TRANSFER MATRIX APPROACH TO METAL SURFACES VIBRATIONS

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Surface phonons propagating in arbitrary directions in the surface of FCC metals are studied via vibrational Green's functions obtained through the definition of transfer matrices. The dynamical matrix is described in the central force model. The method is applicable to any direction in the surface and is specially efficient for high symmetry directions. Ni (111) surface phonons are obtained with excellent agreement with previous experimental results.

In recent years there has been a large increase of the interest in the study of surface and interface vibrations. This was partially motivated by technological reasons and has been possible due to the significant improvement both in the growing and characterization techniques. The development of experimental probes with high surface sensitivity has made it possible to study localized vibrations and to analyse interesting features associated with surface phenomena.

The adsorption of foreign atoms in clean surfaces has been examined successfully in Electron Energy Loss Spectroscopy (EELS) experiments producing a clear picture of the adsorption sites.¹ The surface vibrations are also a valuable tool to characterize surface phase transitions and reconstructions.^{2,3}

The main characteristic of surface experimental methods is the use of probing particles with very small penetration depths. A clear physical picture of the scattering is provided in most cases by single surface phonon processes. This is the case in EELS experiments and also in experiments involving the scattering of helium atoms off the surface. In both cases the scattering is produced by surface phonons propagating in a fixed direction.

The inelastic scattering of heavy atoms with low energy involves surface modes with large wave vectors, ranging from the centre of the Brillouin zone to the edges, and requires the knowledge of the surface spectrum away from the Γ point. The inelastic scattering of Helium atoms⁴ is one of the most valuable experimental methods and allows a

complete sampling of the surface spectrum.

The theoretical approaches for surface vibrations include complete diagonalization of the Dynamical Matrix for thin slabs, based in Van der Waals forces between the atoms⁵ or the use of Green's functions in semi-infinite systems. The first approach is limited due to the small number of planes which can be considered in the slab to reduce the computational effort. The fine details of the surface spectrum are not represented and the relative weight of the resonances and local modes in the surface, which is an important information to analyze spectra, is not calculated either. Vibrational Green's functions give this information in a convenient way. This technique has been used in the framework of the Continued Fraction Method⁶ and also for particular directions in the surface, when it is possible to decouple the equations of motion using symmetry transformations.⁷

Our purpose is to present a method which is valid for a general direction in the surface. The surface vibrations are studied via densities of states obtained from displacement-displacement Green's functions calculated using transfer matrices previously used in the context of electronic properties of surfaces and amorphous systems.⁸⁻¹¹ It is therefore a unified method to describe a wide range of surface excitations.

The basic structure of the surface spectra of transition metals can be described very accurately in most cases by central force interactions between nearest neighbour (nn) atoms. This model is particularly good for Cu and Ni vibrations due to an efficient

shielding effect by the conduction electrons.^{12,13} We therefore consider the elastic energy given by

$$U = \sum_{lm} (\alpha/2) \{ [u(l) - u(m)] \cdot n(l,m) \}^2 \quad (1)$$

where $u(l)$ is the displacement of the atom at site l , $n(l,m)$ is the unit vector in the direction joining site l and m and α is the central force constant. α was chosen in order to fit the maximum frequency of the Ni vibrations (295 cm^{-1}).¹⁴ The upper limit of the Ni spectrum is at the X point and the frequency is given by $\omega(X) = \sqrt{8\alpha/M}$, where M is the mass of a Nickel atom. $\alpha = 0.6385$ in units chosen such as to give the frequency in inverse wave numbers and the mass in atomic units.

The force-constant matrix, involving the interactions of pairs of atoms is given by

$$\phi_{\gamma\beta}(l,m) = \frac{\partial^2 U}{\partial u_\gamma(l) \partial u_\beta(m)} \quad (2)$$

where $u_\gamma(l)$ is the displacement of the atom at position l in the direction γ . The displacement-displacement Green's functions are defined by the matrix equation

$$(M\omega^2 - \Phi)G = I \quad (3)$$

in which each entity is a $3N \times 3N$ matrix, where N is the number of atoms in the crystal. The translational periodicity parallel to the surface allows a partial diagonalization of equation (3). This is accomplished by a Bloch transformation to a basis consisting of phonons propagating in each plane parallel to the surface. After the transformation the equations of motion for the Green's functions are

$$(M\omega^2 - \Phi_{nn}) G_{nm}(k) = \delta_{nm} + \Phi_{nn+1} G_{n+1m}(k) + \Phi_{nn-1} G_{n-1m}(k) \quad (4)$$

where all the entities are 3×3 matrices and Φ_{nm} and G_{nm} describe the coupling and the Green's functions involving waves with wave number k propagating in planes n and m . In this mixed representation the degrees of freedom parallel to the surface are considered by the Bloch transformation and the direction perpendicular to the surface is treated in real space, resulting in an infinite set of equations coupling the Green's functions for a given k . To form a semi-infinite solid in the region $n \geq 0$, we simply impose that the self-interaction at the surface plane, Φ_{00} , is different from

the self-interaction in the bulk, due to the smaller coordination number at the surface, and that there is no coupling with the plane $n=-1$ (above the surface).

The stacking of (111) planes in the fcc lattice involves a single kind of coupling between adjacent planes. The twelve nearest neighbours of a given atom are distributed in the two adjacent planes (each containing three neighbours) and in the same plane.

The elastic forces are here represented by the matrices Φ_{nn} , Φ_{nn+1} and Φ_{nn-1} . If no relaxation or reconstruction is considered, all but the self-interaction matrices are constant and given by the bulk values. For simplicity we call Φ_{00} , Φ_0 , the self-interaction matrices (surface plane and bulk) and Φ_+ (Φ_{nn+1}) and Φ_- (Φ_{nn-1}) the coupling between adjacent planes. The relevant matrix elements are given by

$$\Phi_{0\gamma\beta}(k) = \sum_R \phi_{\gamma\beta}(0,R) \exp(ik \cdot R) \quad (5)$$

$$\Phi_{+\gamma\beta}(k) = \sum_R \phi_{\gamma\beta}(0,R_+) \exp(ik \cdot R_+) \quad (6)$$

where the vectors R and R_+ denote the positions of nn atoms and $\Phi_- = (\Phi_+)^*$.

The equations of motion can be decoupled through the use of a plane independent transfer matrix $T(k)$ defined by

$$G_{n+1m}(k) = T(k) G_{nm}(k) \quad (n \geq 0) \quad (7)$$

which obeys the equation

$$T(k) = (M\omega^2 - \Phi_0 - \Phi_+ T(k))^{-1} \Phi_- \quad (8)$$

Surface densities of states are obtained from appropriate Green's functions. For the surface plane, for instance, the spectral density of states in a selected direction (k) is given by

$$\rho(\omega,k) = -(2M\omega/\pi) \text{Im } G_{00}(\omega,k) \quad (9)$$

The Green's functions in the first few planes from the surface are very easily obtained from $T(k)$. In the first two planes they are given by

$$G_{00}(\omega,k) = (M\omega^2 - \Phi_{00} - \Phi_+ T(k))^{-1} \quad (10)$$

and

$$G_{11}(\omega,k) = (M\omega^2 - \Phi_0 - \Phi_- (M\omega^2 - \Phi_{00})^{-1} \Phi_+ - \Phi_+ T(k))^{-1} \quad (11)$$

The bulk spectrum can be obtained as well. This requires an extra transfer matrix $Q(k)$ defined by

$$Q(k) = (M\omega^2 - \Phi_0 - \Phi_- Q(k))^{-1} \Phi_+ \quad (12)$$

and the local density of states in the bulk is obtained from an average of

$$G(\omega,k) = (M\omega^2 - \Phi_0 - \Phi_+ T(k) - \Phi_- Q(k))^{-1} \quad (13)$$

The bulk spectrum is a useful aid in determining the nature of the relevant features in the surface spectrum. One

may decide, for instance, whether a given peak in the surface spectral density is a gap mode or a resonance, by comparing the surface spectral density with the bulk density.

The solutions of equations (8) and (12) were obtained iteratively starting with $T(k)=0$, $Q(k)=0$ for each frequency. The iteration number is generally small, except for frequencies near singularities in the surface spectrum. For high symmetry directions the iteration process is specially fast due to the fact that the coupling matrix Φ_+ and the self-interaction matrix Φ_0 are block-diagonal in these directions. Vibrations polarized perpendicularly to (111) planes (z direction) are decoupled from in-plane vibrations (x and y directions).

We have chosen the Ni(111) surface to apply the method in order to make a comparison with electron energy loss experiments on oxygen covered surfaces. Furthermore Ni bulk vibrational spectrum can be fitted well by the central force model restricted to first neighbours. The method applies to other FCC metals as well. In some cases it may be necessary to extend the interaction to second neighbours and to introduce angular forces.

The densities of states at selected points in the Brillouin zone are useful in interpreting electron energy loss experiments. As pointed out by Evans and Mills¹⁵ the dipole moment for the elastic scattering is mainly due to the coherent vibration of surface atoms in the direction perpendicular to the surface. Therefore the scattering must reflect the density of states in the Γ point in the surface. The presence of adsorbed atoms, though, can induce scattering by local modes propagating in special directions away from the zone centre. This was first

proposed by Ibach and Bruchman¹ as an explanation to interesting experiments involving the adsorption of Oxygen atoms in the Ni(111) surface. They considered two different coverages. The oxygen adlayer for low coverage was shown to consist of a (2x2) pattern while for higher concentration of Oxygen the adlayer has the $(\sqrt{3} \times \sqrt{3})R30$ structure (see fig.3 of Ibach and Bruchman). They proposed that the spectra is dominated by phonons at special points in the surface Brillouin zone (points K and M), due to the coupling between the oxygen adlayer coherent motion and the substrate. We selected these points to make a comparison with their experiment. The spectral densities of states are shown in figs.1-2. We obtain excellent agreement with the experimental results by Ibach and Bruchman¹. Our results are consistent with the previous theoretical

Fig.1 Densities of states for the M point in the Ni(111) surface. (a) Vibrations in the (111) plane: polarized in the x direction (full line) and polarized in the y direction (broken line). (b) Vibrations polarized in the [111] direction. In the insert we show the two-dimensional Brillouin zone for the (111) surface of an FCC crystal.

models by Alen et al.⁵ and by Black et al.⁷ The leading features of the spectrum are peaks corresponding to local modes. In fig.1 for the spectral density of states in the point M, we notice two bands corresponding to the projection of bulk bands on the surface and two peaks associated to surface modes. The surface modes take practically all the weight of the surface density and correlate well with the observed peaks in the EELS spectra. The peak at 130 cm⁻¹ is the Rayleigh wave, polarized in the direction z (normal to the surface). It has been observed at 135 cm⁻¹. It takes practically all the weight of the motion perpendicular to the surface. A very small projection of bulk states is seen near the top of the spectrum (295 cm⁻¹). We calculated densities of states along the direction ΓM and observed that it exists throughout the Brillouin zone and is below the bottom of the bulk band for any given value of the parallel wave vector k. The second peak at 272 cm⁻¹

Fig. 2 Densities of states for the K point in the Ni(111) surface (a) Vibrations polarized in the (111) plane. (b) Vibrations polarized in the [111] direction.

was observed at 265 cm^{-1} . It is a gap mode very near the bottom of a bulk band and its polarization vector lies in the (111) plane. The other point of interest is the corner of the Brillouin zone, the point K. The densities shown in fig. 2 have the same features as before, showing projection of bulk bands and local mode peaks. The Rayleigh mode is seen at 137 cm^{-1} , at almost the same frequency as in the point M, corresponding to a flat dispersion away from the zone centre. The peak at 229 cm^{-1} is a gap mode, below the projection of bulk states in the surface. The second peak, with approximately half the weight of the first, seen at 238 cm^{-1} , is a surface resonance. It was observed at 240 cm^{-1} and it is associated to the active mode in the electronic scattering for the $(\sqrt{3} \times \sqrt{3})\text{R}30$ surface. The small differences between the calculated values of surface mode frequencies and the observed ones are expected since we are comparing a clean Ni(111) surface calculation with experiments made on an oxygen covered surface. The coupling to oxygen atoms may lead to modifications on the frequencies of the substrate modes.

The method presented here is also useful to examine the decay of the surface modes into the bulk, since the densities in the first few planes from the surface can be obtained from a single transfer matrix. We observe in fig. 3 that most of the features of the surface spectrum are very localized. The surface local density (full curve) has a

Fig. 3 Ni(111) local density of states: surface plane (full curve) and second plane (dashed curve).

Fig. 4 Ni- Local bulk spectrum

large weight in the low frequency region, where the Rayleigh wave dominates the spectrum. The density at the second plane (dashed curve) is already very similar to the bulk density shown in fig.4. The local densities of states were obtained from an average of spectral Green's functions. The points in the irreducible part of the surface Brillouin zone were chosen according to Cunningham's scheme.¹⁶

Among alternative methods to study surface excitations the present one is particularly efficient because it provides the Green's functions for fixed values of k very easily, specially along high symmetry directions, and is valid for any value of k . Local properties can also be obtained without much computational effort, specially for surfaces of high symmetry in which the irreducible part of the Brillouin zone is a small fraction of the entire zone.

The model can be extended to include interactions between more distant atoms or to consider the

presence of adsorbed layers. It is also possible to include surface relaxation provided that an estimate of the stiffening of the force constants near the surface is available. Dispersion relations for surface modes can be obtained as well, by simply following a given pole of the surface Green's function as a function of k . This is useful to interpret atom scattering results. A calculation of the dispersion of Ag(111) surface modes as well as of surface densities of states appropriate to interpret inelastic helium scattering experiments is in course, and will be the subject of a future communication.

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