

ASSIGNMENT 5: MONTE CARLO

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Written in X_YL^AT_EX

Monte Carlo

INTRODUCTION

In this tutorial, we will write a simple Monte Carlo simulation for single-jump diffusion of an adsorbate on a square lattice. This is the precursor to more advanced methods of modelling surface diffusion, such as molecular dynamics, while offering a testable model for the behaviour of a particle on a surface.

THEORETICAL BACKGROUND

Consider a particle diffusing between sites on a surface. In the context of single-jump diffusion on a square lattice, it is assumed that only jumps to adjacent sites are possible. We assume that jumping to each of the four neighbouring sites is equally likely, and governed by a constant-probability Arrhenius equation. This is the essence of the entire problem - in each step, the particle randomly jumps to an adjacent site. This type of model is known as a “Monte Carlo” model of surface diffusion.

In principle, it may be possible for a given adsorbate to jump over more than one lattice site in the time taken for a helium spin-echo measurement to be made, so it is of interest to also model such systems. Intuitively, the probability of jumping several lattice sites in a given timestep should be lower than jumping a single site. Implementing this possibility is explored in the extension questions.

TASK

1. Construct a Monte Carlo simulation of idealised hopping. Generate the trajectory of a diffusing adsorbate as a function of time. The surface is modelled as a discrete square lattice, with a lattice parameter of 2.5 \AA .
2. For an isolated particle, plot the position of the particle along each axis as a function of time. Plot the two-dimensional trajectory of the particle.

3. Repeat task 1 for a triangular lattice (*i.e.* a lattice of tessellated equilateral triangles).
4. Repeat task 2 for a hexagonal lattice. Why is this more difficult?

Tips

1. It is convenient to generate three vectors, x , y and t , describing the positions of the particle, and their corresponding time variable. We assume the particle starts at the origin. For each timestep, we must decide whether or not the particle jumps, using the probability p of hopping (*e.g.* $p \approx 0.01$). This can be done by sampling a value h from the Bernoulli Distribution $\text{Ber}(p)$. If the value of this sample h is 1, the particle hops. If the sample h is 0, then it does not. We also need to know which direction it will jump in. This can be done by taking a random integer from 1 to 4.

EXTENSION

1. Write a subclass that allows for double jumps on the square lattice. Intuitively the probability of performing multiple jumps is smaller than single jumps, but experiment with varying the probability distribution.
2. Construct a class that allows for jumps of infinite length with a Gaussian distribution and standard deviation of 1 jump.

ISF FROM MONTE CARLO

INTRODUCTION

In this tutorial, we will use the Monte Carlo trajectories, determined in the chapter above, to calculate the intermediate scattering function (ISF) for quasi-elastic helium atom scattering (QHAS). We will analyse the behaviour of the ISF for different parallel momentum transfers.

THEORETICAL BACKGROUND

ISF as Autocorrelation

The knowledge of the trajectories of adsorbed atoms on a surface can allow us to model the scattering of incident helium atoms from the sample. Fortunately, this is the information we obtained in the first task! In this section, we will discuss the theory related to the intermediate scattering function for our system, allowing us to make sense of this data. Given we are considering quasi-elastic scattering, momentum can be transferred from the beam to phonons in the lattice; consequently the parallel momentum transfer $\Delta\mathbf{K}$ can take many values. In typical experiments, the parallel momentum transfer ΔK ranges from 0 \AA^{-1} to 4 \AA^{-1} , and it can point along any direction in the surface.

How do we find the amplitude of the scattered beams? Using a simple kinematic scattering model, the scattered amplitude A is given by:

$$A = FS,$$

where F is a “form factor” for scattering; it determines the distribution of scattered intensity from a given scattering centre. S is the structure factor for the surface. In general, we do not know the form of the atomic factor F - we can assume it is 1. It is straightforward to discuss the surface, but what about the inside of the solid? We assume the solid’s internal structure has little effect on scattering. Thus it is not taken into consideration for our calculations.

What is the structure factor S ? It is a quantity that encodes the phase change due to the relative positions of particles. For slow-

moving adsorbates, it is given by:

$$S = e^{-i\Delta\mathbf{K}\cdot\mathbf{R}_a(t)},$$

where \mathbf{R}_a is the trajectory of a particle. Thus for any trajectory $\mathbf{R}_a(t)$, the expression for the complex scattered amplitude A reduces to

$$A(\Delta\mathbf{K}, t) = e^{-i\Delta\mathbf{K}\cdot\mathbf{R}_a(t)}.$$

What use is this formalism in experiment? The observable quantity in spin-echo experiments is the intermediate scattering function (ISF). The ISF can be described, among other things, as the autocorrelation of the time-dependent scattering amplitude $A(t)$. What does this mean? Given that the autocorrelation of a function is the convolution of the function with its complex-conjugate, with time as a variable, the convolution theorem suggests that we can write the ISF $I(\Delta\mathbf{K}, t)$ as:

$$\begin{aligned} I(\Delta\mathbf{K}, t) &= A(\Delta\mathbf{K}, t) * A(\Delta\mathbf{K}, t)^*; \\ &= \mathcal{F}^{-1} [\mathcal{F}[A(t)] \cdot \mathcal{F}[A(t)^*]]; \\ &= \mathcal{F}^{-1} [\mathcal{F}[A(t)] \cdot \mathcal{F}[A(-t)]^*]. \end{aligned}$$

Can we simplify this further? The complex scattered amplitude $A(t)$ is symmetric about $t = 0$, as the motion of the particles is random. Thus, the expression for the ISF above reduces to

$$I(\Delta\mathbf{K}, t) = \mathcal{F}^{-1} [|\mathcal{F}[A(\Delta\mathbf{K}, t)]|^2].$$

This formulation can equivalently be obtained from the inverse temporal Fourier transform of the dynamic structure factor.

Statistical Approach

The ISF provides a complete statistical description of adsorbate motion on a surface. However, there is usually more information contained in this data than can be feasibly extracted. How do we get around this issue? In QHAS experiments, we fit the ISF with an exponentially decaying function; the exponential prefactor α in this function is called the “dephasing rate”. The behaviour of the prefactor α as the parallel momentum transfer ΔK varies is drastically different for distinct types of motion on the surface.

A useful description of the motion of a particle is the van Hove pair correlation function. We define (classically) the van Hove pair correlation function $G(\mathbf{R}, t)$ as the probability of finding a particle at the position \mathbf{R} at a time t , given there was a particle at the origin at $t = 0$. Since we are only considering a single isolated adsorbate, we can write the van Hove pair correlation function as the trajectory of the particle (as the probability of finding it at that point is 1), as

$$G(\mathbf{R}, t) = G_s(\mathbf{R}, t).$$

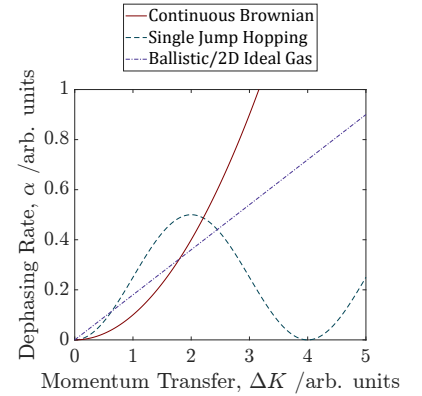


Figure 1 | Variation of the measured dephasing rate with parallel momentum transfer for simple diffusion models.

The position of the particle as a function of time depends on the diffusive regime it experiences while diffusing on the surface. Summarily, these can be generally classified as continuous Brownian motion, single jump hopping, and “ballistic” motion. These will be explored individually below.

- The simplest model for a diffusing particle is continuous, random, Brownian motion. For this regime, we expect the form of the van Hove pair correlation function G_s to be:

$$G_s(\mathbf{R}, t) = \frac{1}{4\pi D|t|} \exp\left(-\frac{R^2}{4D|t|}\right),$$

where D is a constant. By Fourier transforming, this yields the intermediate scattering function (ISF) as

$$I_s(\Delta\mathbf{K}, t) = \exp(-\Delta K^2 D|t|).$$

From this, the dephasing rate α evidently obeys the relation

$$\alpha(\Delta\mathbf{K}) \propto \Delta K^2$$

(i.e. it is proportional to the modulus squared of the parallel momentum transfer). This behaviour occurs in the limit of large length-scales and temperatures, or measurements of sufficiently small momentum transfers ΔK .

- At sufficiently low temperatures, adsorbate motion becomes dominated by the periodic arrangement of substrate atoms; we expect to see the adsorbates undergoing discrete jumps as a result. This follows the rate equation for instantaneous jumps:

$$\frac{\partial G_s(\mathbf{R}, t)}{\partial t} = \sum_{\mathbf{j}} v_{\mathbf{j}} [G_s(\mathbf{R} + \mathbf{j}, t) - G_s(\mathbf{R}, t)],$$

where \mathbf{j} are the allowed jump vectors on the lattice. This can be solved to give the dephasing rate as

$$\alpha(\Delta\mathbf{K}) = 2 \sum_{\mathbf{j}} v_{\mathbf{j}} \sin^2\left(\frac{\Delta\mathbf{K} \cdot \mathbf{j}}{2}\right).$$

Can we make any remarks on this equation? This sinusoidal behaviour gives zeroes at a discrete set of points; these points satisfy the condition that the parallel momentum transfer $\Delta\mathbf{K}$ is the same as any reciprocal lattice vector \mathbf{G} . It is reassuring to see that the dephasing rate is periodic with position, especially in a way that respects the periodicity of the lattice.

What happens if the adsorbate jumps further than one spacing in a time interval? We would need to include more components in the series for α . It is trivial that in the limit of small ΔK we recover the quadratic dependence.

- There is one more case to consider. When the substrate corrugation is small compared to the energy of the adsorbate, then “ballistic” motion is expected for the adsorbate. This is especially clear for small length scales and time scales. The van Hove pair correlation function is then predicted by statistical mechanics to be:

$$G_s(\mathbf{R}, t) = \frac{1}{\pi(v_0 t)^2} \exp\left(-\frac{R^2}{(v_0 t)^2}\right),$$

where the temperature is related to the root mean square velocity of the particles through the equipartition theorem as:

$$k_B T_s = \frac{1}{2} m v_0^2,$$

where v_0 is the root mean square velocity of the adsorbates. This assumes that there are no additional quadratic potential energies acting as degrees of freedom (such as chemical bonds). Following through with calculating the intermediate scattering function through the Fourier transform suggests that the dephasing rate α can be written as

$$\alpha(\Delta \mathbf{K}) = \sqrt{\ln 2} v_0 \Delta K.$$

In this case, the dephasing rate α is proportional to the magnitude of the parallel momentum transfer ΔK .

CURVE FITTING

The Matlab `fit()` function uses iterative optimisation to calculate the coefficients for a fitted function to a set of data. Providing `fit()` with a known set of data points, along with a function to fit it to, MATLAB can produce a fitted curve. It can also provide the calculated coefficients in the fitted curve.

```

1 % Setup the x axis and a function
2 x = linspace(-2,2)';
3 y = cos(x);
4
5
6 % Define the type of function to be fitted
7 g = fittype('1-a*x^2');
8
9
10 % This command fits the data to the curve
11 % Initial guess for parameter a is the final argument
12 fit_g = fit(x, y, g, 'startpoint', [0.4]);
13
14
15 % Returns vector of fit coefficient values
16 a_est = coeffvalues(fit_g);
17
18
19 % Plot and save
```

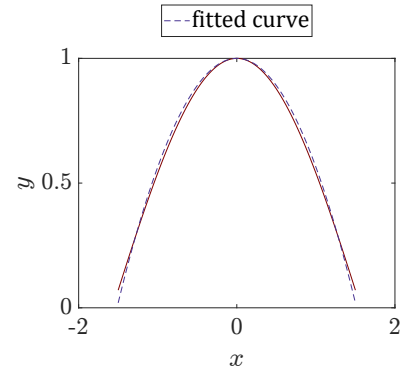


Figure 2 | A fitted curve matches closely to a set of data.


```

20 plot(x, y);
21 hold on;
22 plot(fit_g);

```

which produces the following fit, with $a_{\text{est.}} = 0.4704$:

TASK

- Using the trajectory $\mathbf{R}(t)$ of an isolated adsorbate on a square lattice, calculate and plot the scattered amplitude $A(\Delta\mathbf{K}, t)$ as a function of time for a particular value of the parallel momentum transfer ΔK (use 2 \AA^{-1} as the parallel momentum transfer).
- Using the analytic expression for the ISF in terms of the complex scattered amplitude $A(\Delta\mathbf{K}, t)$, calculate the ISF for the same value of ΔK as used above. Note that the timebase of the ISF is half that of the amplitude. Why is this?
 - Redefine your ISF to only include the first time-base, then plot your ISF against time for the new time-base. Your plot should look like an exponential decay, descending into noise with increasing time.
 - Use the matlab `fit()` function to fit

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

to the calculated ISF, and plot the fitted curve over the simulation curve to check that it fits theoretical prediction.

- Try varying the following parameters and observe how they affect the ISF:
 - Lattice parameter a
 - Parallel momentum transfer ΔK
 - Hopping probability p
 - Scattering direction $\arg(\Delta\mathbf{K})$
 - Timestep between points in the trajectory
 - Total length of the simulation
- By iterating over the code you have already written, either with a loop or using vector operations, calculate α for a series of values of ΔK , then plot α as a function of ΔK . You should find that your plot has a similar form to the single-jump diffusion model.
- Try plotting the same curve for triangular and hexagonal lattices. What do you notice about the new dephasing rate curves?
- You may notice that, despite following the theoretical curve on average, the dephasing curves become significantly more noisy for lower numbers of timesteps. Why is this?

EXTENSION

1. Try plotting the dephasing rate curve for the double-jump simulation. Add higher Fourier components to your fitted curve, as suggested in the theoretical background section. Experiment with varying the probability distribution.