ASSIGNMENT 14: SOLUTION

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Written in XeLaTeX

ROTATING MOLECULES

INTRODUCTION

This tutorial has two main aims:

- To introduce some analytical models for the intermediate scattering function (ISF) of an adsorbate undergoing rotational diffusion
- To bring together the discussions in Assignment 5 and Assignment 8, summarising how the ISF measured in spin-echo experiment provides signatures for different types of surface diffusion (in both the translational and rotational cases)

THEORETICAL BACKGROUND

The ISF of a rotating adsorbate

In the molecular dynamics simulation used by the Cambridge group (where the overall package is known as PIGLE), the rotational degrees of freedom of a diffusing molecule are modelled in a similar way to the translational degrees of freedom [1]. This means that in a rotating molecules simulation, the rotational ISF of an adsorbate is found by numerically integrating a generalised Langevin equation. This is done in exactly the same way as for finding the ISF of translational diffusion. For most systems, simulations such as PIGLE can be used to analyse and interpret experimental measurments of the ISF of a rotating adsorbate.

However, for the case of an adsorbate rotating within a uniform potential energy surface, there is also an analytical form of the ISF that can be used as a starting point for interpreting experimental data. This model, called the Langevin model, is given by:

$$I(\Delta K, t) = \sum_{n=-\infty}^{+\infty} J_n^2(\Delta K r) \exp -\frac{k_B T n^2}{I\gamma} t,$$

where ΔK is the parallel momentum transfer imparted by the particle, t is the spin-echo time, J_n is the nth Bessel function of the first kind, r is the radius of the adsorbate, T is the temperature of the substrate,

I is the moment of inertia of the adsorbate, and γ is the atomic scale friction coefficient [1].

The Ballistic-Brownian Transition

In the assignment on Monte Carlo simulations, we discussed how translational diffusion can be understood in terms of different diffusion regimes. The Monte Carlo simulation used predicts that the ISF should be a decaying exponential with respect to time (albeit with a $\alpha(\Delta\mathbf{K})$ signature that changes with the diffusive regime). However, in a molecular dynamics simulation, and in experimental measurements, we also expect the diffusive regime to change the shape of the ISF in the time domain. In particular, for low corrugation (which applies to the system used here), we can identify two possible diffusive regimes [2]:

- In the ballistic regime, we expect that the ISF takes a Gaussian form. We expect to see this regime when looking at small spin-echo times (corresponding to small timescale diffusion) and small momentum transfers (corresponding to small lengthscale diffusion), and in cases where the frictional coefficient is low.
- In the Brownian regime (also known as the continuous regime or the diffusive regime), we expect that the ISF takes an exponential form. We expect to see this regime emerging over longer timescales and lengthscales, and in cases where the frictional coefficient is high

(note that neither of these models work well when the PES is strongly corrugated - in this case, jump diffusion models, such as the Chudley-Elliott model, are the most accurate analytical models for predicting the ISF. The different diffusive regimes are summarised in [2]).

Given that the PIGLE simulation models rotational diffusion in the same way as it models translational diffusion, we would expect that it would find a similar ballistic-Brownian transition for rotational diffusion. In this tutorial, we will use the analytical form of the ISF of a rotating molecule provided in the section *§ Theoretical Background* (which is consistent with simulation results in the case of a flat PES [1]) to investigate the transition between ballistic and Brownian motion for rotational diffusion.

TASK

1. Use the Langevin model provided to evaluate the ISF for a system in the ballistic regime. Evaluate the extent to which it is in a ballistic regime.
2. Repeat task 1 for a system in the Brownian regime.

Tips

There are many methods you may use to analyse the Langevin model, and to determine whether it shows a ballistic-Brownian transition. As a starting point, you may wish to look up the `fit()` function.

REFERENCES

1. N.Avidor, P.S.M.Townsend, D.J.Ward, A.P.Jardine, J.Ellis, W.Allison, 2019. PIGLE - Particles Interacting in Generalized Langevin Equation simulator. Comp. Phys. Comm. 242, pp.145-152.
2. Jardine, A.P., Hedgeland, H., Alexandrowicz, G., Allison, W., and Ellis, J., 2009. Helium-3 Spin-Echo: Principles and Application to Dynamics at Surfaces. Prog. Surf. Sci., 84(11-12), pp.323-379.

SOLUTIONS

MAIN TASK

The first task is to write a function that evaluates the Langevin model for a given set of parameters. Given that the model includes a sum over Bessel functions, one way to implement this would be using a `for` loop. An alternative approach, presented here, is to use a `meshgrid` to evaluate the model at every value of the spin-echo time t and at every Bessel function index n that we are interested in, and then sum over the Bessel functions for each value of the time t. The ISF can be calculated with:

```
1  function isf=incoh_langevin_rot(r,I,kb,T,g,N,DK,t)
2
3  % function to return the incoherent isf for a molecule of moment
       of inertia I, radius r
4
5  %Inputs:
6  %r: radius of molecule
7  %I: moment of intertia of molecule
8  %kb: Boltzmann constant
9  %T: Temperature
10 %g: 'gamma' (frictional coefficient)
11 %N: number of bessel functions to include in sum
12 %DK: momentum transfer
13 %t: spin-echo time (may be a column vector for multiple se times
       )
14
15
16 %Making t into a row vector (where each element in t is a se
       time at which to evaluate the ISF)
17 t=(t(:))';
18
19 %Defining the limits of the sum (where each element in n is a
       Bessel function to sum over)
20 n=-N:N;
21
22 %Making n into a column vector
23 n=n(:);
24
25 %Creating a grid that spans n-t space (where each point in the
       grid represents a particular Bessel function AND a
       particular se time)
26 %n becomes a grid that gives the value of n at each point in n-t
       space
```

```
%t becomes a grid that gives the value of t at each point in n-t space
[n,t]=meshgrid(n,t);

%Reversing the dimensions of the grids
n=n'; t=t';

%Evaluating the Langevin model at every point in the grids
isf=besselj(n,DK*r).*besselj(n,DK*r).*exp(-kb*T*n.^2.*(exp(-g*t)+g*t-1)/(I*g^2));

%Summing over the values evaluated at each n value (for a given t value) to find the ISF at each t value
isf=sum(isf,1);
```

In order to complete tasks 1 and 2, we will first define the values of some parameters that we do not wish to change:

```
%Parameters that we won't be changing

%Radius of molecule (in Angstroms)
r=4;

%Moment of inertia, in the form n*m*r^2 where n = num atoms, m = atomic mass (in amu), r = molecular radius
I=104.15*4^2;

%Boltzmann constant in [Angstrom^]2 amu ^ps-2 ^K-1
kb=0.8314;

%Temperature in Kelvin
T=298.92;

%Number of Bessel functions to include in sum
N=3000;

%Range of spin-echo times
t=0:0.05:1000;
```

We then evaluate the Langevin model at parameters where we expect to see ballistic motion. In this case, we use a low frictional coefficient `g`, and a low momentum transfer `DK`.

```
%Looking for ballistic diffusion

%Parameters that should produce ballistic diffusion
g=1;
DK = 1;

%Evaluating the Langevin model at these parameters
isf=incoh_langevin_rot(r,I,kb,T,g,N,DK,t);

%Plotting the result
figure(1)
p1 = plot(t,isf);
```

To see whether the model output may be described as ballistic motion, we then attempt to fit this curve to a Gaussian model using the `fit()` function. Given that we only expect the motion to be ballistic over short timescales, we exclude spin-echo times that are greater than

10ps from the fitting function:

```
%Fitting the Langevin model to a Gaussian model, excluding se
    times greater than 10ps
f1 = fit (t', isf', 'a*exp(-((x-b)/c)^2)+d', 'Exclude', t>10);

%Plotting the fitted function
p2 = plot (f1);

%Adding axis labels and a legend
xlabel('Spin echo time/$ps$')
ylabel('ISF')
legend([p1 p2], 'Langevin model', 'Fitted Gaussian');
```

We then repeat this process, but this time we evaluate the Langevin model at parameters that we would expect to give us Brownian diffusion. This means choosing a high frictional coefficient and a high momentum transfer. To evaluate the extent to which the model predicts Brownian motion, we attempt to fit the model output to an exponential model, this time excluding spin-echo times that are less than 200ps from our fit:

```
%Looking for Brownian diffusion

%Parameters that should produce Brownian diffusion
g=30;
DK = 5;


%Evaluating the Langevin model at these parameters
isf=incoh_langevin_rot(r,I,kb,T,g,N,DK,t);

%Plotting the result
figure(2);
p3 = plot(t,isf, 'linestyle', '-', 'marker', 'none', 'color',
    color1);

%Fitting the Langevin model to an exponential model, excluding
    se times less than 200ps
f2 = fit(t', isf','exp1', 'Exclude', t<200);

%Plotting the fitted function
p4 = plot (f1);

%Adding axis labels and a legend
xlabel('Spin echo time/$ps$')
ylabel('ISF')
legend([p3 p4], 'Langevin model', 'Fitted exponential');
```

The results of these two plots are shown in Figures 1 and 2 respectively.

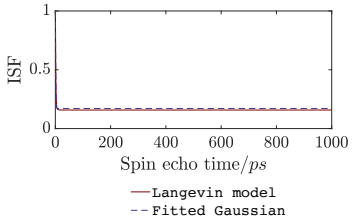

Figure 1 | The Langevin model evaluated at a low frictional coefficient and a low momentum transfer, with a Gaussian (*i. e.* ballistic) model fitted at small spin-echo times

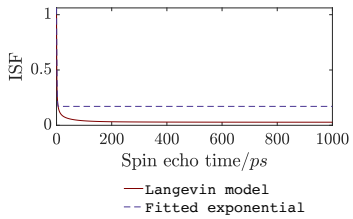

Figure 2 | The Langevin model evaluated at a high frictional coefficient and a high momentum transfer, with a exponential (*i. e.* Brownian) model fitted at large spin-echo times