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Quantum and classical study of surface characterization by three-dimensional helium atom scattering

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Exact time-dependent wavepacket calculations of helium atom scattering from model symmetric, chiral, and hexagonal surfaces are presented and compared with their classical counterparts. Analysis of the momentum distribution of the scattered wavepacket provides a convenient method to obtain the resulting energy and angle resolved scattering distributions. The classical distributions are characterized by standard rainbow scattering from corrugated surfaces. It is shown that the classical results are closely related to their quantum counterparts and capture the qualitative features appearing therein. Both the quantum and classical distributions are capable of distinguishing between the structures of the three surfaces. © 2011 American Institute of Physics. [doi:10.1063/1.3519811]

I. INTRODUCTION

Low energy helium atom scattering from surfaces is by now a well-established field.1–6 The helium atom interacts directly with the topmost layers of the surface serving as a sensitive probe of the surface charge density. For example, helium scattering is often used to extract the structure of surface adsorbates through analysis of the diffraction pattern that results from adsorbate induced changes in the corrugation of the helium-surface potential.1 Furthermore, measurements of the final energy and angular distributions obtained while varying the surface temperature provide information on the coupling to the surface phonons.7–9 Because of its sensitivity to surface details, helium atom scattering is often used in parameterizing models for the atom-surface potential and it serves as a stringent test of approximate theoretical methods.10–13

There continues to be a large focus on the scattering of atoms from clean surfaces, but measurements with adsorbed atoms or molecules can also provide a wealth of information on dynamical processes occurring on surfaces.14–16 The experimental extensions into quasilastic helium atom scattering and very recently, the spin-echo technique, have allowed for detailed observations of diffusion processes occurring on surfaces through time-resolved measurements of the diffraction peak line shapes.17, 18 These experiments provide some of the most sensitive measurements to date of surface processes occurring at atomic length and time scales.

The interpretation of these experimental measurements is far from trivial even when the scattering is elastic. No method exists to invert the diffraction data directly and give the helium–surface interaction potential. In many cases, the analysis proceeds through the definition of an effective hard-wall whose corrugation is adapted to best describe the diffraction intensities.1,19,20 The hard-wall is then taken to be a replica of a contour of constant surface electronic charge density.19 While this procedure is useful for simple adsorbate structures,21 it necessarily fails to account for features of a realistic potential, such as the softness of the wall and the existence of the attractive well. Exact calculations for a realistic potential are possible but they require significant computational resources and are rarely employed in practice. It is of interest to have computations of the helium scattering process available in order to aid in the experimental interpretation as well as to serve as a benchmark for approximate theoretical methods.

Classically, the scattering of atoms from corrugated surfaces leads to the well-known rainbow scattering distributions.22 For in-plane scattering, the rainbow features in the angular distribution occur where the derivative of the final scattering angle with respect to the impact parameter vanishes. In three-dimensional scattering, the rainbows lie along the lines where the Jacobian of the transformation from the impact parameters to the final scattering angles vanishes. Intersections of the rainbow lines lead to the phenomenon of “super-rainbows.”22–24 Recently, theoretical results for both the in-plane and full three-dimensional scattering distributions have been formulated for the classical scattering of atoms from realistic surfaces within perturbation theory.24–27 The results are in quantitative agreement with a number of experimental measurements of the in-plane scattering of heavy noble gases from a variety of surfaces.26 In the hard-wall limit, the theory provides analytic estimates for the locations of the rainbow features.21

Here we present exact time-dependent quantum mechanical calculations of three-dimensional helium scattering from model symmetric, chiral, and hexagonal surfaces and compare the results with numerical simulations of classical scattering. Additionally, the analytical predictions for the scattering distributions obtained from a hard-wall model for the surface are provided. The results show that the qualitative information available in the classical scattering distributions closely corresponds with the exact quantum distributions. Strong diffraction peaks lie along the classical rainbows and the most intense diffraction is found at the super-rainbows. Both the classical and quantum
calculations are capable of distinguishing between the symmetric, chiral, and hexagonal surfaces. The classical deflection function may provide a useful tool for structural analysis, which provides straightforward insights into the quantum results that are not readily discernible otherwise. The hard-wall model provides at best only a qualitative description of the scattering distributions.

In the following section, the scattering system and surface potentials are presented along with the details of the quantum and classical simulations. Following this, analytical estimates are provided for the classical rainbow structure obtained from a hard-wall model of the surface. The resulting scattering distributions are presented in Sec. III where the similarities between the quantum and classical approaches as well as the deficiencies of the hard-wall model become evident. The analysis of the resulting diffraction pattern is much simpler with the aid of the accompanying classical simulations. They provide a clear physical interpretation of the scattering distributions in terms of classical rainbows.

II. THEORY

A. Quantum dynamics

The standard Hamiltonian for the three-dimensional helium scattering system is given by

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2M} + V(x, y, z), \quad (1)$$

where $M$ is the mass of the helium atom. The $z$ coordinate characterizes the motion perpendicular to the surface while $x$ and $y$ lie in the plane of the surface. The interaction of the atom with the surface is taken to be of the corrugated Morse form\textsuperscript{[11,25]}

$$V(x, y, z) = \tilde{V}(z) + \frac{\partial \tilde{V}(z)}{\partial z} h(x, y), \quad (2)$$

where the Morse potential takes the usual form

$$\tilde{V}(z) = V_0(e^{-2\alpha z} - 2e^{-\alpha z} + 1). \quad (3)$$

The corrugation functions characterizing the symmetric, chiral, and hexagonal surfaces are

$$h_s(x, y) = h_1\left( \sin \frac{2\pi x}{l_x} + \sin \frac{2\pi y}{l_y} \right), \quad (4)$$

$$h_c(x, y) = h_1\left( \sin \frac{2\pi y}{l_y} - \sin \frac{2\pi x}{l_x} \right) + h_2\left( \sin \frac{4\pi y}{l_y} - \sin \frac{4\pi x}{l_x} \cos \frac{4\pi y}{l_y} \right), \quad (5)$$

$$h_h(x, y) = \frac{2h_1}{3}\left( \cos \frac{4\pi y}{l_y} + 2 \cos \frac{2\pi x}{l_x} \cos \frac{2\pi y}{l_y} \right), \quad (6)$$

where $l_x$ and $l_y$ are the respective lattice constants. Examples of the three corrugations are displayed as contour plots in Fig. 1. The solid lines superimposed on each panel depict the primitive units cells of each surface.

![Corrugation functions shown as contour plots for the (a) symmetric, (b) chiral, and (c) hexagonal surfaces. A primitive unit cell is indicated by solid black lines in the center of each figure.](image)

The parameters for the surface potential are based upon a model for the in-plane scattering of helium from a copper surface.\textsuperscript{[11,28]} The Morse well depth is 6.35 meV with a stiffness parameter $\alpha = 1.05 \, \text{Å}^{-1}$. For all three model surfaces, the lattice length $l_x = 3.6 \, \text{Å}$. For the symmetric and chiral surfaces, the lattice lengths along $x$ and $y$ are equivalent $l_x = l_y$, while for the hexagonal surface $l_x = \sqrt{3} l_y$. The corrugation heights are $h_1 = 0.2$ a.u. and $h_2 = h_1/2$. The value for $h_1$ is chosen to be large enough to emphasize the differences among the various corrugation functions in the scattering calculations.

The initial helium wavepacket is a Gaussian coherent state defined by

$$\langle x, y, z | \psi \rangle = \left( \frac{\gamma_x \gamma_y \gamma_z}{\pi^3} \right)^{1/4} \exp \left( -\frac{\gamma_x}{2}(x - x_0)^2 - \frac{\gamma_y}{2}(y - y_0)^2 - \frac{\gamma_z}{2}(z - z_0)^2 \right) \exp \left( i\frac{p_{x_0}}{\hbar} (x - x_0) + i\frac{p_{y_0}}{\hbar} (y - y_0) + i\frac{p_{z_0}}{\hbar} (z - z_0) \right). \quad (7)$$
Calculations are presented for two angles of incidence, \( \theta_i = 0^\circ \) and 45°, where the angle \( \theta \) is defined with respect to the surface normal. The angle \( \phi \) is defined in the plane of the surface and for the symmetric and chiral surfaces, \( \phi_i = 45^\circ \), while for the hexagonal surface, \( \phi_i = 60^\circ \). The initial momenta are defined by the energy of the incident beam (125 meV) and the specified initial scattering angles. The initial vertical coordinate is taken to be far enough from the surface such that the interaction with the wavepacket is negligible. The width parameters are \( \gamma_x = \gamma_y = \gamma_z = 0.05 \) a.u.\(^{-2} \) which results in a wavepacket that spans several lattice lengths in position space and is highly localized in momentum space. The simulations are run for a sufficiently long amount of time such that the scattered wavepacket is again free from the surface interaction. Under the present scattering conditions, we observed no evidence of resonant scattering.

The quantum calculations are performed using a standard split-operator method with a grid size of 256\(^3 \).\(^{20} \) The results obtained from a larger grid of 512\(^3 \) displayed little difference compared with the results from the smaller grid. We have shown that one of the most useful quantities to calculate is the final momentum distribution of the scattered wavepacket.\(^{28} \) From this, it is possible to obtain the angular distribution, energy distribution, or any other energy-related quantities directly from only a single simulation. In the quantum case, this is simply the absolute-value squared of the time-evolved wavefunction in momentum space\(^{28} \)

\[
P(\vec{p}_x, \vec{p}_y, \vec{p}_z) = \lim_{t \to \infty} |\langle \vec{p}_x, \vec{p}_y, \vec{p}_z | \psi(t) \rangle |^2.
\]

The momentum changes parallel to the surface provide the most relevant information for the characterization of surface structure. As a result, below we present only the two-dimensional momentum distributions obtained after integrating over the vertical momentum,

\[
P(\vec{p}_x, \vec{p}_y) = \int_{-\infty}^{\infty} d\vec{p}_z P(\vec{p}_x, \vec{p}_y, \vec{p}_z).
\]

**2. Hard-wall scattering**

As is well-known, classical scattering from corrugated surfaces leads to rainbow features in the resulting distribution functions.\(^{22} \) The classical rainbows in the final momentum distribution occur wherever the Jacobian of the transformation from the impact parameters to final momenta vanishes.\(^{23} \) For the potential given in Eq. (2), the dynamics reduces to scattering from a hard-wall when the stiffness parameter of the Morse potential \( \alpha \to \infty \). In this limit, the perturbation theory results of Ref. 24 provide analytical estimates for the dependence of the final momenta on the initial coordinates. The final momentum after scattering can be written in the general form

\[
\begin{align*}
px &= px_0 + \delta p_x(x, y), \\
py &= py_0 + \delta p_y(x, y),
\end{align*}
\]

where the respective momentum shifts are explicitly given by

\[
\delta p_x(x, y) = 2px_0 \frac{\partial h(x, y)}{\partial x}, \\
\delta p_y(x, y) = 2py_0 \frac{\partial h(x, y)}{\partial y}.
\]

Therefore, the Jacobian of the transformation from the impact parameters to the final momenta is proportional to the determinant of the Hessian of the corrugation function,\(^{23, 24} \)

\[
J(p_x, p_y; x, y) = 4p_x^2 \left( \frac{\partial^2 h(x, y)}{\partial x^2} \right)^2 + 4p_y^2 \left( \frac{\partial^2 h(x, y)}{\partial y^2} \right)^2 - \left( \frac{\partial^2 h(x, y)}{\partial x \partial y} \right)^2.
\]

The rainbow lines occur at the values of \( x \) and \( y \) where Eq. (15) vanishes and the corresponding features in the momentum distribution are provided from Eq. (13).
The symmetric surface of Eq. (4) provides a simple illustrative example. In this case, the Jacobian has zeroes along the lines \( x = 0 \) and \( l_i/2 \) and \( y = 0 \) and \( l_j/2 \). This leads to rainbows in the momentum distribution located at

\[
\begin{align*}
px_i &= \pm 2 \xi_i h_1 / l_x, \\
py_i &= \pm 2 \xi_i h_1 / l_y.
\end{align*}
\]

It is easily seen that the momentum rainbows form the four sides of a square in this case since the lattice constants are equivalent. The super-rainbows occur at the corners where the individual rainbow lines along \( p_x \) and \( p_y \) intersect leading to even more intense peaks at these points. For the more complicated cases of the chiral and hexagonal surfaces, the zeros of the Jacobian are found numerically.

III. RESULTS

The classical final momentum distributions obtained for helium scattering from the symmetric surface at normal incidence and at \( \theta_i = 45^\circ \) are presented in Figs. 2(a) and 2(b), respectively. The dashed line superimposed on the latter indicates the scattering plane. In each case, the results are presented in terms of the change in wavevector with respect to those of the initial beam, that is \( \Delta K = (p_f - p_i)/\hbar \).

The results at normal incidence shown in Fig. 2(a) form a fourfold symmetric structure centered about the specular peak (\( \Delta K = 0 \)) that clearly reflects the underlying \( p4m \) symmetry of the surface unit cell. The predictions for the location of the rainbow lines based upon the hard-wall model outlined in the previous section are indicated as the solid lines superimposed on the classical distribution. For the hard-wall model, the rainbows also occur symmetrically around the specular peak forming a square as shown. The hard-wall rainbows in Fig. 2(a) lie close to the intensity maxima of the full classical calculation which indicates that the regions of largest intensity in the classical calculation are manifestations of classical rainbows. Super-rainbows, where the largest intensity peaks are observed, occur near the corners of the hard-wall square while standard rainbows exist near the edges of the square.

The results shown for \( 45^\circ \) incidence in Fig. 2(b) retain some of the structure seen in the scattering at normal incidence. The incident direction, shown dashed in the figure, lies along a mirror plane of the surface so the out-of-plane scattering must be symmetric with respect to this axis. However, other symmetry elements are lost. The classical intensity is displaced slightly in the backscattering direction and the forward scattering and backscattering directions are no longer equivalent, as expected for non-normal incidence. In the plane of parallel momentum transfer, the predicted positions of the hard-wall rainbows are independent of the angle of incidence. As a result, the hard-wall rainbows are still symmetrically displaced around the specular peak. The probability for striking the surface at a particular location in the unit cell is not uniform for off-normal scattering.\(^{21,26}\) There is a larger probability of scattering from the part of the surface that faces the initial beam, which would indicate that the back scattering (subspecular) peak should have a larger intensity than the forward scattering (superspecular) peak. However, Fig. 2(b) seemingly displays the opposite behavior. The origin of this phenomenon is analyzed in more detail in the Appendix.

The corresponding quantum momentum distributions obtained for the helium scattering from the symmetric surface at an incident angles of \( \theta_i = 0^\circ \) and \( 45^\circ \) are presented in Figs. 3(a) and 3(b), respectively. As with the classical distributions, the results are presented in terms of the change in wavevector with respect to those of the initial beam, that is \( \Delta K = (p_f - p_i)/\hbar \). The conditions for Bragg scattering require that the diffraction peaks are separated by the constant factor \( 2 \pi n / l \). The underlying square symmetry of the surface is clearly reflected in both diffraction patterns. For \( \theta_i = 45^\circ \), the out-of-plane scattering is symmetric as it must be since the incident beam direction (dashed line) lies along one of the mirror planes of the surface as in the classical case. The width of the diffraction peaks arises from the finite width of the initial wavepacket and because the vertical momentum has been integrated over.

Comparison of Figs. 2 and 3 shows clear similarities between the classical and quantum results. Of course, the classical Wigner simulations are not able to capture the interference effects leading to the discrete peaks in the quantum distribution. Nevertheless, the qualitative features of the quantum distributions have clear counterparts in the classical distributions and the interpretation of the former are greatly facilitated with the aid of the latter. The quantum diffraction peaks of largest intensity occur at or near the super-rainbow positions in the classical distribution, while the remaining standard rainbows provide the basic structure of the quantum results.
Results for the classical helium scattering from the chiral surface at normal incidence and $\theta_i = 45^\circ$ are presented in Figs. 4(a) and 4(b), respectively. The analogous quantum distributions are presented in Fig. 5. The dashed lines in the relevant figures indicate the incident scattering plane and the solid lines superimposed on the classical distributions display the predictions for the location of the hard-wall rainbows. The chiral surface has no mirror or glide symmetry and the absence of symmetry elements is clearly evident in the momentum distributions. Scattering from the chiral surface is very sensitive to the orientation of the initial beam and the results at $\theta_i = 45^\circ$ bear little resemblance to the distributions generated at normal incidence in either the classical or quantum case. The rainbow lines displayed in Fig. 4 predicted by the hard-wall model provide little insight into the structure of the classical momentum distributions. Even at normal incidence, the agreement between the hard-wall model and the numerical simulations is rather poor. As with the symmetric surface, it is seen that the quantum distributions closely follow their classical counterparts, except that distinct diffraction peaks are absent from the latter. The largest diffraction peaks have clear analogues in the classical distributions. There are also clear differences between the momentum distributions generated from the chiral and symmetric surfaces indicating the sensitivity of the helium atom to surface structure. The chiral surface approaches a symmetric one as the magnitude of $h_2$ is lowered. As a result, in the case of weak chirality or low beam energy, measurements of the diffraction pattern—either classically or quantum mechanically—may not be able to distinguish between the two surface structures.

The results for the scattering from the hexagonal surface are presented in Figs. 6 and 7 for the classical and quantum cases, respectively. Figures 6(a) and 6(b) display the momentum distributions obtained at normal incidence and at $\theta_i = 45^\circ$. The scattering plane is chosen along one of the mirror planes of the corrugation function and is shown as the dashed line in the relevant figures. As expected, the out-of-plane scattering in both the quantum and classical distributions is symmetric with respect to this axis. As in the previous figures, the hard-wall rainbow structure has been superimposed on the classical momentum distributions. In this case, the hard-wall model is in
FIG. 6. Final classical momentum distributions for helium scattering from the hexagonal surface. (a) corresponds to scattering at normal incidence and (b) is obtained at $\theta_i = 45^\circ$. The remaining notation is the same as in Fig. 2.

excellent agreement with the numerical simulations at normal incidence as seen in Fig. 6(a). The classical scattering distribution reflects the symmetry of the structure within the unit cell. The circular rainbow structure corresponds to scattering from the large circular peaks of the corrugation function while the sixfold symmetric structure inside is due to scattering from the two small triangular depressions seen in each unit cell [Fig. 1(c)]. At $\theta_i = 45^\circ$, the classical momentum distribution is shifted towards the backscattering direction and the rainbow structure deviates from the hard-wall prediction. The quantum and classical results display similar orientations with respect to the location of the hard-wall rainbows and comparable distributions of scattered intensity. The quantum distributions are, of course, only sampled at the diffraction positions. The underlying hexagonal structure of the surface is clearly evident from the diffraction pattern and the results are markedly different from those obtained for the scattering from either the square symmetric or the chiral surfaces. As a final example, in Fig. 8 the quantum mechanical momentum distribution calculated at $\theta_i = 45^\circ$ and half of the beam energy, 62.5 meV, is presented. As expected, the hexagonal structure of the corrugation function is still distinguishable and the distance between the peaks is necessarily the same as at the higher energy. The only difference is that fewer diffraction peaks are observed and the distribution is more compact since fewer diffraction channels are energetically accessible.

IV. DISCUSSION

Three-dimensional time-dependent wavepacket calculations of helium scattering from model square symmetric, chiral, and hexagonal surfaces were presented. As has been confirmed many times before, helium diffraction is a sensitive probe of surface structure and can be used to determine the configuration of the scattering centers. The momentum distributions presented here clearly support this observation. The differences in the diffraction patterns generated from the three model surfaces are qualitative and reflect the symmetry of each respective surface. The classical distributions capture almost all of the relevant qualitative features apparent in their quantum counterparts. The classical results are strongly influenced by the local structure within the unit cell and give rise to rainbow effects whose theoretical understanding is well established. In all three cases, the correspondence between the classical and quantum distributions are readily apparent. Of course, the discrete diffraction peaks arising from quantum interferences are absent, but the essential features remain.

The agreement between the classical and quantum results is largely due to the persistence of the classical rainbow structure in the quantum distributions. Observing the rainbow features in the quantum case requires that the separation between the rainbow lines be much larger than the spacing.
between the diffraction peaks. The latter can only take on the discrete values $2\pi rhn/l$ where $l$ is the lattice constant. In the hard-wall limit, the separation between the classical rainbow lines is proportional to the vertical energy of the initial beam and the corrugation height. The value of $h_1$ was chosen to be quite large in the numerical simulations presented here. This results in a large separation between the momentum rainbows and allows several quantum diffraction peaks to fit under the envelope of the classical rainbow structure. It is this choice which is largely responsible for the correspondence between the classical and quantum distributions observed in the results.

In Ref. 28, the in-plane scattering of helium from a copper surface was studied using a model potential very similar to that of the symmetric surface. In that case, the classical and quantum distributions were not even in qualitative agreement, unlike the present results. The classical diffraction was a result of the usual rainbow scattering with the maxima of the classical distribution located at the rainbow angles. The corresponding quantum distribution, however, displayed a maximum at the specular angle along with several peaks lying outside the rainbow structure. The corrugation in Ref. 28 was much smaller than the value used here causing the effect of the rainbows to play a lesser role relative to the quantum diffraction. This implies that it should be easier and perhaps more informative to perform the experiments at not too low an incident beam energy so that the diffraction peaks will reflect the underlying rainbow features.

In surface characterization studies, the hard-wall model is often used in order to determine the surface corrugation function, and thus infer the surface structure. 1,19,20 The results presented here indicate that a hard-wall model of the surface can be used, in some restricted cases, to provide a qualitative prediction for the classical scattering distributions. This is particularly clear from the momentum distributions obtained at normal incidence from the hexagonal and symmetric surfaces. However, as the angle of incidence increases to more realistic experimental values, the agreement becomes significantly worse. For the chiral surface, the hard-wall model provides little useful information either at normal incidence or at $\theta_i = 45^\circ$ and should be applied with caution in such systems.

The computations presented in this paper were at energies sufficiently high so that trapping by the physisorbed well is not important. Such trapping can lead to a smearing of the scattered distribution which tends to hide the underlying surface structure. This would be further accentuated if one includes the role of surface temperature. Phonons not only lead typically to a broadening of the distribution, they can induce trapping. They may also lead to a shift to sub- or superspecular scattering.25 Including the bath modes in classical simulations is not too difficult, but the quantum mechanical calculations quickly become impractical due to the exponential scaling with respect to system size.

In Ref. 24, it was suggested that it may be possible to use the classical scattering of heavier atoms in surface structure studies. Here, we have shown that the classical distribution for elastic scattering provides similar structural sensitivity to the quantum case. Thus, the present work provides further arguments for the use of heavier atoms in structural studies, provided the effects of strong inelastic scattering can be avoided. Classical scattering is much easier to simulate and interpret than the corresponding quantum case. The rainbows and super-rainbows are very sensitive to the underlying potential just as are the quantum diffraction peaks. Therefore, it is expected that little sensitivity will be lost when using "classical atoms."

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APPENDIX: ASYMMETRIC SCATTERING

This appendix is intended to provide a more in depth analysis of the somewhat counterintuitive peak intensities observed in the scattering distributions obtained at off normal incidence angles. As mentioned in the main text, there is a larger probability to scatter from the portion of the surface that faces the initial beam. This should lead to a larger subspecular peak relative to the superspecular peak. For one-dimensional systems, the argument is clear; however, two-dimensional corrugation combines forward- and backward-scattering processes with both in-plane and out-of-plane scattering. In order to study this behavior in more detail, a hard-wall model of the symmetric surface with an attractive square well of depth $D$ is presented. Despite the simplicity of the model it captures all of the salient features of the more complicated systems studied in the main text. As shown below, the intensities of the superspecular peaks are greater than the subspecular peaks even for the case of hard-wall scattering. The conclusion here is that the simple picture based on the relative probabilities for striking the surface is not a sufficient criterion to determine the corresponding peak intensities when out-of-plane scattering is involved.

Klein and Cole have provided an exact analytical expression for the final angular distribution in Ref. 36. The scattered intensity into the solid angle $\Omega$ is given by

$$\frac{dI}{d\Omega} = \frac{1}{\pi^2} \left[ 1 - \frac{f \sin(\theta_i)}{\sqrt{D^* + \cos^2(\theta_i)}} \right] \cos(\theta_i) \cos(\phi_i) \frac{W_1 W_2 h^2}{W_1 W_2 h^2} \times \left[ 1 + \frac{f \sin(\theta_i) \cos(\phi_i) + g \sin(\phi_i)}{\sqrt{D^* + \cos^2(\theta_i) \cos^2(\phi_i)}} \right], \quad (A1)$$

where the subscripts $i$ and $r$ denote the incident and reflected angles respectively, and $D^* = D/E_i$. The additional variables introduced in Eq. (A1) are given by

$$W_1 = [C^2 - \cos(\phi_i) f + \sin(\phi_i) g]^2]^{1/2},$$

$$W_2 = [C^2 - \cos(\phi_i) g - \sin(\phi_i) f]^2]^{1/2},$$

$$f = [\sin(\theta_i) \cos(\phi_i) - \sin(\phi_i)] / h, \quad (A2)$$

$$g = \sin(\phi_i) / h,$$

$$h = [D^* + \cos^2(\theta_i) \cos^2(\phi_i)]^{1/2} + [D^* + \cos^2(\theta_i)]^{1/2},$$
where \( C = 2 \pi h_1 / l \). The rainbow angles are found when \( W_1 \) or \( W_2 \) vanish. However, the angles specified in these equations are not same as the spherical polar coordinates used in the numerical results presented in the main text. The coordinates specified in Eq. (A1) are defined such that the incident beam lies along the \( \phi_i \) plane. McClure has shown that the two coordinate systems are related by

\[
\sin^2(\theta_i) = \frac{\sin^2(\theta) \cos^2(\phi)}{1 - \sin^2(\theta) \sin^2(\phi)},
\]

\[
\sin(\phi) = \sin(\theta) \sin(\phi),
\]

where the angles without subscripts denote the standard spherical polar angles. The Jacobian of the transformation relating the two is given by

\[
\frac{\partial (\theta_i, \phi_i)}{\partial (\theta, \phi)} = \frac{\sin(\theta)}{\sqrt{1 - \sin^2(\theta) \sin^2(\phi)}}.
\]

Figure 9 displays the results for the final angular distribution obtained from the equations above at incidence angles of \( \theta_i = 45^\circ \) and \( \phi_i = 0^\circ \) with the attractive well depth of \( D = 0 \). The distribution has been artificially broadened by a Gaussian of variance 0.0005 rad\(^2\) in order to avoid the divergences at the rainbow angles. The results of trajectory calculations obtained by ignoring the attractive part of the Morse potential in Eq. (2) and taking the stiffness parameter to be very large are indistinguishable from the analytical results presented here. It is clearly seen in Fig. 9 that the intensity at lower scattering angles is smaller than that of the larger angles similar to the results presented in the main text. Nevertheless, when one integrates over the out-of-plane scattering as shown in Fig. 10, a larger scattering intensity is found in the subspecular peak as expected. These results are independent of the particular coordinate system since the angle \( \theta \) is always defined relative to the surface normal. As a final comparison, the angular distributions calculated at incidence angles of \( \theta_i = \phi_i = 45^\circ \) from Fig. 2(b) as well as from the hard-wall model are shown in Fig. 11. In this case, the distribution is dominated by the two super-rainbows arising from out-of-plane scattering. They are symmetrically equivalent as seen from Fig. 2(b) and contain contributions from both forward- and back-scattered trajectories. Thus any enhancement of the subspecular scattering is less evident in Fig. 11 than in Fig. 10.

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