Atomic Probes of Surface Structure and Dynamics

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Introduction:

Atom scattering from surfaces remains a unique and powerful tool for the study of surface structure and dynamics. Inelastic atom scattering is the method of choice for studying surface phonons. Some of the more recent applications have included binary metal surfaces¹ and inelastic scattering from surface steps.² Novel studies of surface diffusion have also been reported recently, both self-diffusion³ and adatom diffusion.⁴ This is a very important area since atom scattering makes it possible to measure very rapid diffusion. An exciting prospect is to distinguish between various diffusion mechanisms (one- vs. two atom mechanisms). Atom scattering is also an important tool for studying structure of 'fragile' surfaces, where other tools such as STM and electron scattering are too destructive. Some examples are molecular overlayers,⁵ rare gas overlayers,⁶ and Langmuir films.⁷ Atom scattering has furthermore proved to be a powerful tool for studying *in situ* the growth of surfaces from vapor where rate dependent phenomena are of critical importance and the use of slow and intrusive measuring procedures such as STM are less effective. The deposition of various metals on surfaces has been studied in several laboratories⁸⁻¹¹ and even the growth of an overlayer of Buckey balls on mica.¹² Most surface growth measurements use RHEED (reflection high energy electron diffraction) but the interpretation of the RHEED signal is ambiguous because of refraction as well as reflection events.¹³ A recent and novel application of atom scattering is the study of structure and dynamics of liquid surfaces,¹⁴ an area where very few experiments have been done and very few experimental techniques can be applied.¹⁵

1. New semiclassical method for scattering calculations:

We have been developing methods which will allow much faster and more accurate three dimensional atom surface scattering calculations, both elastic and inelastic (section 3 of our previous proposal). For full 3D elastic scattering, our goal is to be able to semiclassically describe not only the diffractive scattering, which previously could be handled by Gaussian wavepacket technology, but also the selective adsorption resonances, which could not be handled by those techniques. This will be made possible by the newer 'Cellular Dynamics' approach,¹⁶ which is much more accurate. It has been shown to give excellent results even for chaotic motion over rather long times.^{17,18}

Progress has been gratifying on semiclassical methods which will be of direct consequence for application to surface scattering processes. The 'Cellular Dynamics' method, which involves direct construction of the semiclassical Green's function has proven to be viable and accurate beyond anyone's hope. Even completely chaotic dynamics have been shown to be well within its grasp. This bodes well for both elastic and inelastic surface scattering. For the elastic case, the ability to handle all the complexity of multiple collisions from surface features, selective adsorption, and arbitrary defects will be a significant advance.

2. *Application to inelastic scattering:*

The future looks bright for inelastic atom-surface scattering (section 5 of our previous proposal) using the new semiclassical method. The Cellular Dynamics approach has been applied to correlation function spectroscopy, in work which is now being written up with a second year graduate student, Miguel Sepulveda. The correlation function methods will be used for the treatment of inelastic atom scattering from surfaces. The efficacy of the approach was first demonstrated by Drolshagen and Heller.¹⁹ However at that time a Gaussian wavepacket approach was used,^{20,21} and now we have a much more accurate and flexible scheme. The inelastic scattering cross sections are obtained as autocorrelation functions of the target motion after it has been struck by the probe atom. Since individual quantum eigenstates are never observed, a time dependent approach is ideal.

We have started working on an intriguing problem closely related to the atom-surface inelastic scattering problem that is not as complex and is a useful test problem: the scattering of helium atoms from buckyballs. The experiment is being conducted by Dr. A. Scheidemann in this Department as well as in other laboratories.²² Although this is atom-molecule, not atom-surface scattering, there are many technical similarities. The treatment of buckyball scattering will allow us to graduate much closer to the atom-solid state situation. We have used the semi-empirical He-C atom-atom potential of Jónsson and Weare, which was obtained from various kinds of experimental and theoretical data on atom scattering from graphite surfaces.²³ So far the elastic total and differential cross sections have been evaluated. These calculations coupled with the experimental data of Scheidemann will tell us how the atom-buckyball interaction compares with the atom-graphite surface interaction, and by comparing the inelastic scattering with experiment we will learn about the carbon lattice interactions. Miguel Sepulveda, is now working on this problem.

The theory for semiclassical treatment of infrared absorption has been worked out and is ideal for surface spectroscopy. As of now, we have no plans to push this capability, for lack of time, but it remains very interesting. The same holds true for DIET (desorption induced by electronic transitions), which is in a rather sorry state in the literature. However, until the inelastic scattering is well underway or a new student joins the group, this too will remain on hold.

3. *He atom scattering from defective Pt surfaces:*

We have started working on atom scattering from defects on metal surfaces, described in section 8 of our previous proposal. We are in particular analysing a very interesting recent experiment using He atom beam scattering to monitor vapor deposition of Pt. Several experiments indicate layer-by-layer growth of metal surfaces at surprisingly low substrate temperatures.^{8,29} Particularly intriguing is the 'reentrant' behaviour of the layer-by-layer growth of Pt(111) observed by He atom scattering: While layer-by-layer growth is

observed at temperature below room temperature and at sufficiently high temperature, the growth seems to be three-dimensional (not layer-by-layer) at intermediate temperatures.⁸

We are doing Molecular Dynamics and Monte Carlo simulations of the vapor deposition of Pt on Pt(111). The simulations show that the latent heat of condensation (ca. 4 eV) can lead to several direct impact mechanisms that enhance layer by layer growth. It is not, however, effective in increasing the diffusive mobility of the deposited atoms, as has been suggested previously.²⁴ Diffusion barriers for the migration of adatoms from on-top of islands are found to be very large (ca 0.8 eV), irrespective of the shape and size of the island. At higher temperatures, diffusion leads to the formation of larger islands and the direct impact ordering mechanisms become less effective. This possibly explains the puzzling atomic scattering measurements. A second year graduate student, Marie Villarba, is working on this project.

We are doing calculations, using the Gaussian wavepacket method,²⁰ to relate the measured atom scattering signal to the surface morphology. An important question is how defective the surfaces are when the deposition is carried out at low temperature. There are several advantages to low temperature deposition, for example in electronic device manufacturing, such as reduced damage and interdiffusion between layers, but the quality of the deposited layers is also a concern. Atom scattering is a very important tool here. The measured signal is dependent on the growth rate, so stopping the experiment and applying intrusive and slow techniques such as STM is less than optional. Currently, the most commonly used technique for *in situ* monitoring of growth is RHEED, but the measured signal is difficult to interpret in terms of surface structure, due to multiple scattering (refraction effects).¹³

A central problem for doing the atom scattering calculations is to find potential functions that describe the interaction with the surface defects. Purely theoretical, *ab initio* estimates of atom and molecule interaction with perfect surfaces have given qualitative but not quantitative agreement with experimental data.²⁵⁻³⁰ Semiempirical interaction potentials have, however, been very successful in reproducing a wide range of experimental data on surfaces.^{24,31-34} While some properties such as the long range attraction and the steepness of the short range repulsion can be well estimated theoretically, it is important to combine those with careful analysis of experimental measurements.

We have developed a semiempirical potential function that can be used to construct interaction potentials for defects on metal surfaces such as vacancies, steps and adatoms, in the following way: Several theoretical treatments of the atom-surface interaction have indicated that the repulsive interaction is proportional to the surface electron density.^{26,28} At the low electron densities relevant here, this can be approximated quite well with a superposition of atomic densities, even for metal surfaces.²⁸⁻³¹ Thus a pairwise additive form for the repulsive potential is justified. The work function is used to determine the softness of the exponential repulsive interaction³² while we leave the preexponential as a free parameter determined by comparison with measured scattering data.

The long range dispersion (London) interaction has the asymptotic form, $C_3/(z-z_0)^3$, with C_3 obtained from the dielectric function.²⁵ Close to the surface it is important to include short range corrections to this long range form. A simple model for the electronic response of a transition metal surface considers the conduction electrons as a ho-

homogeneous electron gas while the localized d-electrons are treated as a lattice of point polarizabilities.⁴⁵ It has been shown theoretically that the dispersion interaction of *He* and *H*₂ with the localized d-band electrons, even in the very smooth Ag(111) surface, has appreciable corrugation.³⁵ A simple continuum dielectric model has been used to estimate the contribution of the conduction electrons to the attractive interaction of *He* atoms with adatoms and vacancies on metal surfaces.³⁶ Our potential is consistent with the results of that calculation, even though it is based on a local oscillator approach. Finally, a damping factor is included that accounts for effects of the electron overlap and turns off the divergence of the multipole expansion. All parameters in this model for the dispersion interaction can be estimated theoretically from the dielectric function of the metal. It has been argued that short range, corrugated attractive interaction in addition to the dispersion interaction, arises from hybridization.²⁹ We choose an exponential pairwise form for this short range attraction and leave the parameters as adjustable parameters. Finally, vacancies and steps carry a permanent dipole due to the electron smoothening effect (Smoluchowsky effect).³⁷ For example, the value of 0.6 *Debye* has been determined for a vacancy on Pt(111) by measuring the effect of ion sputtering on the surface work function. This gives a negligibly small attractive contribution to the surface interaction potential.

The free parameters have been determined by comparison with measured scattering data on periodic surfaces with known structure. For *Pt* we have used data on the highly corrugated missing row *Pt*(110)*x*(1 $\times$ 2) surface.³⁸ The corrugation of the *Pt*(111) surface is predicted to be very small using the same set of parameters, in agreement with the available experimental data.³⁹

We have evaluated the *He* atom scattering cross sections for various defects on *Pt* surfaces using this semiempirical potential. Unfortunately, there is only very limited experimental data to compare with here. The calculated cross section for diffuse scattering from steps agrees with the experimental measurements on *Pt*⁴⁰ as well as *Cu*⁹ surfaces to within 10%.

However, the cross section for vacancies which has been estimated from the scattering from surface undergoing ion sputtering,^{41,42} is a factor of 4.5 larger than our calculated value. We believe this is because several defects other than monovacancies are created on the surface. We are doing molecular dynamics simulations of *He*⁺ and *Ar*⁺ ion sputtering of Pt(111) surfaces in the energy range of 400 – 1000 eV with emphasis on analysing the structure of the resulting surface. In particular, we want to analyze the experimental data taken at 80 K by Comsa and coworkers,⁴¹ who simultaneously monitored the reflectivity of low energy (60 meV) *He* atoms from the surface. Several questions need to be answered that are crucial for the correct interpretation of those and any other experiments on surface defects induced by ion bombardment at low temperature. First of all it is important to know what defects are created on a surface at low temperature. In addition to mono-, di-, and larger vacancies one might have adatom/vacancy pairs, interstitials, embedded neutralized ions, etc. It is also important to understand sputtering of a defective surface as opposed to sputtering of a perfect surface. The types of defects formed and the sputtering yield can be quite different. Conclusions drawn in the experimental *He* scattering investigation⁴¹ about spatial correlations of vacancies will be tested by combining the sputtering simulations and calculations of atom scattering from the defective surfaces.

An undergraduate student, Eric Schug, is working on the sputtering calculations.

4. *He atom scattering from Xe overlayers on metal surfaces:*

Atomic beam scattering (in particular *He* atom scattering) has proved to be a uniquely powerful tool for studying the structure of rare gas overlayers. We have been working on a calculation of *He* atom scattering from *Xe* overlayers on Pt(111) and Ag(111). We have previously done extensive analysis of atom scattering from rare gas overlayers on graphite and found very good agreement between experiment and theory^{42,43} when the surface potential is constructed by adding up gas-phase He-Xe potential for each overlayer atom and applying the Axilrod-Teller-Muto three-body correction. However, using the same approach for the monolayer on these metals leads to clear discrepancy with experiment.⁴⁴⁻⁴⁶ We have found that the surface potential turns out to be much too corrugated in those cases. The discrepancy can be explained by a substantial redistribution of the electrons around the *Xe* atoms. The repulsive part of the He-surface potential is to a good approximation proportional to the surface electron density. This indicates that the *Xe*-metal interaction in those systems goes beyond 'physisorption' interaction and has a more 'chemical' character. Indirect evidence from the statistical mechanics of incommensurate *Xe* overlayers on Pt(111)⁴⁷ and *ab initio* density functional calculations⁴⁸ have lead other workers to conclude that the *Xe* atoms sit on top of Pt atoms rather than in the threefold hollow sites, consistent with a strong, 'chemical' interaction. Furthermore, studies of *Ag*₂-raregas complexes, such as *Ag*₂ - *Xe* have shown that the *Xe* interaction is anomalously strong, ca. two times stronger than the Drude model would predict,^{49,50} again indicating more 'chemical' interaction.

We will go on to analyse experimental data on incommensurate and superlattice layers of the *Xe* on Pt(111) to obtain models of their atomic structure. This will provide more information about the *Xe*-Pt interaction. A very clear superlattice diffraction pattern has been seen, indicating a unit cell that is 5 times larger than the commensurate unit cell in each direction. The challenge now is to interpret this in terms of the atomic structure within the unit cell. We will use a recently formulated *Xe*-Pt(111) potential⁵¹ to generate structural models for the overlayers and then verify, by comparing calculated and measured scattering, the atomic structure of the layers.

5. *Thermalized dissociation of H₂ on Cu(110):*

We have started studies of tunneling from physisorbed (precursor) state of molecules to the chemisorbed state on surfaces as described in section 4 of our previous proposal. We are particularly interested in the interaction of *H*₂ with metal surfaces and the dissociative

sticking process. At present there is no technique that allows us to do a full quantum mechanical simulation of the dynamics. We hope that the new 'Cellular Dynamics' approach will provide us with that tool.

At present we are doing a quantum simulations of the dissociative sticking of thermally equilibrated H_2 molecules on Cu(110). This experiment has been carried out in the laboratory of Prof. Charles T. Campbell here in this Department (and is DOE funded).^{52,53} These calculations are based on Feynman Path Integrals^{54,55} and will allow us to identify the statistically relevant tunneling path and evaluate the effective barrier for dissociation, including quantum mechanical effects. The simulations are fully three dimensional and include full averaging over the surface atom vibrations, but no temporal information is obtained about dynamic processes from these simulations.

This thermally equilibrated treatment can be appropriate in many circumstances. It has, for example, been hypothesized⁴² that dissociative sticking of H_2 is a two step process when the smooth surface gives rise to low sticking probability: (1) First the molecule is trapped in a physisorbed state and diffuses readily on the surface until, (2), it dissociates at a defect site. Since the molecule would thermally equilibrate with the surface in the physisorbed state, the second step, the dissociative sticking process, can be studied using equilibrium Feynman Path Integrals.

Applying the equilibrium Feynman Path Integrals (as opposed to the real time Path Integrals) is a well established computational technique that has been applied to various problems, such as H atom diffusion in bulk metals⁵⁶ and electron tunneling in proteins.⁵⁷ The method can be described as quantum transition state theory.⁵⁸ The dissociation of H_2 molecules is an interesting application of the technique because it involves two quantum particles. An efficient representation of the potential energy surface has been used to make the calculations doable without large CPU requirements. The potential surface⁵⁹ reproduces several *ab initio* calculations of H_2 dissociation on metal clusters⁶⁰ as well as experimental binding energies. Previous theoretical work on dissociative adsorption of H_2 has largely been confined to classical trajectory simulations⁵⁹ and quantum wavepacket simulations with restricted geometries (to reduce the dimensionality of the problem).⁶¹⁻⁶⁴

A first year graduate student, Greg Mills, is working on these calculations.

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