Chapter 5

Elastic and Inelastic Helium Atom Scattering Theory

Introduction

A comprehensive understanding of the fundamental physics and chemistry of solid surfaces requires a detailed knowledge of the atomic forces which bind atoms into and onto a surface. Surface bonding, in general, differs substantially from bulk. A measurement of interatomic force constants at the surface therefore provides important input for accurate modeling and understanding of numerous surface properties and processes including, for both clean and adsorbate-covered surfaces, surface relaxation and reconstruction; surface diffusion; adsorption and desorption of surface and adsorbate atoms; momentum and energy transfer to and through the surface; phase transitions of clean or adsorbate-covered surfaces or of overlayers; and even electronic transitions insofar as they are phonon-mediated.

Low energy helium atoms have several attributes that render them uniquely suitable to the study of surfaces in general and surface vibrations in particular. First and foremost, atoms are strictly surface sensitive. Particularly for a lightweight atom such as helium, there is absolutely no penetration into the bulk. Any information carried away by the scattered atom, whether due to the structure or dynamics, will relate only to the outermost layer of the crystal. Further, a helium atomic beam provides a chemically, electrically, magnetically, and (at the thermal beam energies employed) mechanically inert probe. It is therefore possible to study the surface structure or dynamics of virtually any material, to do so for reactive or metastable surfaces or in the presence of electromagnetic fields, and even to make measurements during UHV processing without altering the process. The latter might include measurements during sputtering or annealing, deposition of adsorbate overlayers, chemical reactions through molecular adsorption, or even optical or electrical excitation through laser or electron beams. In addition, helium atom has no rotational or vibrational degrees of freedom and no accessible electronic transitions at thermal collision energies.

Only the translatory motion of the incident and scattered beam need to be analyzed to extract information on energy and momentum exchange. For inelastic scattering studies, as seen in *Fig.1*, He atoms are particularly well-matched in momentum and energy to surface phonons. This ensures that the resultant changes in scattered beam momentum are large and easily resolved. Yet, the inelastic scattering cross-sections are sufficiently low that, over a reasonable range of source temperatures and scattered angles, only single surface phonons are excited or deexcited, thus allowing an unambiguous mapping of inelastic energy loss/gain onto vibrational frequency and wavelength.

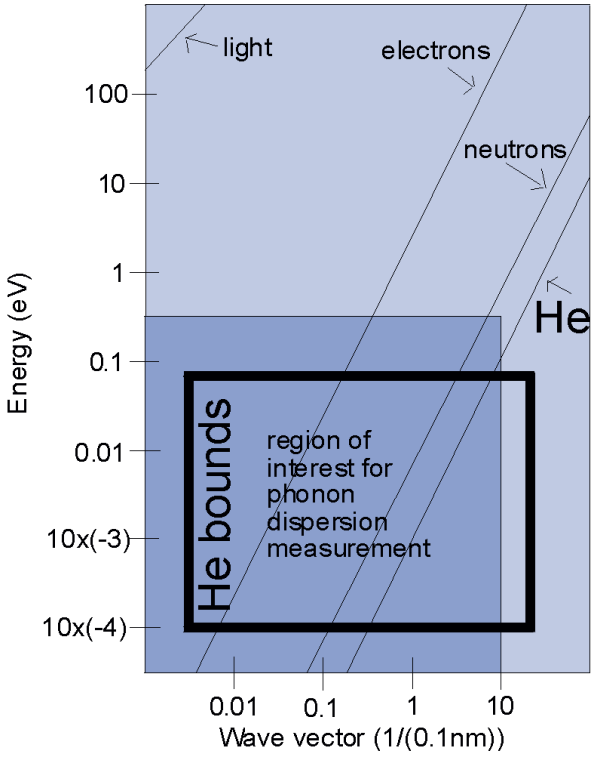

Fig.1

Energy-momentum relation for various probe particles commonly employed in making phonon measurements. Dark blue indicates the region of interest in measuring of full phonon dispersion curves. Approximate bounds for He atoms are shown by the dark violet line.

Helium nozzle beam produces an especially narrow velocity distribution, giving excellent energy resolution and high spectral intensity. The low natural abundance of helium makes it possible to reduce the background levels at the detector to quite low levels through differential pumping. This is very important for detecting the small inelastically scattered intensities.

A major disadvantage of He beams and, generally speaking, of all atomic beams is that atoms are, relatively speaking, big and slow. One can characterize the normal mode excitation in a

surface-scattering process by considering the deformation of the surface produced by the incoming beam particle. Probe species which travel with high speed (electrons, ions, photons) or interact with short-range forces (neutrons) produce an impulsive, local deformation. In contrast the lattice displacement produced by the impact of an atom against a surface varies slowly in both time and space. This deformation can be expanded as a sum of normal modes. When the probe-surface interaction is more impulsive (electrons, ions), the penetration into the sample will also be deeper and the surface sensitivity lower (*Fig.3*). In general the probe atom should be as light in the mass as possible (to produce a high speed at thermal energies) and as small as possible. Helium is thus the ideal choice among the rare gases and is surpassed overall only by H and H_2 (which suffer from insurmountable problems in generating an intense monoenergetic beam and from the tremendous natural background levels on mass 1 and 2) and remains the ideal choice for inelastic surface scattering to measure low-energy surface vibrations.

Elastic scattering

For any perfect surface e.g. a metal, semiconductor or insulator, the elastic scattering event for He atom is governed by conservation of energy and of the momentum component parallel to the surface plane.

$$E_f = E_i \tag{1}$$

$$\vec{K}_f = \vec{K}_i + \vec{G} \tag{2}$$

where $G = n_1\vec{b}_1 + n_2\vec{b}_2$, $(n_1, n_2 = 0, \pm 1, \pm 2...)$ is a reciprocal lattice vector, with the basis vectors of the real space $\vec{a}_1$ and $\vec{a}_2$ which satisfy the condition

$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$ $(i, j = 1,2)$. δ_{ij} is a Kronecker symbol.

The scattering geometry and the Ewald-construction for diffraction from surfaces are shown in *Fig .2*.

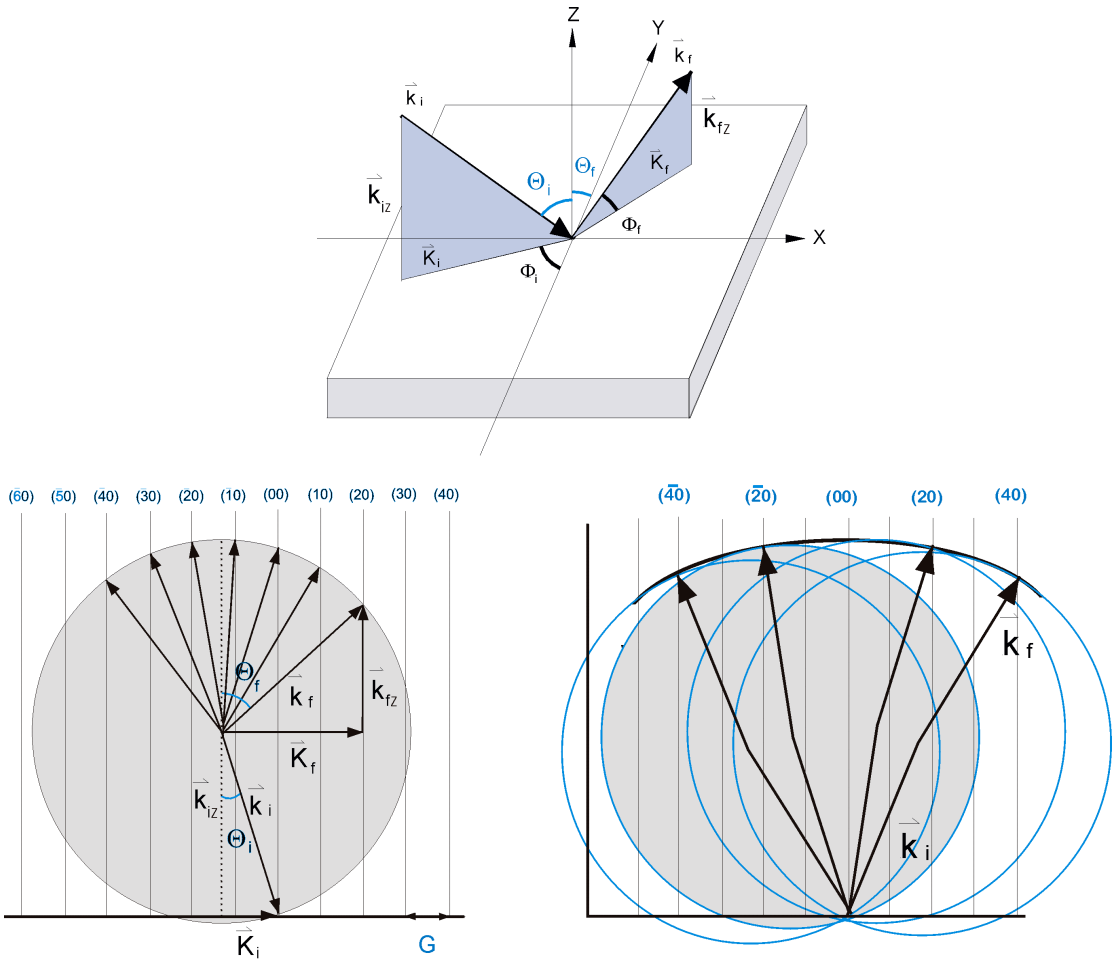

Fig.2

The scattering geometry and the Ewald-construction for diffraction from surfaces.

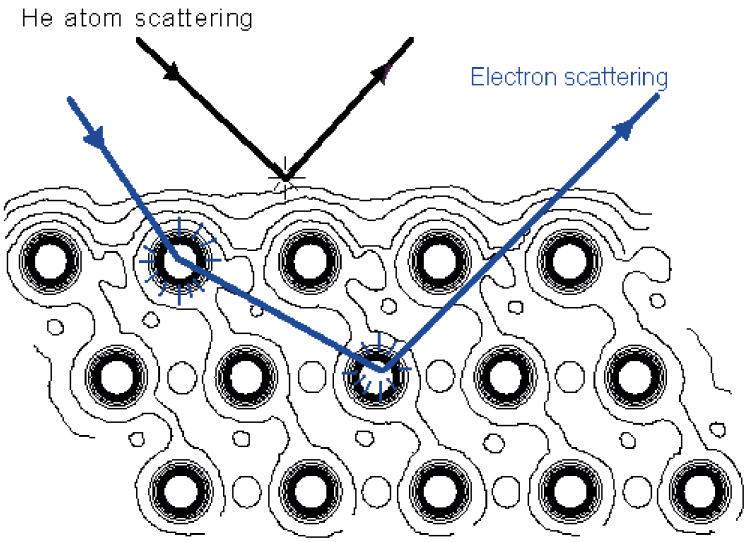

Fig.3

The schematic illustration of scattering of He atoms (black) and electrons (blue) at a metal surface.

The detection of the He atoms is much less efficient than that of electrons. So at any time the scattered intensity can be determined only for a single point in k-space. Between the diffraction peaks no elastic intensity is expected for an ideal surface. Any elastic intensity scattered in these regions of k-space is due to a lack of perfection at the surface and the presence of adatoms and steps, i.e. lattice defects.

Inelastic scattering

Schematically, an inelastic helium scattering experiment takes the form indicated in *Fig.4*. An intense, nearly monoenergetic beam of He atoms is directed onto a target surface at a particular angle of incidence and the scattered intensity measured at a given angle of reflection. So in general helium atoms can be scattered either elastically, with no energy transfer to or from the internal degrees of freedom of the crystal surface, or inelastically, by excitation (phonon creation, Stokes process) or deexcitation (phonon annihilation, anti-Stokes process) of surface vibrational modes. To monitor the elastic scattering it is necessary to energy-analyze the scattered beam. The most common-used technique is the time-of-flight (TOF) analysis which entails pulsing a beam with a mechanical 'chopper' at some point in its transit from source to detector and measuring the chopper-detector flight time.

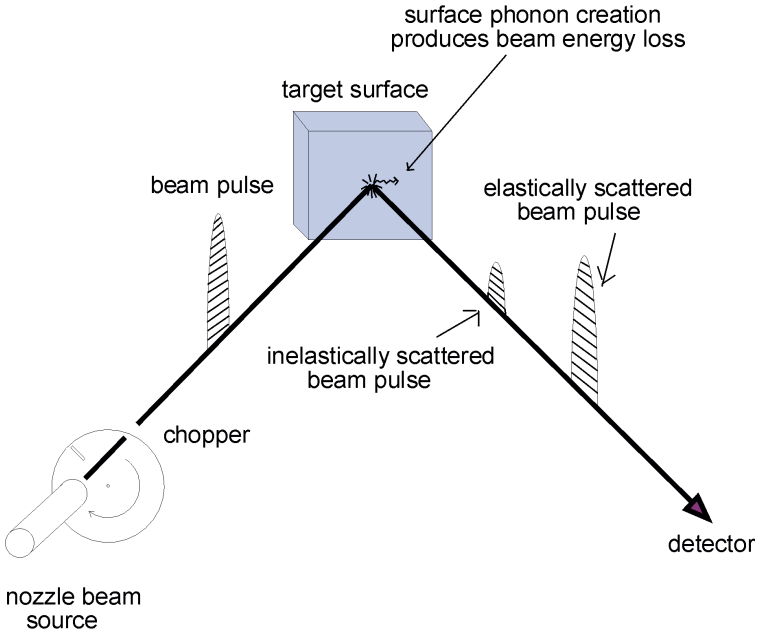

Fig.4

Schematic depiction of a surface phonon measurement using inelastic He scattering with TOF analysis.

Beam atoms which scatter inelastically will leave the target surface with velocities different from that of the incident beam producing time-shifted peaks at the detector. So the creation or annihilation of surface phonons will produce discrete shifts in the energy of the scattered beam. Experimental conditions are chosen to ensure that single phonon scattering dominates, in which energy analysis of the scattered beam yields directly the energy of the surface phonons.

From the measured energy exchange and knowing the angles of scattering, the momentum of the phonon is also easily computed to provide one point $\omega(Q)$ on the phonon dispersion curve. By varying kinematic parameters (beam energy, scattering angles) it is possible to sample other $\omega(Q)$ points and map out the full dispersion relation.

$\upsilon_i = \frac{x_{cd}}{t_{cd}}$ where x_{cd} is the flight path from chopper to detector, t_{cd} is the transit time of an elastically scattered atom over the flight path. Inelastic scattering at the target surface transfers energy to or from atoms, changing their velocity and thereby their flight time from target to detector. So TOF spectra display peaks which are shifted relative to the elastic flight time.

The salient features of the preceding data can be understood on the basis of the simple kinematic relations. The scattering geometry is shown in *Fig.2*. An atom incident onto the surface at polar angle Θ_i (with respect to the surface normal), azimuthal angle Φ_i and wavevector K_i scatters to emerge at Θ_f, Φ_f with the wavevector K_f. Conservation of energy requires

$$\frac{\hbar^2 k_f^2}{2m} = \frac{\hbar^2 k_i^2}{2m} + \Delta E \qquad (3)$$

$\Delta E = \hbar\omega$

$\Delta E > 0$: phonon annihilation and gain of energy by the beam atom,

$\Delta E < 0$: phonon creation and loss of energy by the beam atom.

Within the plane of the surface conservation of momentum requires $K_f = K_i + \Delta K$ where ΔK is the scattering vector in the surface plane. The projections into the surface plane are $K_a = k_a \sin\Theta_a$, where $a = i, f$ and angles are measured with respect to the surface normal. Most inelastic scattering measurements are made in an 'in-plane' scattering configuration, $\Phi_i = \Phi_f$ in which case the total source-target-detector scattering angle is $\Theta_{sd} = \Theta_i + \Theta_f$. Since the helium atoms are nonpenetrating, however, they sample the lattice periodicity in this direction only in the rudimentary form of step interference. One cannot formulate the selection rules for the perpendicular momentum transfer.

The conservation laws can be combined to give an expression that specifies the values of energy exchange ΔE and parallel momentum exchange ΔK, consistent with the conservation of momentum and energy,

$$\Delta E = \frac{\hbar^2}{2m}\left(\frac{\left|K_i + \Delta K\right|^2}{\sin^2\Theta_f} - k_i^2\right) \tag{4}$$

This expression is generally referred to as a scan curve and plotted as $\Delta E(\Delta K)$ for given values of K_i and scattering angles. For the in-plane scattering, $K_f \text{II} K_f \text{II} \Delta K$ and $\Theta_{sd} = \Theta_i + \Theta_f$ the scan curve relation becomes

$$\frac{\Delta E}{E_i} = \left(\frac{\sin\Theta_i + \dfrac{\Delta K}{k_i}}{\sin(\Theta_{sd} - \Theta_i)}\right)^2 - 1 \tag{5}$$

A complete set of the scan curves is shown in *Fig.5* for a $\Theta_{sd} = 60°$ fixed-angle geometry. This set spans the full range of accessible Θ_i, Θ_f values for this Θ_{sd}: the leftmost curve corresponds to $\Theta_i = 90°$ and the rightmost curve corresponds to $\Theta_f = 90°$.

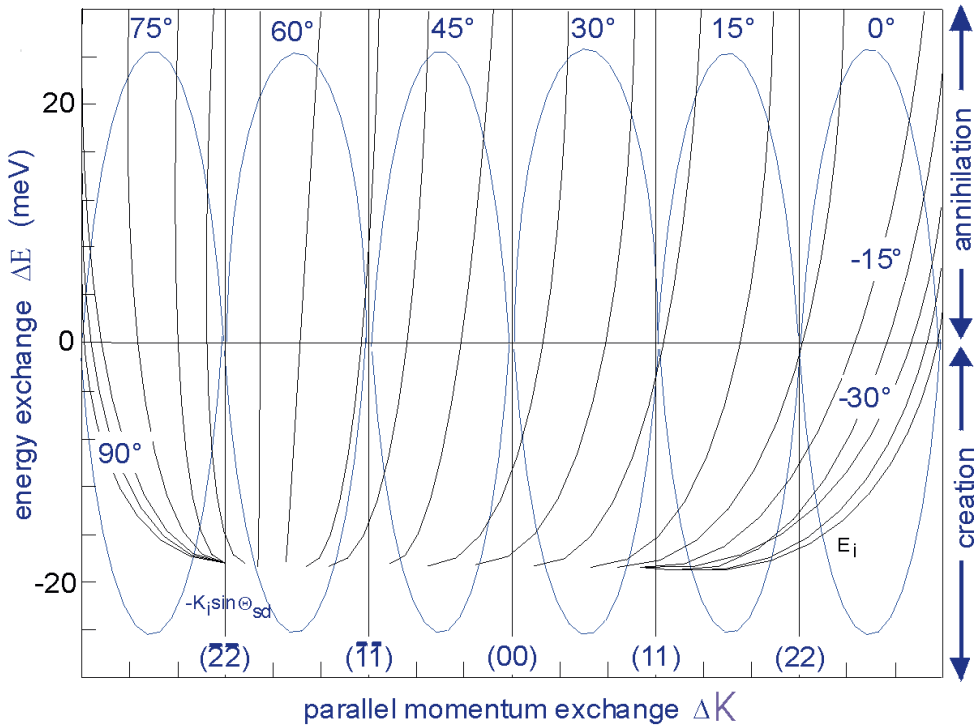

Fig.5

Representative set of scan curves (black parabolic line curves) for $\Theta_{sd} = 60°$, $k_i = 6.0\,\text{Å}^{-1}$ *(liquid nitrogen cooled nozzle) spanning the full range of possible scattering angles. The blue curves represent phonon dispersion curves. For* $\Theta_{sd} < 90°$, *as in this instance setting* $\Theta_f = 0°$ *produces a 'constant Q' scan at* $\Delta K = -k_i \sin\Theta_{sd}$. *Phonon creation* $(\Delta E < 0)$ *can occur only for* $\Delta E > E_i$, *where* E_i *is the incident beam energy.*