to Fig. 1 b) gray solid circles, experimental data from Ref. [30].

C. Experimental comparison

In order to test the reliability of the proposed model, in Fig. 5 we contrast P0-SIVR and SIVR differential probabilities, as a function of the deflection angle $\Theta_f$, with the available experimental spectrum [30] for the incidence conditions $E = 1.3$ keV and $\theta = 0.55 \text{ deg}$, which correspond to the normal energy $E_\perp = 0.12$ eV. Like in the previous Subsection, in this case the theoretical and experimental distributions display only supernumerary peaks, associated with intra-channel interference, without any trace of Bragg interference.

In Fig. 5 the P0-SIVR spectrum is very similar to that for a static crystal derived by means of the SIVR approach, both showing a very good agreement with the experimental data. This behavior, together with the absence of interference sub-structures in the P0-SIVR supernumeraries, might indicate that the thermal contribution on GIFAD patterns becomes smaller as $E_\perp$ decreases, since the atomic projectiles move farther from the surface plane.

However, notice that the $\Theta_f$- spectra displayed in Fig. 5 were also obtained by integrating the corresponding 2D-angular distributions, shown in Fig. 6 inside an annulus of central thickness 0.03 deg [30]. When the distributions of Figs. 6 a) and 6 b) are compared, it is found that even though for this low perpendicular energy there are no visible signatures of interference sub-structures, the thermal motion of the crystal ions still introduces a wide polar-angle dispersion in the P0-SIVR distribution. It gives rise to a P0-SIVR pattern formed by elongated vertical streaks, instead of the nearly circular spots of the SIVR distribution, which is in good accord with the experiment of Fig. 1 a) of Ref. [30].
contrasting Figs. 4b) and 7 we found that the incoherent addition of thermal effects destroys the interference sub-pattern observed in the central region of P0-SIVR distribution of Fig. 4b). Moreover, the thermally-incoherent approach introduces a significant broadening of the supernumerary maxima along $\phi_f$, while the $\theta_f$ dispersion is similar to that displayed by the P0-SIVR distribution. Although there is no available experimental distribution for this case, an analogous calculation for the case of Fig. 6 shows that this noticeable $\phi_f$ widening of the interference peaks, associated with the incoherent thermal contribution, does not agree with the reported experiments [30]. Therefore, the thermally-incoherent SIVR approximation [32] seems not to be suitable to reproduce thermal effects on GIFAD patterns.

IV. CONCLUSIONS

We have developed the P-SIVR approximation, which is a semi-quantum method that takes into account the contribution of the vibrational modes of the crystal to the GIFAD patterns. The P-SIVR probability was expressed as a sum of partial scattering probabilities, $P_n$, each of them involving the exchange of a different number $n$ of phonons. Formulas for the probabilities corresponding to zero- and one-phonon scattering have been presented.

The P0-SIVR approach for zero-phonon scattering was employed to investigate the effect of the thermal lattice vibrations on GIFAD distributions for the Ne/LiF(001) system. At room temperature it was found that, depending on the incidence conditions, the relative intensities of the Bragg peaks can be affected by the thermal fluctuations of the LiF(001) crystal. Within the P0-SIVR model, the thermal vibrations introduce a polar-angle dispersion into the angular distributions, which contribute to transform the interference spots into elongated structures, in concordance with the experimental observations [30]. For high normal energies, such a polar-angle spread can also alter the shape of the supernumerary maxima, giving rise to the appearance of interference sub-patterns in the central region of the GIFAD spectra.

In conclusion, present P0-SIVR results demonstrate that thermal vibrations affect the aspect of the GIFAD patterns from insulator surfaces, a finding that is especially relevant for the use of GIFAD as a surface analysis technique. But notice that there are other effects, like phonon excitations [22, 23] or the presence of terraces in the crystal sample [37], not considered in this article, which can modify the interference structures too. Therefore, further experimental and theoretical work to investigate the different decoherence mechanisms in GIFAD would be valuable.
Acknowledgments

The authors acknowledge financial support from CONICET and ANPCyT of Argentina.

Appendix: P-SIVR model for grazing atom-surface scattering with phonon exchange

In this Appendix we explain the steps and assumptions that lead to the P-SIVR approximation for GIFAD from an insulator target. Let us consider an atomic projectile \( P \), with initial momentum \( K_i \), which is scattered from a crystal surface \( S \), ending in a final state with momentum \( K_f \). The scattering state of the projectile-surface system at the time \( t \), \(|\Psi_i(t)\rangle\), is governed by the time-dependent Schrödinger equation

\[
\frac{d}{dt} |\Psi_i(t)\rangle = i \left[ \frac{P^2}{2m_P} + H_S + V_{PS} \right] |\Psi_i(t)\rangle,
\]

where \( P \) denotes the momentum operator of the projectile with mass \( m_P \), \( H_S \) is the unperturbed surface Hamiltonian, and \( V_{PS} \) is the perturbation produced by the projectile-surface interaction. The Hamiltonian \( H_S \) reads

\[
H_S = \sum_{r_B} \frac{P^2(r_B)}{2m(r_B)} + W_S(u),
\]

where the sum runs over the positions \( r_B \) of the occupied Bravais lattice sites. In Eq. (A.2) \( P(r_B) \) indicates the momentum operator of the crystal ion that oscillates about \( r_B \) and \( m(r_B) \) is its mass, with \( m(r_B) = m_1 \) or \( m_2 \) to include two different ions in the crystallographic basis. The potential \( W_S(u) \) represents the potential energy of the crystal as a function of the multi-dimensional vector \( u \), which is determined by the spatial deviations \( u(r_B) \) of the crystal ions from their equilibrium positions \( r_B \), for all the occupied lattice sites [29].

As initial condition, at \( t = 0 \), when the projectile is far away from the surface, the scattering state \(|\Psi_i(t)\rangle\) tends to the state \(|\chi_i(0)\rangle\), where

\[
\chi_j(t) = e^{iK_j \cdot R_p} \phi_j(u) \exp(-iE_j t), \quad j = i(f),
\]

is the initial (final) unperturbed wave function with total energy

\[
E_j = K_j^2/(2m_P) + \epsilon_j, \quad j = i(f)
\]

which satisfies the energy conservation, i.e., \( E_i = E_f \).

In Eq. (A.3), \( R_p \) is the position vector of the center of mass of the incident atom and the wave function \( \phi_j(u) \), for \( j = i(f) \), is the initial (final) eigenstate of \( H_S \) with eigenvalue \( \epsilon_j \).

By considering that the surface behaves like a harmonic crystal, \( H_S \) can be expressed as a sum of independent harmonic-oscillator Hamiltonians, each of them corresponding to a different normal mode of the lattice, with wave vector \( k \), frequency \( \omega_l(k) \), and \( l \) denoting the phonon branch. Hence, the unperturbed crystal state \( \phi_{jl} \), for \( j = i, f \), is determined by the excitation numbers \( n_{kl}^{(j)} \) of the normal modes and the corresponding crystal energy reads

\[
\epsilon_j = \sum_{k,l} \omega_l(k) \left[ n_{kl}^{(j)} + \frac{1}{2} \right], \quad j = i, f,
\]

where the sum runs over all the \((k,l)\) normal modes of the crystal [29].

1. P-SIVR scattering state

Within the P-SIVR method, the scattering state \(|\Psi_i(t)\rangle\) is approximated by means of the IVR method [35]. It is expressed as

\[
|\Psi_i^{(P-SIVR)}(t)\rangle = \int dR_o f(R_o) \int dK_o g(K_o)
\]

\[
\times \int dS_o \int dK_o \int dP_o [J(t)]^{1/2} \exp(iK \cdot R_o) \times \exp(iS_o \phi(u_o) |R_o\rangle \otimes |u_o\rangle),
\]

where the position ket \( |R_o\rangle \) is associated with the time-evolved position \( R_i \) of the incident atom at a given time \( t \), which is derived by considering a classical trajectory with starting position and momentum \( R_o \) and \( K_o \), respectively. In a similar way, the deviation ket \( |u_o\rangle \) is determined from the classical deviations \( u_i(r_B) \) of all the crystal ions, starting at \( t = 0 \) from initial deviations and momenta \( u_o(r_B) \) and \( p_o(r_B) \), respectively. In Eq. (A.6), \( u_i(r_B) \) denotes the 3N-dimension vector determined by such deviations (momenta) for the \( N \) ions contained in the crystal target. In fact, note that we are dealing with a many-particle problem, in which the classical motions of the projectile and the crystal ions are related through their mutual interactions. Consequently, the classical trajectories \( R_i \) and \( u_i(r_B) \), for the different \( r_B \)-values, depend on the initial positions and momenta of all the particles in the system.

Furthermore, in Eq. (A.6) the functions \( f(R_o) \) and \( g(K_o) \) describe the shape of the position- and momentum-wave packet associated with the incident projectile, while \( S_i \) represents the classical action along the trajectory, reading

\[
S_i = \int_{t_0}^{t} dt' \left[ \frac{K^2}{2m_P} - V_{PS}(R_{i'}, u_{i'}) \right]
\]

\[
+ \sum_{r_B} \frac{P^2(r_B)}{2m(r_B)} - W_S(u_{i'}) \right],
\]

corresponding to \( \sum_{r_B} \frac{P^2(r_B)}{2m(r_B)} - W_S(u_{i'}) \)
where \( \mathbf{K}_i = m_P d \mathbf{R}_i / dt \) and \( \mathbf{p}_i(\mathbf{r}_B) = m(\mathbf{r}_B) d \mathbf{u}_i(\mathbf{r}_B) / dt \) are the classical projectile and crystal ion momenta, respectively, at the time \( t \). The Jacobian factor
\[
J(t) = \det \left[ \frac{\partial \mathbf{R}_i}{\partial \mathbf{K}_o} \frac{\partial \mathbf{u}_o}{\partial \mathbf{p}_j} \right]. \tag{A.8}
\]
is a determinant evaluated along the classical path, which takes into account the motions of the projectile and all the crystal ions. This Jacobian factor can be related to the Maslov index \([39]\) by expressing it as
\[
\langle \Phi_f(t) | V_{PS}(\mathbf{R}_t, \mathbf{u}_o) | \Phi_i(t) \rangle,
\]
where \( \Phi_j(t) = \phi_j(\mathbf{u}) \exp(-i \epsilon_f t) \), for \( j = i, f \), \( \mathbf{Q} = \mathbf{K}_f - \mathbf{K}_i \), and
\[
\varphi_t = \int_0^t dt' \left[ \frac{(\mathbf{K}_f - \mathbf{K}_i)^2}{2m_P} - V_{PS}(\mathbf{R}_t, \mathbf{u}_o) \right]. \tag{A.14}
\]
is the SIVR phase at the time \( t \). By contrasting Eq. (A.12) with the SIVR partial amplitude for a static surface, given by Eq. (6) from Ref. [3], notice that, apart from the dependence of \( \mathbf{R}_i \) and \( \varphi_t \) on \( \mathbf{u}_o \), the P0-SIVR partial amplitude differs from the SIVR one by the substitution of the projectile-surface potential by the crystal factor \( F_{i_f}^{(c)} \), which is related to the first-order Born amplitude for the crystal-state transition \( |\phi_i\rangle \rightarrow |\phi_f\rangle \).

2. P-SIVR transition amplitude

By using the P-SIVR scattering state, given by Eq. (A.6), within the framework of the time-dependent distorted-wave formalism \([40]\), the P-SIVR transition amplitude reads
\[
A^{(PSIVR)} = -i \int_0^{+\infty} dt \left[ \chi_f(t)|V_{PS}|\Psi_i^{(PSIVR)}(t) \right]. \tag{A.9}
\]
For the evaluation of Eq. (A.9) a meaningful simplification can be obtained by considering that in GIFAD the interaction time of the projectile with the crystal surface is much shorter than the characteristic time of phonon vibrations \([29]\). Therefore, we can assume that the crystal ions remain at their initial positions \( \mathbf{u}_o(\mathbf{r}_B) \) during the collision, leading to
\[
J(t) \approx J_P(t) = \det \left[ \frac{\partial \mathbf{R}_i}{\partial \mathbf{K}_o} \right]. \tag{A.10}
\]

Then, by introducing the closure relation for the initial deviations of the crystal ions, the P-SIVR transition amplitude can be expressed, except for a normalization factor, as
\[
A^{(PSIVR)} = A^{[a_{if}]} = \int d\mathbf{R}_o \ f(\mathbf{R}_o) \int d\mathbf{K}_o \ g(\mathbf{K}_o) \times \int d\mathbf{u}_o \ a_{if}, \tag{A.11}
\]
where
\[
a_{if} = \int_0^{+\infty} dt \ |J_P(t)|^{1/2} e^{i\nu t \pi/2} F_{i_f}^{(c)}(\mathbf{R}_t, t) \times \exp \left[ i \left( \varphi_t - \mathbf{Q} \cdot \mathbf{R}_o \right) \right] \tag{A.12}
\]
is the partial amplitude associated with the classical path \( \mathbf{R}_t = \mathbf{R}_i(\mathbf{R}_o, \mathbf{K}_o, \mathbf{u}_o) \), which was derived by assuming that the initial deviations \( \mathbf{u}_o \) are decoupled from \( \phi_i(\mathbf{u}) \). In Eq. (A.12), the function \( F_{i_f}^{(c)} \) is defined as
\[
F_{i_f}^{(c)}(\mathbf{R}_t, t) = \langle \Phi_f(t) | V_{PS}(\mathbf{R}_t, \mathbf{u}) | \Phi_i(t) \rangle, \tag{A.13}
\]
where \( \Phi_j(t) = \phi_j(\mathbf{u}) \exp(-i \epsilon_f t) \), for \( j = i, f \), \( \mathbf{Q} = \mathbf{K}_f - \mathbf{K}_i \), and
\[
\varphi_t = \int_0^t dt' \left[ \frac{(\mathbf{K}_f - \mathbf{K}_i)^2}{2m_P} - V_{PS}(\mathbf{R}_t, \mathbf{u}_o) \right]. \tag{A.14}
\]
is the SIVR phase at the time \( t \). By contrasting Eq. (A.12) with the SIVR partial amplitude for a static surface, given by Eq. (6) from Ref. [3], notice that, apart from the dependence of \( \mathbf{R}_i \) and \( \varphi_t \) on \( \mathbf{u}_o \), the P0-SIVR partial amplitude differs from the SIVR one by the substitution of the projectile-surface potential by the crystal factor \( F_{i_f}^{(c)} \), which is related to the first-order Born amplitude for the crystal-state transition \( |\phi_i\rangle \rightarrow |\phi_f\rangle \).

3. P-SIVR differential probability

The P-SIVR differential probability for scattering with final momentum \( \mathbf{K}_f \) from a crystal surface in the initial state \( |\phi_i\rangle \), is obtained from Eq. (A.11) as
\[
\frac{dP_i^{(PSIVR)}}{d\mathbf{K}_f} = \sum f' \left| A^{[a_{if}]} \right|^2, \tag{A.15}
\]
where the sum over \( f' \) involves the addition of all the final crystal states \( |\phi_{f'}\rangle \) satisfying the total energy conservation.

In order to derive a more easy to handle expression for Eq. (A.15), we introduce a pairwise additive model to represent the projectile-surface interaction. Within the pairwise model, \( V_{PS} \) is built by adding the binary interatomic potentials that describe the interaction of the atomic projectile with individual ionic centers of the crystal. It reads
\[
V_{PS}(\mathbf{R}_t, \mathbf{u}) = \sum_{\mathbf{r}_B} v_{r_B} (\mathbf{R}_t - \mathbf{r}_B - \mathbf{u}(\mathbf{r}_B)), \tag{A.16}
\]
where \( v_{r_B}(\mathbf{r}) \) denotes the binary projectile-ion interaction as a function of the relative vector \( \mathbf{r} \), with \( v_{r_B} = v_1 \) or \( v_2 \) to consider the two different ions of the crystallographic basis. Replacing Eq. (A.16) in Eq. (A.13), the crystal factor can be expressed as
\[
F_{i_f}^{(c)}(\mathbf{R}_t, t) = (2\pi)^{-3/2} \sum_{\mathbf{r}_B} \hat{v}_{r_B}(\mathbf{q}) e^{i\mathbf{q} \cdot (\mathbf{R}_t - \mathbf{r}_B)} \times \langle \phi_f | \exp[-i \mathbf{q} \cdot \mathbf{U}_t(\mathbf{r}_B)] | \phi_i \rangle, \tag{A.17}
\]
where $\tilde{v}_{n}(q)$ is the Fourier transform of $v_{n}(r)$ and $U_{i}(r_{B}) = \exp(iH_{St})u(r_{B})\exp(-iH_{St})$ is the deviation operator within the Heisenberg picture.  

Finally, to compare with the experiments the differential probability $dP_{i}^{(p-SIVR)}/d\mathbf{K}_{f}$, given by Eq. (A.15), must be averaged over the equilibrium distribution of the $\psi_{i}$-wave functions. Following a procedure similar to that given in the Appendix N of Ref. [29], after some steps of algebra that involve the use of Eq. (A.17), we obtain an averaged probability $dP_{i}^{(p-SIVR)}/d\mathbf{K}_{f}$, which includes a correlation factor

$$C(q, r_{B}, t; q', r_{B}', t') = \left\{ \exp \left[ i q' \cdot U_{i}(r_{B}) \right] \exp \left[ -i q \cdot U_{i}(r_{B}) \right] \right\} \exp \left[ -W_{n}(q) - W_{n}(q') \right]$$

(A.18)

where the averaged value $\langle X \rangle$ of any operator $X$ at the equilibrium temperature $T$, is given by Eq. (N.13) of Ref. [29]. The factor $C(q, r_{B}, t; q', r_{B}', t')$ can be then expanded as a power series

$$C(q, r_{B}, t; q', r_{B}', t') = \exp \left[ -W_{n}(q) - W_{n}(q') \right] \times \sum_{n=0}^{+\infty} c_{n}(q, r_{B}, t; q', r_{B}', t')$$

(A.19)

with

$$c_{n}(q, r_{B}, t; q', r_{B}', t') = \left\{ \left[ q' \cdot U_{i}(r_{B}) \right] \left[ q \cdot U_{i}(r_{B}) \right] \right\}^{n}$$

(A.20)

and $W_{n}(q)$ being the Debye-Waller function, defined as

$$W_{n}(q) = \frac{\left\langle q \cdot u_{n}(r_{B}) \right\rangle^{2}}{2}$$

(A.21)

where the dependence on $r_{B}$ indicates that its value changes for the different species of the crystallographic basis, as well as for bulk or surface positions.

Using the expansion given by Eq. (A.19), the P-SIVR probability can be expressed as a series

$$\frac{dP_{i}^{(p-SIVR)}}{d\mathbf{K}_{f}} = \sum_{n=0}^{+\infty} \frac{dP_{n}}{d\mathbf{K}_{f}},$$

(A.22)

where $dP_{n}/d\mathbf{K}_{f}$ accounts for the partial probability corresponding to the $\mathbf{K}_{i} \rightarrow \mathbf{K}_{f}$ transition with the exchange of $n$ phonons. It reads

$$\frac{dP_{n}}{d\mathbf{K}_{f}} = \int_{r_{B}, r_{B}'} dq \int_{t} dt' \left[ \int_{0}^{+\infty} dt \right] c_{n}(q, r_{B}, t; q', r_{B}', t') \times A[b_{i}(q, r_{B})] A[b_{i}(q', r_{B}')]$$

(A.23)

with $A[b]$ defined by Eq. (A.11) and

$$b_{i}(q, r_{B}) = [JP(t)]^{1/2} e^{iQ \cdot r_{B}} \tilde{v}_{n}(q) \exp \left[ -W_{n}(q) \right] \times \exp \left[ i (\varphi + Q \cdot R_{o} + q \cdot (R_{z} - R_{B})) \right].$$

(A.24)

From Eq. (A.23) we derive more compact expressions for the orders $n = 0$ and $n = 1$, corresponding to the partial probabilities for zero- and one-phonon scattering, which are given in the text by Eqs. (1) and (2), respectively.
Scattering of Fast Helium Atoms from an Oxygen Covered Mo(112) Surface. *Phys. Rev. Lett.*, 108:065503, 2012.

[13] J. Seifert, M. Busch, E. Meyer, and H. Winter. Surface Structure of Alanine on Cu(110) Studied by Fast Atom Diffraction. *Phys. Rev. Lett.*, 111:137601, 2013.

[14] A. Zugarramurdi, M. Debiossac, P. Lunca-Popa, A. J. Mayne, A. Momeni, A. G. Borisov, Z. Mu, P. Roncin, and H. Khemliche. Determination of the geometric corrugation of graphene on SiC(0001) by grazing incidence fast atom diffraction. *Appl. Phys. Lett.*, 106:101902, 2015.

[15] A. Momeni, E. M. Staicu Casagrande, A. Dechaux, and H. Khemliche. Ultrafast Crystallization Dynamics at an Organic-Inorganic Interface Revealed in Real Time by Grazing Incidence Fast Atom Diffraction. *J. Phys. Chem. Lett.*, 9:908–913, 2018.

[16] A. Schüller, S. Wethkaam, D. Blauth, H. Winter, F. Aigner, N. Simonović, B. Solleder, J. Burgdörfer, and L. Wirtz. Rumpling of LiF(001) surface from fast atom diffraction. *Phys. Rev. A*, 82:062902, 2010.

[17] M. Debiossac, A. Zugarramurdi, Z. Mu, P. Lunca-Popa, A. J. Mayne, and P. Roncin. Helium diffraction on SiC grown graphene: Qualitative and quantitative descriptions with the hard-corrugated-wall model. *Phys. Rev. B*, 94:205403, 2016.

[18] A. Schüller, D. Blauth, J. Seifert, M. Busch, H. Winter, K. Gärtner, R. Wlodarczyk, J. Sauer, and M. Sierka. Fast atom diffraction during grazing scattering from a MgO(001) surface. *Surf. Sci.*, 606:161–173, 2012.

[19] M. Debiossac, A. Zugarramurdi, H. Khemliche, P. Roncin, A. G. Borisov, A. Momeni, P. Atkinson, M. Eddrief, F. Finocchi, and V. H. Etgens. Combined experimental and theoretical study of fast atom diffraction on the β3(2 × 4) reconstructed GaAs(001) surface. *Phys. Rev. B*, 90:155308, 2014.

[20] M. S. Gravielle and J. E. Miraglia. Semiquantum approach for fast atom diffraction: Solving the rainbow divergence. *Phys. Rev. A*, 90:052718, 2014.

[21] M. del Cueto, A. S. Muzas, M. F. Somers, G. J. Kroes, C. Díaz, and F. Martín. Exploring surface landscapes with molecules: rotationally induced diffraction of H2 on LiF(001) under fast grazing incidence conditions. *Phys. Chem. Chem. Phys.*, 19:16317–16322, 2017.

[22] P. Roncin and M. Debiossac. Elastic and inelastic diffraction of fast atoms, Debye-Waller factor, and Mössbauer-Lamb-Dicke regime. *Phys. Rev. B*, 96:035415, 2017.

[23] P. Roncin, M. Debiossac, H. Oueslati, and F. Raouafi. Energy loss and inelastic diffraction of fast atoms at grazing incidence. *Nucl. Instr. Methods Phys. Res. B*, 427:100–107, 2018.

[24] A. Al Taleb, G. Anemone, W. W. Hayes, J. R. Manson, and D. Farias. Multiphonon excitation and quantum decoherence in neon scattering from solid surfaces. *Phys. Rev. B*, 95:075414, 2017.

[25] M. C. Schram and E. J. Heller. Approach to coherent interference fringes in helium-surface scattering. *Phys. Rev. A*, 98:022137, 2018.

[26] G. A. Bocan, J. D. Fuhr, and M. S. Gravielle. van der Waals effects on grazing-incidence fast-atom diffraction for H on LiF(001). *Phys. Rev. A*, 94:022711, 2016.

[27] L. Frisco, J. E. Miraglia, and M. S. Gravielle. Spot-beam effect in grazing atom-surface collisions: from quantum to classical. *J. Phys.: Condens. Matter*, 30:405001, 2018.

[28] G. A. Bocan and M. S. Gravielle. GIFAD for He/KCl(001). Structure in the pattern for (110) incidence as a measure of the projectile-cation interaction. *Nucl. Instr. Methods Phys. Res. B*, 421:1–6, 2018.

[29] N. W. Ashcroft and N. D. Mermin. *Solid State Physics*, chapter 23. Brooks/Cole, Belmont, 1976.

[30] M. S. Gravielle, A. Schüller, H. Winter, and J.E. Miraglia. Fast atom diffraction for grazing scattering of Ne atoms from a LiF(001) surface. *Nucl. Instr. Methods Phys. Res. B*, 269:1208–1211, 2011.

[31] M. S. Gravielle, J. E. Miraglia, and L. Frisco. Coherence-Length Effects in Fast Atom Diffraction at Grazing Incidence. *Atoms*, 6:64, 2018.

[32] J. E. Miraglia and M. S. Gravielle. Reexamination of the interaction of atoms with a LiF(001) surface. *Phys. Rev. A*, 95:022710, 2017.

[33] H. Winter and A. Schüller. Fast atom diffraction during grazing scattering from surfaces. *Prog. Surf. Sci.*, 86:169–221, 2011.

[34] M. Debiossac and P. Roncin. Image processing for grazing incidence fast atom diffraction. *Nucl. Instr. Methods Phys. Res. B*, 382:36–41, 2016.

[35] A. Schüller, H. Winter, M. S. Gravielle, J. M. Pruneda, and J. E. Miraglia. He-LiF surface interaction potential from fast atom diffraction. *Phys. Rev. A*, 80:062903, 2009.

[36] M. S. Gravielle and J. E. Miraglia. Single- and double-slit collimating effects on fast-atom diffraction spectra. *Nucl. Instrum. Methods Phys. Res. B*, 382:42–48, 2016.

[37] B. Lalmi, H. Khemliche, A. Momeni, P. Soulisse, and P. Roncin. High resolution imaging of superficial mosaicity in single crystals using grazing incidence fast atom diffraction. *J. Phys.: Condens. Matter*, 24:442002, 2012.

[38] W. H. Miller. The Semiclassical Initial Value Representation: A Potentially Practical Way for Adding Quantum Effects to Classical Molecular Dynamics Simulations. *J. Phys. Chem. A*, 105:2942–2955, 2001.

[39] R. Guantes, A. S. Sanz, J. Margalef-Roig, and S. Miret-Artés. Atom-surface diffraction: a trajectory description. *Surf. Sci. Rep.*, 53:199–330, 2004.

[40] D.P. Dewangan and J. Eichler. Charge exchange in energetic ion-atom collisions. *Phys. Rep.*, 247:59–219, 1994.

[41] C. Cohen-Tannoudji, B. Diu, and F. Laloe. *Quantum Mechanics*, chapter III. Willey-VCH, Paris, 2011.