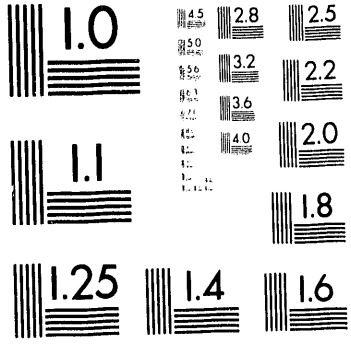
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Atomic Probes of Surface Structure and Dynamics

Technical Progress Report

for the period

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Introduction:

Atom scattering from surfaces remains a unique and powerful tool for the study of surface structure and dynamics. A particularly successful effort in the last few years has been its application to studies of *in situ* growth of crystals from vapor.[1–5] Rate dependent phenomena are of critical importance here and the use of slow and intrusive measuring procedures such as STM are problematic. The deposition of various metals on surfaces has been studied in several laboratories and even the growth of an overlayer of Buckey balls on mica.[5] Workers using atom scattering have been able to devise deposition schemes (including intermediate sputtering) for growing layer-by-layer metals which otherwise exhibit 3-D growth.[6] Most surface growth measurements use RHEED (reflection high energy electron diffraction) but the interpretation of the RHEED signal is ambiguous and not as surface sensitive because of refraction as well as reflection events.[7] Scanning tunneling microscopy can of course give more detailed information on the atomic structure of the deposited layers, but is confined to small surface areas and requires interrupting the deposition experiment and rapid quench of the system to prevent annealing during the measurement process.

Inelastic atom scattering is the method of choice for studying surface phonons. Some of the more recent applications have included binary metal surfaces[8] and inelastic scattering from surface steps.[9] Novel studies of surface diffusion have also been reported recently, both self-diffusion[10] and adatom diffusion.[11] 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,[12] rare gas overlayers,[13] and Langmuir films.[14] A recent and novel application of atom scattering is the study of structure and dynamics of liquid surfaces,[15] an area where very few experiments have been done and very few experimental techniques can be applied.[16]

1. New semiclassical method for scattering calculations:

Last year, we reported on new breakthroughs in development of semiclassical methods which would be of direct utility to surface scattering processes. The direct construction of the semiclassical Green's function has proven to be viable and accurate beyond anyone's hope. Work by S. Tomsovic, M. Sepulveda and Heller[17–19] has demonstrated this. Moreover the use of the semiclassical Green's function to propagate smooth states has proven very successful in the last year. In particular, systems with mixed dynamics (partly chaotic and partly quasiperiodic) have, surprisingly, proven robust semiclassically.

This has opened the way for a graduate student, M. Sepulveda, to begin an investigation of selective adsorption in Helium diffraction from crystalline surfaces. Selective adsorption is a difficult challenge. The classical process of splitting the incoming beam into the directly reflected part plus the indirectly scattered (selectively adsorbed) part is highly nonlinear, especially if the selectively adsorbed atoms emerge at radically different times from the surface. We are confident that the essential quantization of the selectively adsorbed motion will be properly accounted for by interference of the semiclassical

amplitudes.

Sepulveda has built the necessary classical trajectory program with the 'cellular dynamics' semiclassical construction included. Preliminary calculations show promise. Sepulveda will continue working on this project and should be able to obtain definitive results in the next year.

We also hope to implement the inelastic surface scattering through cellular dynamics, correlation function spectroscopy. From this year's experience with semiclassical molecular spectroscopy through correlation functions we are confident that excellent results are possible at low temperature.

A postdoctoral fellow, F. Grossman, has been studying cellular dynamics of a system coupled to a bath at finite temperature. The results have been very promishing. We are now able to include the effects of the harmonic bath in surface scattering, which was much too difficult previously. The idea is to start with the Feynman propagator for the reduced density matrix and reduce it to cellular dynamics. This has been done and we intend to use the new method for inelastic surface scattering at finite temperature.

3. He atom scattering from defective Pt surfaces:

We have been applying the Gaussian wavepacket technique[20–22] to evaluate the scattering cross section for various defects on Pt(111) surface and obtain an estimate of the reflectivity of surface configurations generated by simulated vapor deposition (molecular dynamics and Monte Carlo simulations).[23] The scattering calculations have verified that the morphology of the surfaces obtained from low temperature simulations ($275K$) are comparable to those measured in the laboratory by Poelsema and coworkers.[1] The reflectivity of the first deposited layer is ca. 50%, remarkably high considering the large scattering cross section for surface defects. Currently there is are some apparent inconsistencies between results obtained from laboratories using STM[24] and those using atomic beam scattering.[1] The theoretical scattering calculations have therefore been welcomed by the experimentalists. Possibly, the discrepancy is a result of different growth conditions in the different experiments.

We will continue these calculations and extend them to Cu and Ag surfaces which have also been studied experimentally.

4. He atom scattering from Xe overlayers:

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), Ag(111) and graphite. A very encouraging result in the last year has been the finding that measured diffraction peak intensities for He scattering from Xe overlayers on graphite are reproduced to within 20% both at high (63 meV) and low (8.5 meV) beam energies when the new and revised He-Xe pair potential is used.[25] This makes it possible to establish bounds on the many-body corrections to the repulsice exchange interaction. Such many-body corrections are poorly understood, but are potentialli important in molecular modeling and have been invoked in various systems (including water) to explain discrepancies between experiments

and simulation results.[26]

In the coming months we will obtain ab initio estimates of three body corrections to the exchange and evaluate the effect on the scattering intensities, and continue with the analysis of He atom scattering from Xe overlayers on metal surfaces, where effects of electron redistribution are seen to affect the He-surface interaction potential.

5. Thermalized dissociation of H_2 on Cu(110):

We have extended the 'qunatum transition state theory' method of Gillan[27] to multi-dimensional quantum systems and applied the technique to simulations of the interaction of H_2 with Cu(110) surface. These are quantum statistical mechanics simulations which allow full quantum treatment of all six degrees of freedom of the H_2 molecule and full thermal averaging over the surface degrees of freedom. However, no dynamical information, such as state-to-state cross sections are obtained.

We have used the technique to evaluate the activation free energy of the dissociative process. We found only 10% lowering of the activation energy in going from classical to quantum treatment. The potential energy surface we used has too high a barrier, because the calculated activation energy is higher than the value measured in the laboratory of Prof. Charles T. Champbell here in this Department.[28,29] We have recently finished modifying the potential surface and are repeating the evaluation of the free energy barrier. We hope to finish those calculations and publish the results in the next month. The main problem now in calculating activation free energy of such processes is the uncertainty in the potential energy surface. Below is a discussion of a direction we will be explorint to obtain the potential energy surface from *ab initio* calculations.

A graduate student, Greg Mills, is working on these calculations. He will be spending two months this summer at PNL in Richland in a collaborative effort with the group of Dr. Bruce Garret at the MSRC. The goal is to start building in dynamical corrections into the transition state theory results.

5. Spin flip scattering of atoms from surfaces:

We have started exploring a very new and wide open area of research, the use of spin polarized atomic beams to probe the electro-magnetic fields at surfaces. A few experimental measurements have been carried out,[30] but limited understanding of the processes involved has been an impedance for progress.

We have started developing theory for spin flip scattering from spin labels on surfaces (such as an adsorbed O_2 molecule). We have extended the 'Hard Wall Substrate' theory of Jónsson, Weare and Levi[32] for atom-adsorbate scattering to the spin flip processes. As a test problem we are working on the scattering of spin polarized H atoms from O_2. It is important here to have an accurate estimate of the potential energy surfaces for the various spin configurations. We have finished the evaluation of the doublet surface and are close to done with the quartet surface, using MP-4 calculations in Gaussian-92. We will then be able to compare our calculations with the measured[32] gas phase spin flip cross sections for $H - O_2$ and predict the scattering from an O_2 physisorbed on a surface. A graduate student, Mary Hatcher, has been working on these calculations.

Other intriguing possibilities we are looking at are scattering resonances coupled with spin flip processes, which could give very accurate estimates of magnetic fields local to the surface.

5. Car-Parrinello simulations of surface processes:

We have, in the last year, developed a code for combined molecular dynamics and density functional theory calculations of electronic wavefunctions (within the local density approximation) as proposed by Car and Parrinello.[33] This simulation technique is both used for very large scale calculations of total energy of atomic systems and for carrying out dynamics simulations without having to resort to the use of empirical or semi-empirical potential energy surfaces. Our code is desigend to run on various parallel computers with minimal effort in porting from one computer to another.[34] A graduate student, Jim Wiggs, (a DOE Computational Science Fellow) has written the code partly while doing a practicum at PNL in Richland. The code currently runs on the Delta computer at Caltech (the computer time has been made available by PNL). Unlike other parallel implementations we are aware of, our code distributes the computations on different orbitals onto different nodes or sets of nodes.[34] This opens the possibility of carrying out calculations on much larger systems than can be run, for example, on a CRAY-YMP computer.

Recently, a parallel CP code has been used to map out the potential energy surface for the dissociation of H_2 on a Cu(111).[35]

We will be applying our CP code in the next year on various surface problems. One project is the evaluation of the H_2 on a Cu(110) surface, which relates directly to the FPI quantum simulation project described above. An even more intriguing prospect is the calculation of molecular dynamics (classical) at the surface, such as dissociation of Cl_2 molecules at Si surface with concerted formation and breaking of covalent bonds. With the CP method implemented on state of the art parallel computers, we are now able to attack a wide variety of interesting surface problems. A post doctoral fellow, Arthur Smith (currently at Argonne), will be joining the Jónsson group in August to work on these simulations.

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