ASSIGNMENT 6: THE CHUDLEY-ELLIOTT MODEL

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Written in XeLaTeX

THE CHUDLEY-ELLIOTT MODEL

PREREQUISITES

The previous assignments, and the chapter on *Scattering Functions* from the *Theory Handbook*.

INTRODUCTION

It should not surprise the reader that atoms or molecules may be present on the surface of a solid. To be studied using the helium spin-echo technique, we must obtain the intermediate scattering function (ISF) for their trajectories. This model yields the ISF using the Chudley-Elliot model for surface diffusion - where the diffusion occurs in "jumps" between nearby sites.

THE CHUDLEY-ELLIOT MODEL

The Chudley-Elliott model is an analytical model used to describe the "jump diffusion" of a particle between equivalent adsorption sites in a lattice. What does this statement mean? A set of adsorption sites is considered equivalent if:

- They are energetically identical.
- They form a Bravais lattice with a single site basis (such that each site is a lattice point).

Defining "jump diffusion" is easier. This is the diffusion (*i.e.* "spreading out") of adsorbates on a surface, arising from the instataneous hopping of the adsorbates between nearby sites. The Chudley-Elliott model allows us to generate an analytical expression for the intermediate scattering function (ISF) for a given adsorbate-substrate system. We can compare this function to the ISF data obtained in helium spin-echo spectroscopy measurements, allowing the model to be put under scrutiny in experiment.

Quantitative Description

The Chudley-Elliot model has a simple quantification. We will explore this by first considering the positions that the particles can jump to. Suppose that a particle, initially at the origin, can jump to a finite number of equivalent sites. Let there be n of these equivalent sites. Each site has a position vector $\mathbf{l}_k$, where the subscript index k is an integer between 1 and n (inclusive). What use is the content so far? It can be used to calculate the ISF, allowing us to form an expression relevent to spin-echo spectroscopy. The intermediate scattering function $I(\Delta\mathbf{K}, t)$ is then given by the equation:

$$\frac{\partial}{\partial t} I(\Delta\mathbf{K}, t) = \frac{1}{n\tau} \sum_k I(\Delta\mathbf{K}, t)(e^{-i\Delta\mathbf{K}\cdot\mathbf{l}_k} - 1),$$

where τ is the "site residence time" (a parameter that is inputted into the model), and $\Delta\mathbf{K}$ is the momentum transfer parallel to the plane. The solution to this equation, yielding the ISF, is:

$$I(\Delta\mathbf{K}, t) = I(\Delta\mathbf{K}, 0)e^{-\alpha(\Delta\mathbf{K})t},$$

where the dephasing constant $\alpha(\Delta\mathbf{K})$ is given by:

$$\alpha(\Delta\mathbf{K}) = \sum_k 2\Gamma_k \sin^2(\frac{\Delta\mathbf{K}\cdot\mathbf{l}_k}{2}),$$

where Γ_k is the jump rate to the kth adsorption site.

The dephasing constant α is of interest. It is clear that if we obtain spin-echo data, an exponential function can be fitted with the results. The exponential decay constant can be obtained from this fitting! When calculating the decay constant using the analytic formula, we can split the adsorption sites into shells: each shell consists of a set of sites, all of which are the same distance from the origin. We then assume that the jump rate Γ_k to the kth site, from the origin, is equal for sites in the same shell; we also assume that there is a quantitative relationship between the jump rates for neighbouring shells.

How do we find this relationship between jump rates? We define the probability that the adsorbate jumps from the origin to the ith shell as p_i. We assume that the probabilities of an atom jumping to the 1st, 2nd and 3rd shells from the origin take the form:

$$p_1 = \frac{1}{n};$$
$$p_2 = \frac{s}{n};$$
$$p_3 = \frac{s^2}{n},$$

where the subscript i on p_i represents the ith shell. In these expressions, s is known as the survival probability; this takes a value between 0 and 1. What does this system of equations mean? The most straightforward interpretation of these probabilities is that the probability of jumping to further shells scales as a geometric series. Noting that the common ratio for this series is smaller than 1, it becomes evident that this series represents the exponentially decaying likelihood of jumping as the shell number increases (see appendices).

Can these probabilities be put to use? In addition to assuming the forms of the first three probabilities of jumping, we assume that the probability of the adsorbate jumping any further than the third shell is zero. Consequently, since the total probability of a jump occuring is 1, we see that the sum of the first three probabilities is unity:

$$p_1 + p_2 + p_3 = 1,$$

and so the survival probability for this system satisfies

$$n = 1 + s + s^2.$$

The interpretation of this result is that we can calculate the exact values of each of the probabilities p_1, p_2 and p_3.

We may wish to calculate the jump rate Γ_{ki} for the kth site within the ith shell. It is conceptually straightforward to calculate this quantity. We hope the reader can be pursuaded that the probability of jumping to a particular site is the product of the probability of jumping to the shell the site is in, and the proobability of landing in that site in the shell (rather than any of the others in the shell). This leads to the jump rate Γ_{ki} being given by:

$$\Gamma_{ki} = \Gamma_{tot} p_i \frac{1}{N_i}$$

where the total jump rate Γ_{tot} is:

$$\Gamma_{tot} = \frac{1}{\tau},$$

and N_i is the number of sites in the ith shell.

TASK

Finding the decay constant

1. Using the Chudley-Elliott model, evaluate the dephasing constant $\alpha(\Delta\mathbf{K})$ for a Ru(0001) hexagonal surface. Assume that only the top sites are used as adsorption sites.
   You should consider the momentum transfers $\Delta\mathbf{K}$ that are in the direction of the high-symmetry azimuths, $\langle 11\bar{2}0\rangle$ and $\langle 1\bar{1}00\rangle$, and whose magnitudes are between 0Å^{-1} and 4Å^{-1}.

2. Produce suitable plots of your results.

Tips

You may wish to use some of the functions provided in the solutions to previous tutorials to speed up the coding process. After considering how to approach the task, it is worth looking at the suggested approach below. Consider how your approach compares to the one suggested before starting to code.

We make one more note: a diagram of the shells in a Ru(0001) surface is included in the margin. It is not necessary to reproduce the plot, but it is worth noting the number, and positions, of the sites in each shell. This will allow you to verify your code.

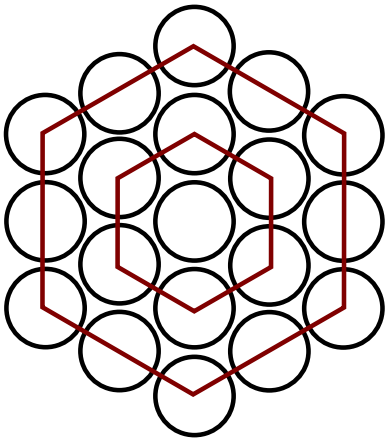

Figure 1 | The first two shells in the close-packed Ru(0001) surface. These are made up of adsorption wells located at the top sites of the surface planes.

Suggested Approach

The approach used in our solution is based around two functions: the so-called `lattice_shell` function, and the `ChudleyElliott` function. Upon writing these functions, your script must call the functions - in the appropriate manner, using the required arguments.

The `lattice_shell` function receives a matrix containing the coordinates of n lattice points (which must include all of the lattice points in the first 3 shells) and returns a $3 \times n$ matrix. The rows of this matrix give, for each lattice point:

1. the x-coordinate,
2. the y-coordinate,
3. the shell number.

Note that these are assigned in this specific order.

Should you opt to use this approach, when writing your function, it is important to note that the function needs to account for how the lattice points in your input matrix may not be ordered by shell number. As described in the theoretical background, we assume that the probability of a jump any further than the third shell is zero. This means that we are only interested in lattice points within the first three shells! It would therefore make sense to order the lattice points by shell number. This will allow it to be easy to see which lattice points are relevant to the model!

The input of the `ChudleyElliott` function is the matrix returned by the `lattice_shell` function, along with a matrix specifying which momentum transfers are to be processed, and a vector of jump rates to each of the first three shells. The Chudley-Elliott function returns the exponential decay constant $\alpha(\Delta\mathbf{K})$. The outputted matrix in our case should be an $m \times 2$ matrix. Each of the two columns in this matrix contains values for the decay constant $\alpha(\Delta\mathbf{K})$, sampled along the two different high-symmetry azimuths at an integer number m values

between 0Å^{-1} and 4Å^{-1}.

SUMMARY

This tutorial introduces the Chudley-Elliott model, describing diffusion as jumps between sites on a surface. This provides an analytic expression for the intermediate scattering function, which holds well when compared with experiment.

FURTHER READING: NON-BRAVAIS LATTICES

As discussed in the *Chudley-Elliott* section, the Chudley-Elliott model works well for jump diffusion between equivalent adsorption sites. This makes the model rather restrictive; in most real adsorbate-substrate systems, the adsorbate can attach to more than one type of site. For example, there are many systems where the adsorbate could attach to the two types of hollow site on a close-packed plane.

Modelling such a system requires the consideration of jump diffusion within a non-Bravais lattice. In this case, the Chudley-Elliott model fails. However, there is a way of extending the model to apply to non-Bravais lattices; this approach is discussed in Tuddenham et al (2010).