

ASSIGNMENT 9: ADSORBATES

E. ARNOLD, M-S. LIU, R. PRABHU & C.S. RICHARDS
THE UNIVERSITY OF CAMBRIDGE

Written in X_YLaTeX

ADSORBATES

PREREQUISITES

The chapter *Adsorbates* from the *Theory Handbook*.

INTRODUCTION

The study of particle adsorption to surfaces is of great importance to atom scattering experiments. As discussed in the theory handbook, the presence of defects on a surface, in the form of adsorbates, has the effect of distorting the surface potential; thus the scattering amplitude from the surface is altered by them. Both the scattered intensity distribution and the intermediate scattering factor (for scanning helium microscopy [SHeM] and helium spin echo spectroscopy [HeSE] respectively) are very sensitive to these perturbations in the surface potential. Adsorption of some kind is inevitable in these experiments, even in high vacuum.

As stated in the *Theory Handbook*, and demonstrated in the tutorial on the Eikonal approximation, information can be extracted about a clean surface for complete adlayers of adsorbates. In general, the surface is not clean: thus we must use a more in-depth study. Furthermore, adsorbates cannot be studied in isolation in practice, as modelled in the Monte Carlo and Molecular Dynamics tutorials.

In this tutorial, we employ a Monte Carlo simulation of Ag adsorbates on a Pt(111) surface, using a very simple ‘nearest-neighbours’ interaction between adsorbates. We calculate the intensity distribution from such a surface and observe how this changes with both momentum transfer and adsorbate coverage.

Many of the simulation techniques used in this tutorial are taken from [1], which also provides some interesting applications of this code if you are interested.

THEORETICAL BACKGROUND

In this tutorial, we will mainly consider two coverage limits. As a prerequisite, we denote the coverage of the adsorbate as Θ . The first of

the coverage limits is the low-coverage limit, where the coverage Θ is much smaller than 1; thus adsorbates are isolated and randomly distributed on the surface. The second limit is the high-coverage limit, where the coverage Θ is much larger than 1. For this regime, successive adlayers are formed on the surface.

Analytic Models for Low Coverage

The theory of adsorbates has been discussed in the *Theory Handbook*. To revise it here, in the low coverage limit, the scattering cross-section of an adsorbate on a flat surface can be expressed as:

$$\Sigma = -\frac{1}{n_s I_0} \left. \frac{dI}{d\Theta} \right|_{\Theta=0},$$

leading to the scattered intensity being expressed as:

$$\frac{I}{I_0} \approx \exp(-n_s \Sigma \Theta),$$

where:

1. n_s is the number of substrate atoms/lattice sites per unit area,
2. Θ is the coverage of adsorbates, which is the number of adsorbates per substrate;
3. I is the specular ($\Delta\mathbf{K} = 0$) intensity with coverage Θ ,
4. I_0 is the specular intensity with zero coverage.

This equation assumes adsorbates are non-interacting, randomly distributed on the surface, and have small cross-sections that do not overlap.

For small cross-sectional overlap, we may apply the ‘overlap approach’; this assumes that the overlap is purely geometrical, giving the equation for the intensity as

$$\frac{I}{I_0} = (1 - \Theta)^{n_s \Sigma}.$$

At higher coverages of the adsorbate, there is no existing analytic model; at sufficiently high coverages, adsorbates generally form ‘adlayers’ of atoms: this generates a quasihard-wall potential, similar to the substrate hard-wall potential. Thus, the specular intensity begins to increase again. This leads to a cycling of specular intensity - the adsorbates form successive adlayers.

Monte Carlo Simulation

In this exercise, we wish to model the scattering of helium from silver adatoms on a Pt(111) surface using a Monte Carlo simulation. Why this surface? The choice of the Pt(111) surface stems from the fact that

the He/Pt(111) surface is rather smooth (modelled as flat, to the first order of the potential); thus the majority of scattering on the surface is due to the Ag adsorbates. Additionally, in the literature there is a reliable potential for the He/Pt(111) surface. This will be useful to us.

How do we model the adsorbates? We could distribute them randomly on the surface. While this is trivial, we need to simulate interactions between adsorbates. In our model we assume that only nearest-neighbour interactions are non-negligible, and that the interaction between two adsorbates depends only on the *number* of their nearest neighbours n . Thus, the energy of a particle in a given configuration is:

$$E(n) = E_0 + n\epsilon,$$

where $E_0 = 5.2$ kcal is the activation energy for diffusion at zero coverage, and $\epsilon = 5.0$ kcal is the nearest-neighbour interaction energy. These values are qualitatively valid as determined by experiment.

The transition probability, per unit time, for a particle to move from site i to a site f is written as:

$$\omega_{i \rightarrow f} = \nu \exp(-E(n_i)/(kT)),$$

where ν is a constant. Note we have assumed that the transition rate depends only on the initial state. This is reasonable because the adsorbate must overcome a potential barrier in hopping between different sites.

Model of Surface Potential

In modelling the potential energy of an impinging helium atom onto a surface at position a $\mathbf{r} = (\mathbf{R}, z)$, we assume the following form for the surface potential:

$$V_{\text{He} \rightarrow \text{Ag/Pt(111)}}(\mathbf{r}) = V_{\text{He} \rightarrow \text{Pt(111)}}(z) + \sum_i V_{\text{He} \rightarrow \text{Ag}_i}(\mathbf{r}, \mathbf{r}_i),$$

where the sum is over all adsorbates (at positions \mathbf{r}_i). We have assumed pairwise interactions for the He with the Ag atoms. We have assumed these are linear.

For the surface, we use a He-Pt Morse potential:

$$V_{\text{He} \rightarrow \text{Pt(111)}}(z) = D_e \left[e^{-2\alpha(z-z_m)} - 2e^{-\alpha(z-z_m)} \right],$$

where $D_e = 2.89 \times 10^{-4}$ a.u., $\alpha = 0.52$ a.u. and $z_m = 11.46$ a.u..

For the adsorbates we use a He-Ag Lennard-Jones potential:

$$V_{\text{He} \rightarrow \text{Ag}}(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6},$$

where r is the distance between the He and Ag atoms. Additionally we use $C_{12} = 6.33 \times 10^6$ a.u. and $C_6 = 29.0$ a.u..

All the above parameters are fitted from experimental results in the literature, where a.u. just means ‘arbitrary units’ in this context. Don’t worry too much about the actual values and units of these constants, they have been chosen to provide a good fit with experiment in our simulation. Feel free to tweak these and observe how they affect your results.

Calculation of the Scattering Intensity

In calculating the intensity, we utilise the so-called *sudden approximation*; this requires that the momentum transfer parallel to the surface is small compared to the momentum transfer normal to the surface. Under this assumption, the intensity distribution from a disordered configuration of N adsorbates with positions \mathbf{r}_i , denoted by $\beta = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$, can be written analytically. This takes the form:

$$I(\Delta\mathbf{K}) = \frac{1}{S^2} \left\langle \left| \int_S \exp(i\Delta\mathbf{K} \cdot \mathbf{R} + 2i\eta_\beta(\mathbf{R})) d^2\mathbf{R} \right|^2 \right\rangle,$$

where:

1. S is the area of the surface over which integration is performed (ideally all of space),
2. $\langle \dots \rangle$ denotes the average over all possible configurations,
3. $\eta_\beta(\mathbf{R})$ denotes the phase shift for He scattering from a configuration β .

In the so-called *WKB approximation*, a common approximation in quantum physics, the phase shift is given by:

$$\eta_\beta(\mathbf{R}) = \int_{\zeta_\beta(\mathbf{R})}^{\infty} \left(\sqrt{k_{iz}^2 - 2mV_\beta(\mathbf{R}, z)/\hbar^2} - k_{iz} \right) dz - k_{iz}\zeta_\beta(\mathbf{R}),$$

where $z = \zeta_\beta(\mathbf{R})$ is the *corrugation function* as seen previously. This is the locus of classical turning points for incident He atoms, given by:

$$(\hbar k_{iz})^2 - 2mV_\beta(\mathbf{R}, \zeta_\beta(\mathbf{R})) = 0.$$

Assuming that only the $z = \zeta_\beta(\mathbf{R})$ contribution to the integral is non-negligible, this expression reduces to

$$\eta_\beta(\mathbf{R}) = -2k_{iz}\zeta_\beta(\mathbf{R}).$$

This is equivalent to applying both the Eikonal and Sudden approximations.

TASK

1. Our first task is to implement a class representing the state of adsorbates on a surface. We can represent the surface as a close-packed

plane of $n \times n$ unit cells (with lattice parameter $a = 3.912 \text{ \AA}$) and periodic boundary conditions (PBCs).

- (a) Create a `Grid` class containing a `meshgrid` of lattice sites on the surface. It should additionally store adsorbate positions on the lattice, along with a function which converts input coordinates to their PBC equivalents. This class should be able to process adsorbates occupying multiple layers above one another (up to a non-periodic upper limit or otherwise).
 - (b) Now we have a way to store adsorbate positions, we need methods to add adsorbates to the surface. Write a function `addParticle(x,y)` which places a particle at a horizontal position on the lattice (at the lowest available z -coordinate). Additionally implement a function denoted `addRandParticle()`, which places a particle randomly on the surface. Take care not to forget the PBCs!
 - (c) We now wish to have some way to allow our adsorbates to settle into an equilibrium arrangement. Implement a `timestep()` function that uses the model discussed in the theoretical background to propagate the system by one timestep. Additionally, make sure that any adsorbates that end up above a vacant site will 'fall' down into it to reduce their potential energy.
 - (d) Experiment with the model. Draw some figures using the function `addParticle()` and observe how they evolve. You may notice that large islands of adsorbates are more stable than individual adsorbates. Where does this effect come from in our model?
2. Now we have a model for adsorbates on a surface, we wish to model scattering from the surface with adsorbates present. To do so, we must define an equation for the potential energy of an impinging helium atom using the model discussed in the theoretical background.

To calculate scattering from a surface:

- Simulate Ag atoms randomly adsorbing to the surface (we suggest starting with the length `len` as 5 and the height `hgt` as 1 for the `Grid`).
- Sum the potential functions across the surface and all the adsorbates thereon to obtain the total surface potential.
- By solving the equation:

$$V(\mathbf{R}, z) = (\hbar k_{iz})^2 / 2m,$$

obtain the classical turning point for each lateral displacement \mathbf{R} on the surface. This will return a set of values $z = \zeta(\mathbf{R})$ - which is the corrugation function.

- Calculate the intensity for a range of momentum transfers $\Delta \mathbf{K}$

using the Eikonal/Sudden approximations.

Try varying the coverage of the surface and observing how this affects the intensity distribution.

3. (a) The final task in this tutorial is to plot an uptake curve of reflectivity against coverage for the surface. To achieve this, we consider only the specular beam, however we must calculate its intensity at a range of coverages (*i.e.* as we add adsorbates to the surface). Alter your code to allow for such a computation by wrapping your existing code in a loop.
- (b) Considering only small coverages, plot an uptake curve and try fitting the two analytic equations for the reflectivity given in the theoretical background to your data. You will get a higher-resolution curve if the number of unit cells is larger (*i.e.* each adsorbate contributes less to the coverage) and the curve will deviate less if you repeat your calculation over multiple cycles of adsorption and take an average over the cycles (*i.e.* average over more adsorbate configurations as in the theoretical background).
For what coverage range is your fit reasonable? How might this be influenced by the assumptions in our model?
- (c) Estimate the Ag cross-section from both of these models. Compare this value with the geometric cross-section.
As a crude approximation, the geometric cross-section can be calculated from the equation for the area of a circle, using the classical turning point in the Lennard-Jones He→Ag potential as the effective radius of the Ag atoms, since it can be assumed that the He is pointlike in comparison to the Ag atoms (due to their large difference in atomic mass).
- (d) Repeat the above but allow for the formation of multiple layers. In particular, try plotting uptake curves for with coverages ranging from 0 to integers larger than 1. Is the resulting curve as you would expect?

Tips

There are two main options here. The first is to represent the positions of each adsorbate in an array of 0s and 1s. Alternatively, one can implement an Adsorbate class containing properties *x*, *y* and *z* for each adsorbate's position. Then the Grid class can simply contain a collection of adsorbates. Whilst the latter of these options will be faster to iterate over, ask yourself which will be simpler to code - don't object-orient your code until it is undecipherable!

You may find it useful to implement a separate `neighbour()` function that returns the state of neighbouring sites. You will also need to

define new properties. Some of these (e.g. the Boltzmann constant k_B) will be constants for all simulations, and should be given in a 'properties(Constant)...end' wrapper. Be careful with units!

You may also find it beneficial to repeat your calculation over multiple cycles of adsorption and take an average over the cycles, since this will cause your data to converge to the analytical solution. The analytical solution in fact requires an average across all possible configurations, however a close approximation is provided for only a few configurations (5 is a good starting point).

You should use similar scattering parameters to those given in previous tutorials, but it is really up to you - what do you wish to model? Many of the parameters in the worked solutions are merely chosen to improve readability of figures more than to model a system of interest (though they are usually of the correct order of magnitude).

EXTENSION

1. Change your code to use the more general form of the WKB approximation, as opposed to the Eikonal/sudden approximation. When does the former approximation give more accurate answers?
2. (a) Modify your simulation such that adsorbates cannot approach within one space of each other. This will require a redefinition of nearest neighbours in your code, as well as when adding particles to the surface. An uptake curve plotted under such a simulation should follow the relation:

$$\frac{I}{I_0} = (1 - m\Theta)^{n_s \Sigma},$$

as described in the Theory Handbook. Recall that $1/m$ is the maximum allowed coverage of the surface under this model.

- (b) You may wish to make the closest distance a variable of your simulation so that you can experiment with different values m .

REFERENCES

1. J. Chem. Phys. 106, 4228 (1997); <https://doi.org/10.1063/1.473513>