ASSIGNMENT 8:
THE ISF

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THE ISF

PREREQUISITES

The chapters on *Fourier transforms* and *scattering functions* from the *Theory Handbook*.

INTRODUCTION

It is a recurring theme to require a model of the *intermediate scattering function* (ISF) to compare against data from helium spin-echo spectroscopy; with this being one of the most important techniques employed by the Cambridge group, it is imperative that the reader (if they study at the university) becomes acquainted with its calculation and interpretation. In a similar spirit to the tutorial on *Monte Carlo* techniques, we will calculate the ISF for the system in the *Molecular Dynamics* tutorial; this will naturally lead to fitting it to a Gaussian distribution, using analytic techniques created in 2004. This will reveal Brownian-like behaviour on increasingly small time scales.

THE SCATTERING AMPLITUDES

When a beam is incident on a surface, it will scatter. Let the amplitude of the scattered beam be A. We can express this scattered amplitude in terms of the parallel momentum transfer $\Delta\mathbf{K}$ of the beam, and the trajectory of a particle $\mathbf{r}(t)$, with the expression

$$A(\Delta\mathbf{K}, t) = \exp(-i\Delta\mathbf{K} \cdot \mathbf{r}(t)).$$

The so-called intermediate scattering function $I(\Delta\mathbf{K}, t)$ is the autocorrelation of the scattering amplitude $A(t)$. This can be written as:

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

where $\mathcal{F}$ is the temporal Fourier transform, and $\mathcal{F}^{-1}$ its inverse.

ANALYTIC FORM OF ISF

Equations

The most simple system we can model is a particle diffusing on a flat surface, undergoing Brownian-like motion. Unusually, there is an analytic solution for the ISF for this system [1]! This analytical solution can be written as:

$$I(\Delta\mathbf{K}, t) = e^{-\chi^2(\eta t - \phi(t))},$$

where $\phi(t)$ is a function of time, and χ is a function of $\Delta\mathbf{K}$. These two quantities are given by:

$$\begin{aligned} \phi(t) &= 1 - \exp(\eta t); \\ \chi(\Delta\mathbf{K}) &= \frac{\Delta\mathbf{K}}{\eta}\sqrt{\frac{k_B T_s}{m}}, \end{aligned}$$

where k_B is the Boltzmann constant, and T_s is the temperature of the substrate surface.

Small Time Scales

What can we do with the analytical expressions above? Given the entire purpose of the ^{3}HeSE experiment is to probe extremely small time scales, it is natural to attempt to calculate the Taylor expansion of the system for small times. This procedure, including simplification, can be written elegantly as:

$$\begin{aligned} I(\Delta\mathbf{K}, t) &= \exp(-\chi^2(\eta t - \phi(t))); \\ &= \exp(-\chi^2[\eta t - (1 - e^{-\eta t})]); \\ &= \exp(-\chi^2[\eta t - 1 + (1 - \eta t + \frac{1}{2}\eta^2 t^2 + \mathcal{O}(t^3))]); \\ &\approx \exp(-\frac{1}{2}\eta^2\chi^2 t^2), \end{aligned}$$

which takes the form we would expect - the ISF is a decaying Gaussian envelope. How does this relate to the position evolution of the particles? Given particles moving under Brownian motion are expected to be normally distributed, it is expected that their van Hove pair correlation function should also be normally distributed. Recalling that the ISF is the Fourier transform of the van Hove pair correlation function, and that the Fourier transform of a Gaussian is also Gaussian, it is reassuring that our analytical expression is normally distributed.

TASKS

Throughout this section, use your data from the *Molecular Dynamics* tutorial.

1. Plot the scattering amplitude $A(\Delta\mathbf{K} \cdot \mathbf{r}(t))$ as a function of time.
2. Calculate, and plot, the intermediate scattering function (ISF) as a function of time.
3. Fit the function I to the ISF, where:

$$I = A_0 \exp(-\alpha|t|),$$

   and A_0 and α are constants, determined by the fitting function. You may notice that this does not fit as well compared to the trajectory calculated in the Monte Carlo simulation. What could be the reason? Try to follow the same train of thought as the discussion on Brownian motion in the theory section of this tutorial.
4. Plot the ballistic part of the ISF. Attempt to fit it to a Gaussian function of the form:

$$I = A_0 \exp(-\frac{x^2}{2\sigma^2}),$$

   where A_0 and σ are constants, determined by the fitting function. Plot the constant σ against ΔK.
5. Attempt the same procedure for the intermediate scattering function after a long time period.

EXTENSION

1. We have provided both an *a priori* and *a posteriori* description of how the scattering particle undergoes ballistic motion. Try to simulate the trajectory again for different surface temperature T_s. How does the change in temperature (corresponding to the system energy - see the equipartition theorem) change the behaviour of the diffusing particles?
2. To eliminate random error, and to improve the quality of the data, repeat the experiment. How can we quantify the behaviour for a large number of particles?
3. Simulations usually involve an absorbate/substrate potential. How would you includea substrate potential ΔV in your simulation? In reality, the assumption used here of the surfaces being flat will not be valid. Thus understanding how to include the potential energy surface is vital.

SUMMARY

In this tutorial, we have seen how it is possible to describe the behaviour of diffusing particles with fitting functions.

REFERENCES

1. Vega et al. J. Phys.: Condens. Matter 16 (2004)