Focused sticking of light mass particles in physisorption

S. Miret-Artes
Instituto de Matemáticas y Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano, 123, 28006 Madrid, Spain

J. R. Manson
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634

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In the scattering of atoms and molecules from surfaces, focusing effects can give rise to a variety of significant features in both the experimentally measured elastic and inelastic scattering intensities. The study of focusing is extended to the case of sticking of atoms upon scattering into the physisorption potential well. It is demonstrated that this focused sticking (FS) should give rise to enhancements of the sticking coefficient for certain well-defined incident conditions.

When a well-defined beam of atomic or molecular projectiles is directed towards a surface, typically a fraction of the beam will be backscattered into outgoing continuum states and the remaining fraction will become trapped in the physisorption well of the interaction potential. The trapping in the physisorption well may be transient, with further rapid transition into a positive energy outgoing continuum state, or the projectile may make transitions leading to a state of negative total energy and become adsorbed at the surface. The fraction of incoming particles that adsorb on a clean surface is the sticking coefficient.

In the last two decades, the role of resonance processes leading to sticking in the physisorption well has been examined in a large number of papers, both experimentally and theoretically as has been chronicled in a recent comprehensive review, see Ref. 1. Entry into the bound states can be via an elastic channel or via a phonon-mediated (inelastic) channel. The sticking coefficient often displays a characteristic feature whenever the incident scattering parameters, e.g., the energy and angles, fulfill the conditions for a selective adsorption process, either elastic or inelastic.2–5 However, the sticking is not a state-to-state transition, rather it must be regarded as a global property of the system because it involves a summation over all elementary processes that can lead to eventual adsorption.

During this same period of time, a number of resonance and focusing enhancement mechanisms have been predicted6–9 for the case of scattering into continuum states, and some of them have been observed experimentally in either the scattering of He atom beams, or in the scattering of small mass molecular beams.10–12 The best known of the resonance effects is selective adsorption, which gives rise to sharp features in the elastic scattering intensities,5,13 and when assisted by a phonon transfer can give rise to significant enhancements of the energy-resolved inelastic scattering intensity.10 Focusing effects, on the other hand, represent a different type of enhancement, one in which the incident beam wave packet is sharply focused into a particular transition.

Up until now, focusing processes have been extensively exploited in continuum state surface scattering11,12 but their role in scattering into bound states and in sticking has not been investigated. The purpose of this paper is to point out conditions, called focused sticking (FS), under which focusing effects can significantly enhance the sticking coefficient of atomic and molecular projectiles.

For any atom-surface scattering event on a periodic surface the kinematical constraints are conservation of total energy \( \Delta E \) and parallel momentum \( \Delta K \) which are expressed as

\[
\Delta E = k_i^2 - k_f^2,
\]

and

\[
\Delta K = k_f \sin \theta_f - k_i \sin \theta_i,
\]

where \( k_i \) and \( k_f \) are the incident and final wave vectors, \( \theta_i \) and \( \theta_f \) are the corresponding scattering angles relative to the surface normal, and the dimensions are chosen so that \( \hbar^2 / 2m = 1 \) where \( m \) is the projectile mass. Equation (2) is written for the special case of scattering in the sagittal plane (the plane defined by the incident beam and the surface normal), however, the extension to full three-dimensional scattering is straightforward.

In the case of scattering into a bound state of the physisorption potential labeled by the quantum number \( n \), the final energy is given by \( k_f^2 = -|\epsilon_n| + (\Delta K + N + k_i \sin \theta_i)^2 \) where \( N \) is a surface reciprocal lattice vector and \( \epsilon_n \) is the bound-state energy. Equations (1) and (2) can then be combined into the so-called resonance curve equation

\[
\Delta E = k_i^2 - (k_i \sin \theta_i + N + \Delta K)^2 + |\epsilon_n|.
\]

Equation (3) represents the locus, for a given set of incident conditions \((\theta_i, k_i^2)\), of all elastic and inelastic processes compatible with the conservation rules in the dispersion \((\Delta E, \Delta K)\) space. Thus, crossings of these curves with the dispersion curves of phonons give rise to inelastic features in angular distributions and/or in time-of-flight inelastic intensity spectra. Conversely, if the energy \( \Delta E \) and parallel momentum \( \Delta K \) of the phonon are regarded as fixed, then the incident parameters \( k_i \) and \( \theta_i \) are consequently related by Eq. (3).

The total sticking coefficient from a given incident beam, regarded as a plane wave of wave vector \( k_i \), is the sum over

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S. Miret-Artes and J. R. Manson

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The total sticking coefficient from a given incident beam, regarded as a plane wave of wave vector \( k_i \), is the sum over
all possible final states that can leave a particle adsorbed on
the initially zero-coverage surface:

$$\sigma(k_i) = \sum_{N,\Delta E, \Delta K} \sigma(k_i; n, N, \Delta E, \Delta K), \quad (4)$$

where \(\sigma(k_i; n, N, \Delta E, \Delta K)\) can be regarded as the transition
probability or the partial sticking coefficient into each well-
defined quantum state, and the sum over \(\Delta E\) includes the
sum over all bound states \(n\). In a real experiment, the in-
cident beam is not a plane wave but a wave packet, and Eq. (4)
must be convoluted over the distribution function \(\rho(k_0)\)
of the incident beam, where \(k_0\) is the central wave vector of
the incident wave packet distribution. Thus the experimentally
measured sticking coefficient \(\Sigma(k_0)\) is given by

$$\Sigma(k_0) = \int_{\Delta k} dk_i \int_{\Delta \theta_i} d\theta_i \rho(k_0) \sigma(k_0). \quad (5)$$

\(\Sigma(k_0)\) can also be written as a sum over the individual quan-
tum transition probabilities \(\Sigma(k_0; n, N, \Delta E, \Delta K)\) just as for
\(\sigma(k_i)\) in Eq. (4).

The question of focusing becomes of importance when
the properties of the incident beam distribution are exam-
ined. Suppose that the incident beam has an angular spread
but the incident energy is well defined at each angle within
this angular spread. In such a case the incident distribution
function can be reasonably approximated by

$$\rho(k_0) = \delta(k_i - k_i(\theta_i))g(\theta_i). \quad (6)$$

The result of carrying out the integral over the angular spread
of the incident beam as in Eq. (5) for each quantum state component is the following:

$$\Sigma(k_0; n, N, \Delta E, \Delta K)$$

$$= \int_{\Delta k} dk_i \int_{\Delta \theta_i} d\theta_i g(\theta_i^*) \sigma(k_i; n, N, \Delta E, \Delta K), \quad (7)$$

where \(\theta_i^*(k_i)\) is the value given by the resonance equation
(3) for specified \(\Delta E\) and \(\Delta K\).

The Jacobian derivative appearing in Eq. (7) can be readily calculated for fixed \(\Delta E\) and \(\Delta K\) and is

$$\frac{d\theta_i}{dk_i} = \frac{k_i \cos^2 \theta_i - (\Delta K + \Delta N) \sin \theta_i}{k_i \cos \theta_i (k_i \sin \theta_i + \Delta K + \Delta N)}. \quad (8)$$

The phenomenon of focusing occurs when this derivative is
singular, and clearly this can occur when the denominator
vanishes. In order to exhibit this singular behavior it is useful
to solve Eq. (3) for \(\theta_i\) as a function of \(k_i\)

$$\theta_i = \arcsin \left( \frac{\sqrt{k_i^2 - \Delta E} + |\epsilon_n| - \Delta K - N}{k_i} \right). \quad (9)$$

This angle must be real and in the range \(-90^\circ < \theta_i < 90^\circ\).
Thus the minimum value of \(\theta_i\) occurs for

$$k_{\text{min}} = \sqrt{\Delta E - (\Delta K + N)^2} \quad (10)$$

It is readily shown that the Jacobian derivative of Eq. (8) is
singular at this minimum point due to the fact that
\(k_{\text{min}} \sin \theta_{\text{min}} + \Delta K + N = 0\). Thus the incident angle and wave
vector determined by \(\theta_{\text{min}}\) and \(k_{\text{min}}\) are the conditions for focusing in the sticking process.

A second condition for focusing is found in the case in
which \(\Delta K + N < 0\) at \(\theta_{\text{max}} = 90^\circ\) with the corresponding value of \(k_i = k_{\text{max}}\) given by

$$k_{\text{max}} = \sqrt{\Delta E - |\epsilon_n|}. \quad (11)$$

This is the case of a beam incident at a grazing angle to the
surface and may be considered of no experimental interest.
However, it should be noted that there have been recent ex-
perimentical measurements, primarily observing scattering by
surface defects, which have been carried out under condi-
tions in which grazing angle final beams have been
observed.\(^{14,15}\) so such a case should not be completely dis-
missed out of hand. Finally, it should be noted that if the parallel momentum \(|\Delta K + N| > \sqrt{\Delta E - |\epsilon_n|}\), i.e., if the parallel
wave vector is above the threshold for entering the bound
state, there are no solutions of interest of Eq. (9).

Shown in Fig. 1 is a calculation for a typical scattering configura-
tion, in this case corresponding to a phonon at the
surface Brillouin zone boundary for He scattering on
Cu(001)(110), in which \(\Delta E = 17\) meV, \(\Delta K = -1.2\)
\[ k_i \rightarrow \theta_i \]

than \( u \)

where \( k_i \)

\(~\)

The partial sticking coefficient, corresponding to Eq. (8), is given by

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in this case the incident distribution function has the following approximate form

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However, for scattering into continuum states, the counterpart of Eq. (15) does not give rise to focusing at physically achievable incident angles. This particular case of focusing in continuum state scattering has been previously studied and it is called the inelastic critical kinematic effect.\(^9\) If \( \Delta E \) and \( \Delta K \) are zero, this same focusing is manifest in the elastic scattering where it is called elastic critical kinematic scattering.\(^7\)

In this paper it is shown that focusing processes, of which several specific cases are now well documented for continuum state molecular- and atom-surface scattering, can be extended to the case of scattering into the negative energy bound states where they affect the measured value of the sticking coefficient or can enhance the intensity of scattering into a particular bound state. The focused sticking presented here can be directly related to similar effects that have been observed in continuum state scattering, hence giving assurance that it will be observed, and can cause significant enhancement of the sticking coefficient under circumstances in which a single phonon mode of energy \( \Delta E \) and parallel momentum \( \Delta K \) makes an important contribution to the sticking. Certain continuum-to-bound state transitions are directly observable as resonances in the continuum scattering, such as phonon assisted selective adsorption processes,\(^10\) and FS may be utilized to enhance these processes. Similarly, since FS occurs at the threshold for which a particular phonon of energy \( \Delta E \) and parallel momentum \( \Delta K \) causes a transition to a well-defined negative energy sticking state, the incident energy and angle can be “tuned” to focus on individual phonons in the surface spectral density. This focusing should be particularly applicable to the case of localized surface modes due to adsorbates and adsorbate layers on the surface.

This focused sticking is not a result of the dynamics of the scattering process, and hence does not depend on details of the interaction potential. Instead, it occurs at particular combinations of incident angle and energy for which the angular spread of the incident beam wave packet is focused into a single quantum transition. This phenomenon should be observable, since its counterparts in continuum state scattering have already been experimentally observed.

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15 D. Farias, M. Patting, K.-H. Rieder, and J. R. Manson (to be published).