ASSIGNMENT 14: ROTATING MOLECULES

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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.