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## RESEARCH ARTICLE

# Rotational Diffusive Motion From a Monolayer of Squalane Adsorbed on Graphite Basal-plane Surface by Fast Fourier Transform Technique.

A. Diama<sup>1,\*</sup>, M. Grafoote<sup>1</sup>, Z. E. Georgina<sup>1,2</sup> and B. Mengjun<sup>3</sup>.

1. Department of Condensed Matter and Technology, University of Felix Houphouët Boigny, Abidjan, Côte d'Ivoire.
2. Department of Crystallography, University of Felix Houphouët Boigny, Abidjan, Cote d'Ivoire.
3. Department of Physics and Astronomy, University of Missouri, Columbia, USA.

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### \*Corresponding Author

Diama.

## Abstract

We present Fast Fourier Transform (FFT) technique from quasielastic neutron spectra measurements of a monolayer of the intermediate-length alkanes; the squalane ( $n\text{-C}_{30}\text{H}_{62}$  denoted C30), adsorbed on a graphite basal-plane surface. The FFT method has been used to make a more direct comparison with the Molecular dynamic simulation and get the microscopic motions from the squalane monolayer adsorbed on graphite substrate. Compare to the molecular dynamics simulation results, we have found that the rotational  $I_s(\vec{q}, t)$  is the main driver of the shape of the total motion of the experimental intermediate scattering.

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## Introduction:-

Decomposition of spectra profiles is a typical task in the spectra profile analysis. The main problem is to separate the instrumental broadening from the measured spectra pattern in order to obtain the pure physical profile containing information on microscopic dynamics or microstructures of the material. This means that the well-know equation for convolution.

$$h = f * g \quad (1)$$

Where  $h$  describes the measured profile, which is in our case the scattering function  $S(Q, \omega)$ ,  $g$  is the instrumental function (our resolution function) and  $f$  represents the shape of the physical profile.

The approach we use to treat the experimental scattering function affected by the instrumental broadening is the one employs the direct deconvolution using the Fast Fourier Transformation (FFT). FFT is simply an algorithm that can compute discrete Fourier transform much more rapidly than other available algorithms [1]. The Fast Fourier Transform of convolution of two functions can be expressed as multiplication of the Fast Fourier Transforms of these functions [2] as express in Equation 2:

$$FFT(h) = FFT(f) \cdot FFT(g) \quad (2)$$

Hence the FFT of the shape of the physical profile which is our intermediate scattering function is defined below:

$$FFT(f) = \frac{FFT(h)}{FFT(g)} \quad (3)$$

Thus, Equation 3 yields:

$$I(Q, t) = \frac{FFT(S(Q, \omega))}{FFT(F_{res}(Q, \omega))} \quad (4)$$

Where  $F_{res}(Q, \omega)$  represents our resolution function.

The computer code for deconvolution routine was written in the MATLAB environment. Fourier transforms were calculated using the internal MATLAB function for the Fast Fourier Transformation and the Inverse Fast Fourier Transformation (iFFT).

This application converts automatically the scattering function for a particular spectrum value  $Q$  to its intermediate scattering function but the conversion from energy to time must be computed by the user and implemented to the program. To achieve this goal the following steps have to be taken.

First we convert the energy from milli-electron volt to electron volt; then we compute the frequency as the following:

$$\hbar\omega = E; \quad \omega = \frac{2\pi}{t}; \quad \nu = \frac{E * 10^{-3}}{2\pi\hbar}; \quad \hbar = 6.56 * 10^{-16} \text{ eV}. \quad (5)$$

The frequency separation between successive abscissas is

$$\Delta\nu = \frac{\nu_N - \nu_1}{N - 1} \quad (6)$$

where  $N$  is the size of the data and  $N - 1$  represents the number of interval.

The time separation in pico second between successive data points is:

$$\Delta t = \frac{10^{12}}{N * \Delta\nu} \quad (7)$$

and the time increment is defined below:

$$t = 0 : dt = (N - 1)\Delta t \quad (8)$$

In order to overcome problems with the FFT result, the experimental data must be pre-processed. In the first step, it is convenient to choose the number of data points according to the relation  $N = 2^\gamma$ , where  $\gamma$  is an integer [1]. For the next step, the data must be interpolated in order to make  $\Delta\nu$  equal value through the  $N - 1$  intervals. The interpolation has been computed with the commercial software OriginPro8.0.

In neutron scattering experiments, it is well known that the scattering intensity is proportional to the coherent and incoherent scattering function. In our quasielastic scattering experiment on the Disc Chopper Spectrometer (DCS), we use a protonated sample ( $\text{C}_{30}\text{H}_{62}$ ) to investigate the diffusive motion. Since hydrogen has a large incoherent scattering cross-section ( $\sigma_{\text{coh}}[\text{barn}] = 1.757$  and  $\sigma_{\text{incoh}}[\text{barn}] = 80.263$ ) for neutron, the contribution of the incoherent scattering is dominant. This means that there is no correlation between a neutron scattered from one hydrogen atom and a second hydrogen atom in the same molecule.

In theoretical point of view, three functions  $G(\vec{r}, t)$ ,  $I(\vec{q}, t)$ , and  $S(\vec{q}, \omega)$  need to be explained in order to understand the physical meaning of the scattering and the intermediate scattering function. All these functions are connected to each other by Fourier transforms in space and in time.

$$\begin{array}{ccccc} G(\vec{r}, t) & \longleftrightarrow & I(\vec{q}, t) & \longleftrightarrow & S(\vec{q}, \omega) \\ \text{Fourier transform in space} & & \text{Fourier transform in time} & & \end{array}$$

$G(\vec{r}, t)$  is the time-dependent pair correlation function. It describes how the correlation between two particles develops gradually with time. It can be split respectively in the self-correlation function  $G_s(\vec{r}, t)$  and distinct correlation function  $G_d(\vec{r}, t)$  [3].

$$G(\vec{r}, t) = G_s(\vec{r}, t) + G_d(\vec{r}, t) \quad (9)$$

$G_d(\vec{r}, t)$  is the probability that after seeing a particle at the origin  $t = 0$ , we see a different particle at  $\vec{r}$  at time  $t$ .

$G_d(\vec{r}, t)$  will not be described, because it does not influence our scattering intensity.

Since our scattering intensity is completely incoherent, we will focus our explanation on the self part of  $G(\vec{r}, t)$ ,  $I_s(\vec{q}, t)$  and  $S_i(\vec{q}, \omega)$ .

$G_s(\vec{r}, t)$  represents the probability that a particle which was at position 0 at time 0 will be found at position  $\vec{r}$  at time  $t$ .

$$G_s(\vec{r}, t) = \frac{1}{N} \sum_{j=1}^N \langle \delta(\vec{r} - [\vec{r}_j(t) - \vec{r}_j(0)]) \rangle \quad (10)$$

$N$  is the number of nuclei in the scattering system.

$\vec{r}_j(t)$  is the position of atom  $j$  at time  $t$ .

$\vec{r}_j(0)$  is the position of the same atom  $j$  at time 0.

The self-intermediate scattering function  $I_s(\vec{q}, t)$  is related to the self-correlation function by the Fourier transform in space.

$$I_s(\vec{q}, t) = \int G_s(\vec{r}, t) \exp(i\vec{q} \cdot \vec{r}) d\vec{r} \quad (11)$$

Substitute Equation 10 in Equation 11, we have Equation 12.

$$I_s(\vec{q}, t) = \frac{1}{N} \int \exp(i\vec{q} \cdot \vec{r}) d\vec{r} \times \sum_{j=1}^N \langle \delta(\vec{r} - [\vec{r}_j(t) - \vec{r}_j(0)]) \rangle \quad (12)$$

$$I_s(\vec{q}, t) = \frac{1}{N} \sum_{j=1}^N \int \exp(i\vec{q} \cdot \vec{r}) d\vec{r} \times \langle \delta(\vec{r} - [\vec{r}_j(t) - \vec{r}_j(0)]) \rangle \quad (13)$$

$$I_s(\vec{q}, t) = \frac{1}{N} \sum_{j=1}^N \int \langle \exp(i\vec{q} \cdot \vec{r}) \delta(\vec{r} - [\vec{r}_j(t) - \vec{r}_j(0)]) \rangle d\vec{r} \quad (14)$$

$$\text{from the property of delta function} \quad \int_{\text{all space}} f(\vec{r}) \delta(\vec{r} - \vec{r}_0) d\vec{r} = f(\vec{r}_0) \quad (15)$$

where  $f(\vec{r}) = \exp(i\vec{q} \cdot \vec{r})$ ,  $\delta(\vec{r} - \vec{r}_0) = \delta(\vec{r} - [\vec{r}_j(t) - \vec{r}_j(0)])$  and  $\vec{r}_0 = \vec{r}_j(t) - \vec{r}_j(0)$

$$\text{if } \vec{r} = \vec{r}_j(t) - \vec{r}_j(0) \text{ then } I_s(\vec{q}, t) = \frac{1}{N} \sum_{j=1}^N \langle \exp[i\vec{q} \cdot (\vec{r}_j(t) - \vec{r}_j(0))] \rangle \quad (16)$$

Now we can easily defined the incoherent scattering function by Fourier transform in time the self- intermediate scattering function found in Equation 16.

$$S_i(\vec{q}, \omega) = \frac{1}{2\pi\hbar} \int I_s(\vec{q}, t) \exp(-i\omega t) dt \quad (17)$$

If the scattering function is known like in our case, we can also Fourier transform it in time to have the intermediate scattering function [4].

$$I_s(\vec{q}, t) = \hbar \int S_i(\vec{q}, \omega) \exp(i\omega t) d\omega \quad (18)$$

From Equations 17 and 18, we can describe how the Fast Fourier Transformation and the inverse Fast Fourier Transformation (iFFT) are connected to  $S_i(\vec{q}, \omega)$  and  $I_s(\vec{q}, t)$ .

$$\begin{array}{ccccc} S_i(\vec{q}, \omega) & \longleftrightarrow & I_s(\vec{q}, t) & \longleftrightarrow & S_i(\vec{q}, \omega) \\ \text{(Fast Fourier transform in time)} & & & & \text{(Inverse Fast Fourier transform in time)} \end{array}$$

The iFFT function will be implemented in two different files routines in order to compute  $I_s(\vec{q}, t)$  back to  $S_i(\vec{q}, \omega)$ .

Our quasielastic scattering experiment and molecular dynamic simulations conducted by Prof. Flemming Y. Hansen and his group have been used to probe the diffusive dynamic in a squalane monolayer absorbed on graphite surface.

We shall first describe briefly the sample we used for the experiment. Squalane ( $C_{30}H_{62}$ ) is a branched alkane of intermediate length consistent of a tetracosane backbone ( $n-C_{24}H_{50}$  or  $C_{24}$ ) and six symmetrically placed side groups. This material is frequently taken as a model lubricant.

To make a more direct comparison with the simulation and get the microscopic motions from the squalane monolayer absorbed on graphite substrate, the experimental data are then Fast Fourier Transformed from neutron scattering law  $S_i(\vec{q}, \omega)$  into intermediate scattering function  $I_s(\vec{q}, t)$ ; this approach has been also taken by different groups to obtain information on microscopic dynamics or microstructure of their material [5, 6, 7].

### Results and discussion:-

Squalane( $C_{30}H_{62}$ ) as it was described before is a branched alkane molecule of intermediate length consisting of a tetracosane backbone ( $n-C_{24}H_{50}$ ) and six symmetrically placed methyl side groups, and is frequently taken as a model lubricant. A cartoon of the molecule is shown in Figure.1.

The QNS experiments were performed on the Disc Chopper Spectrometer (DCS) at 215 K, 230 K, 260 K, 285 K, 300 K, 315 K, and 330 K. This direct geometry chopper spectrometer was operated with an incident neutron wavelength of 5.5 Å, which yielded an energy resolution function with a full width at half-maximum of 100 µeV. In order to calculate the intermediate scattering function  $I_s(\vec{q}, t)$ , the data must first be reduced from  $I(2\theta, t)$  to  $S_i(\vec{q}, \omega)$  using DAVE software (Data Analysis and Visualization Environment); this software was developed at the NIST Center for Neutron Research. A detailed explanation of the data reduction can be found in [8].

Before proceeding to the data analysis, we need to rebin the  $S_i(\vec{q}, \omega)$  data files. We process this for two reasons. First of all, we are interested in a very small range of energies either side to the elastic line and it is unnecessary to keep the full energy range which extends to > 300 meV. The second reason has to do with energy channels being unequally spaced. This can make Fourier transforms more difficult, and much slower, than if the energy channels have identical widths. Our data have been rebinned in two different energies range; first from -3 meV to 1.7 meV and then from -10.0 meV to 1.7 meV; but we present here the second rebinned result. Typical spectrums for  $Q = 2.08 \text{ Å}^{-1}$  for all temperatures are shown in Figure 2.

The experimental data were then fitted using a model for the neutron scattering law  $S_i(\vec{q}, \omega)$  which yields information on the diffusive rate and other parameters. The data were also Fourier transformed as mentioned above.

DAVE software have been used to FFT the inelastic neutron scattering measurements for six  $Q$  values: 0.47, 1.03, 1.32, 1.48, 2.03, and  $2.12 \text{ Å}^{-1}$ .

Prior to applying the FFT, we kept the default energy range of our original data set; the pre and post filter (Gaussian) had been selected to remove the high-frequency noise and we also maintained the default bandwidth; this would not affect our result since our original energy range had been maintained. The results of the transformation for the temperature 215K, 300K and 315 K is presented in Figures [3(a) - 5(a)] which have been compared to our MATLAB results in Figures [3(b) - 5(b)]. Note that for both DAVE and MATLAB programs, we used 512 data points ( $\gamma = 9$ ) and we did not applied filters in the MATLAB program.

Overall, there is a good agreement between DAVE and MATLAB programs on the physical shape of the calculated intermediate scattering functions. The  $I_s(\vec{q}, t)$  decay with  $Q$ . However, the lack of filters in the MATLAB program shows some oscillations in the  $I_s(\vec{q}, t)$  figures.

The second step consists of using the MATLAB program to transform back  $I_s(\vec{q}, t)$  to  $S_i(\vec{q}, \omega)$ , and to achieve that we have taken the following procedures:

First, the intermediate scattering function  $I_s(\vec{q}, t)$  was convoluted with the Fast Fourier Transform of the resolution function as it is displayed in Equation 19.

$$m = I_s(\vec{q}, t) * \text{FFT (resolution function)} \quad (19)$$

Then the scattering function  $S_i(\vec{q}, \omega)$  is obtained by taking the inverse fast Fourier transform of Equation 19 as expressed in Equations (20, 21).

$$S_i(\vec{q}, \omega) = \text{iFFT}(m) \quad (20)$$

$$= \text{iFFT}[I_s(\vec{q}, t) * \text{FFT}(\text{resolution function})] \quad (21)$$

This investigation has been done just for  $T = 330$  K at  $Q = 2.12 \text{ \AA}^{-1}$  using the MATLAB program and the results are displayed below.

Figure (001) represents the measured scattering function for  $Q = 2.12 \text{ \AA}^{-1}$ , Figure (002) is the fast Fourier transform of Figure (001) which gives the intermediate scattering function, and the inverse fast Fourier transform of Figure (002) represents the calculated scattering function which is shown in Figure (003).

We can conclude that, there is no discrepancy between the measured  $S_i(\vec{q}, \omega)$  [Figure (001)] and the calculated scattering function [Figure (003)].

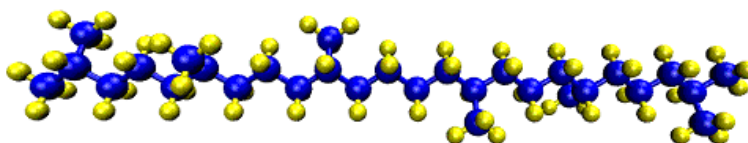
The simulated intermediate scattering function in Figure [4(a) - 6(a)] was done by Prof. Flemming Y. Hansen group [9]; they have calculated  $I_s(\vec{q}, t)$  for the internal, rotational and intramolecular motions [10]. Their results have been compared to our experimental results (DAVE)  $I_s(\vec{q}, t)$  in Figures [6(b)-9(b)]. We believe that the MATLAB result (Figures [6(b)-8(b)]) includes all motions (rotational, center of mass and translational respectively). The comparison have been done at temperatures 215K, 300 K, and 315 K for  $Q = 1.03 \text{ \AA}^{-1}$ .

In the theoretical point of view, it has been shown that the rotational intermediate scattering function  $I_s^R(\vec{q}, t)$  can be split into the time-independent term and a time-dependant one [3, 11].

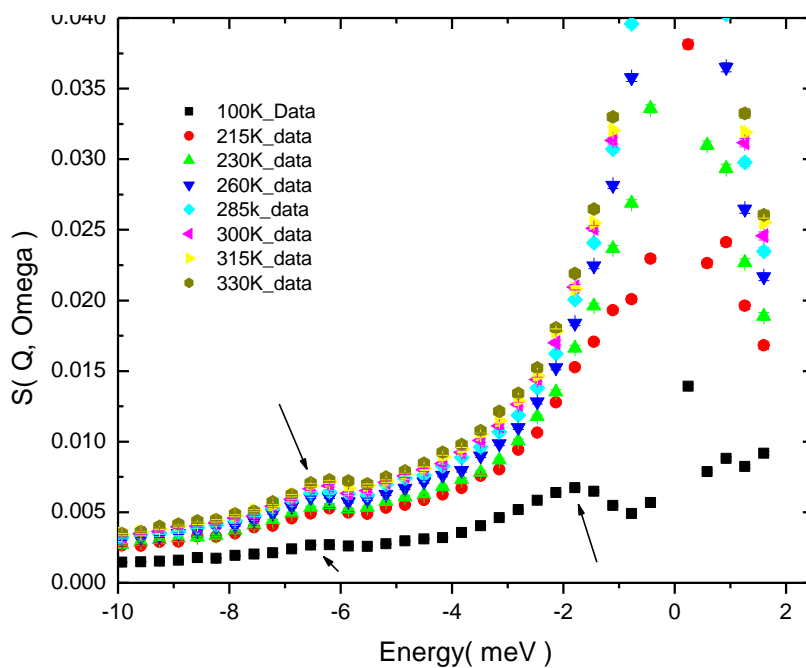
$$I_s^R(\vec{q}, t) = I_s^R(\vec{q}, \infty) + [I_s^R(\vec{q}, t) - I_s^R(\vec{q}, \infty)] \quad (22)$$

Unlike in totally free translational diffusion, the radius vector  $R$  (where the position vector  $\vec{r}_j(t)$  in Equation 16 has been replaced by  $R$ ) is confined to a restricted volume of space which makes the intermediate scattering function  $I_s^R(\vec{q}, \infty)$  different to zero [3].

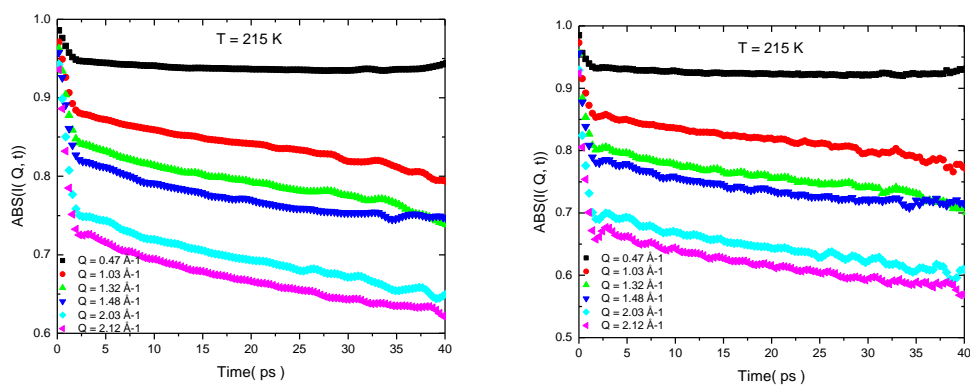
This approach is consistent with our experimental  $I_s(\vec{q}, t)$  values; for a short time (below 10 ps), both Figures [3(a-b) to 5(a-b)] shows time-dependent of the intermediate scattering function; but above 10 ps we also have the evidence of the time-independent term of the  $I_s(\vec{q}, t)$ . For this reason, we conclude that the rotational  $I_s(\vec{q}, t)$  is the main driver of the shape of the total motion of the experimental intermediate scattering function.



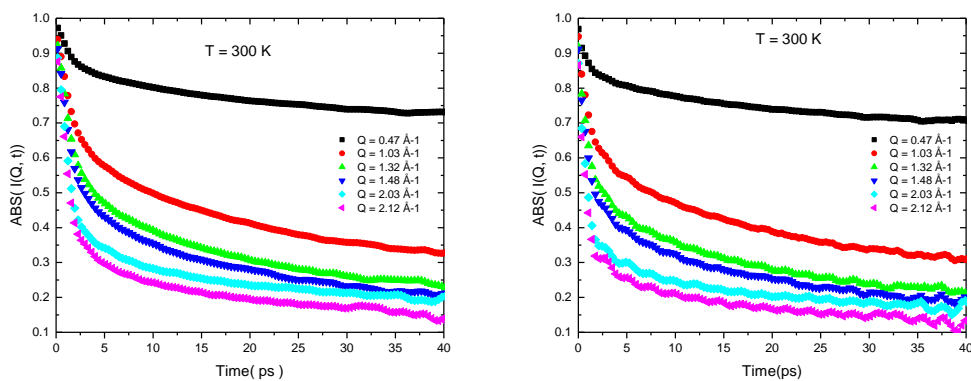
**Fig. 1:-** Squalane; top view



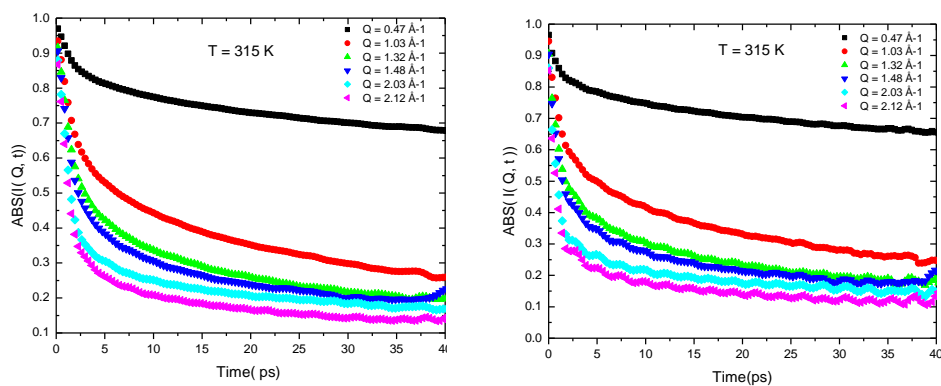
**Fig. 2:-** Scattering function showing an inelastic peak at app. -2 meV at 100 K. DCS instrument.



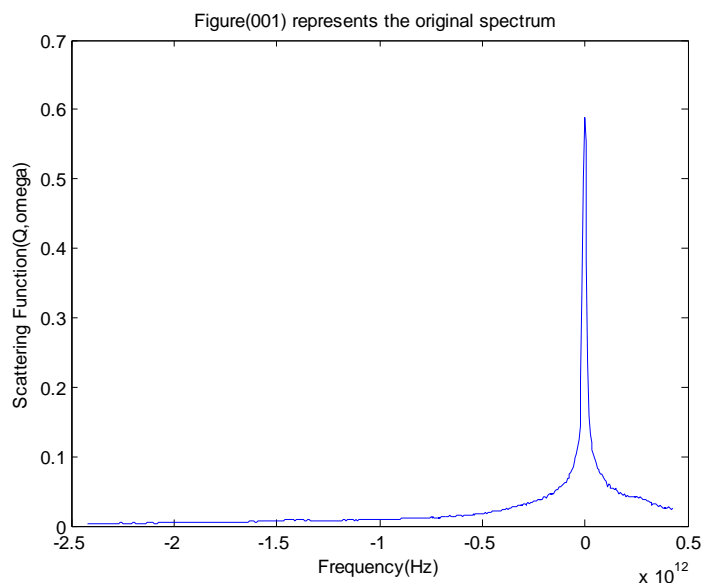
**Fig. 3:-** represent the comparative study of the FFT of the Dave software and the MATLAB algorithm.



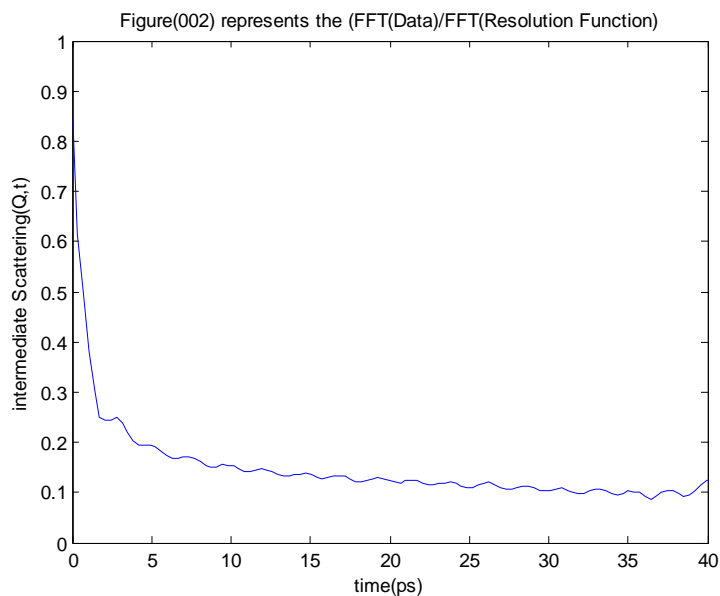
**Fig. 4:-** represent the comparative study of the FFT of the Dave software and the MATLAB algorithm.



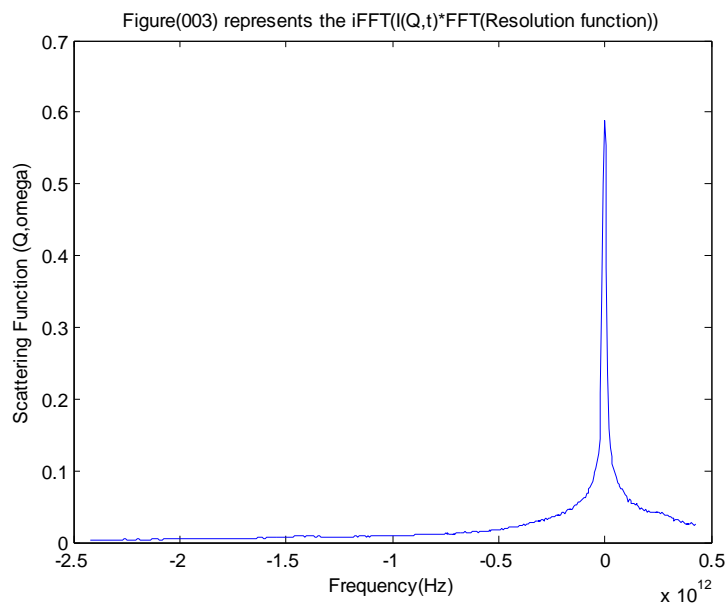
**Fig. 5:-** represent the comparative study of the FFT of the Dave software and the MATLAB algorithm.



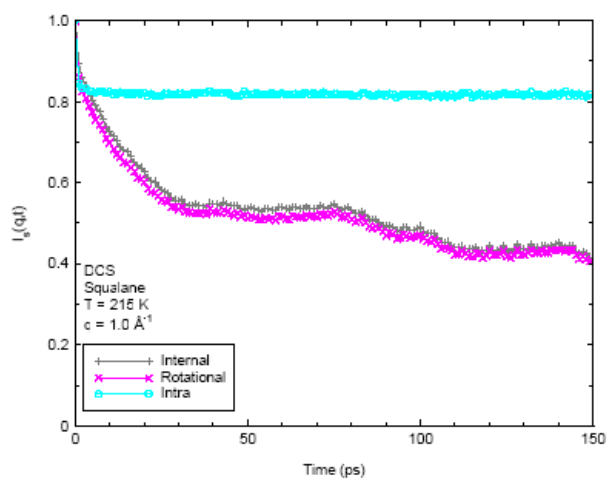
**Fig. (001):-** represents the measured scattering function for  $Q = 2.12 \text{ \AA}^{-1}$



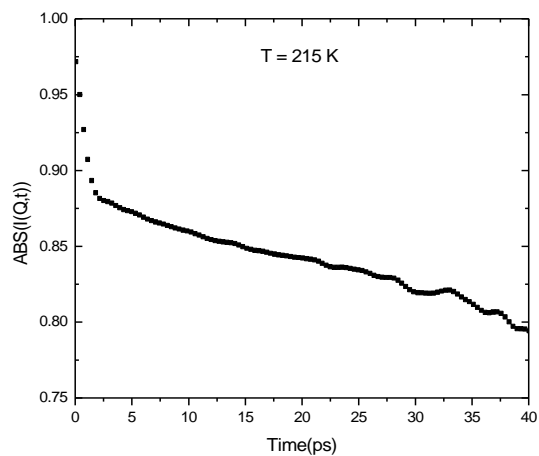
**Fig. (002): -** is the fast Fourier transform of Figure (001) which gives the intermediate scattering function.



**Fig. (003):-** is the inverse fast Fourier transform of Figure (002) and represents the calculated scattering



function.



**Fig. 6(a-b):-** represent the simulated intermediate scattering function.



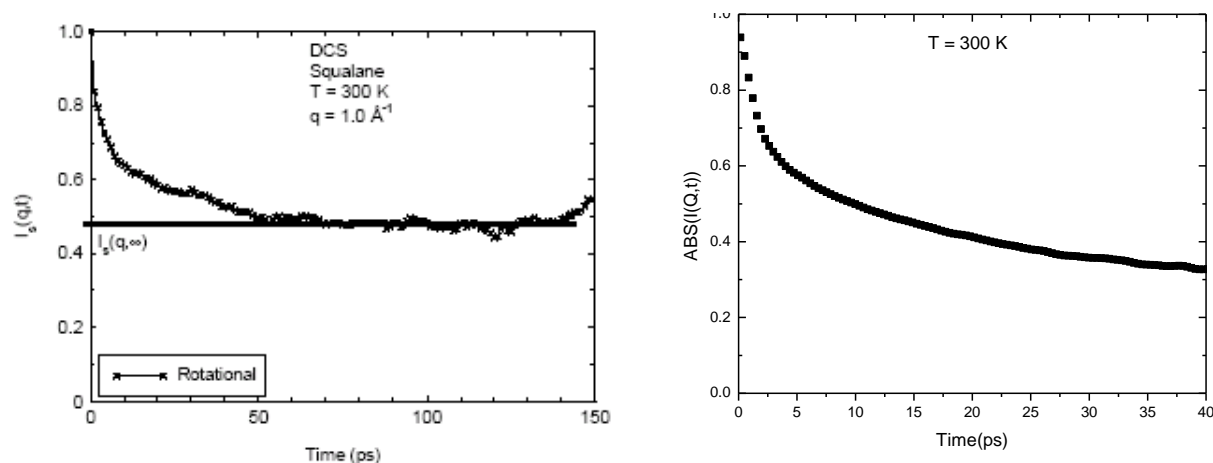


Fig. 7(a-b):- represent the simulated intermediate scattering function.

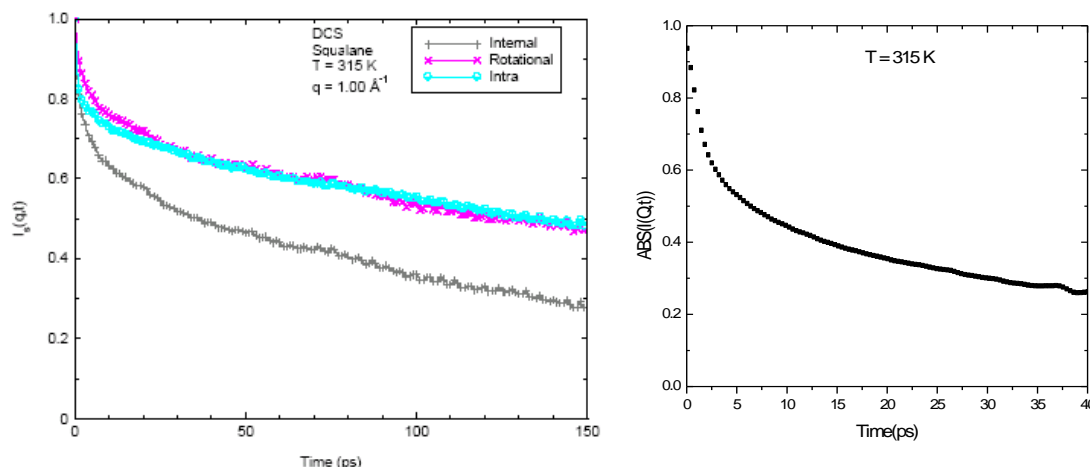


Fig. 8(a-b):- represent the simulated intermediate scattering function.

## Conclusion:-

Comparison of the rotational  $I_s(\vec{q}, t)$  calculated from the simulation in Figures [6(a)-9(a)], shows in overall a minimal agreement with our experimental values in Figures [4(b) - 6(b)] below about 5 ps at 300 K and 315 K. However, the experimental intermediate scattering values decay more quickly than the simulation rotational values beyond 5 ps. There is a significant disagreement between the experimental  $I_s(\vec{q}, t)$  values and the simulation at 215 K. In addition, for the  $Q$  value selected, the experimental  $I_s(\vec{q}, t)$  decay faster as the temperature increases. This evidence is hardly seen in the simulation. At this point, we have no clear explanation for the discrepancy between the experiment and the molecular dynamic simulation results.

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