Experimental report

11/02/2016

Proposal:	**7-05-440**	**Council:**	10/2014
Title:	Diffusion of pyrene molecules: thetransition to ballistic diffusion		
Research area:	Physics		

This proposal is a new proposal

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Samples: $C_{16}H_{10}$/graphite

Instrument	Requested days	Allocated days	From	To
IN6	6	5	22/07/2015	27/07/2015

Abstract:

Graphite surfaces are an ideal playground for studying the fundamentals of two-dimensional diffusion processes and friction using neutron scattering. In a recent experiment we have observed for the first time an almost perfect 2d Brownian diffusion for flat lying benzene molecules adsorbed on exfoliated graphite. In the present experiment we want to investigate a larger aromatic molecule (pyrene) and apply lower coverage with the aim to increase the mean free path which would allow us to observe the expected transition from Brownian to ballistic dynamics. This should tell us more about the influence of eventual substrate friction and the loss of memory.

Diffusion of pyrene molecules: the transition to ballistic diffusion

Scientific background and aim of the experiment

Graphite surfaces are an ideal playground for studying the fundamentals of two-dimensional diffusion processes and friction using neutron scattering [1, 2, 3, 4, 5, 6]. For the first time an almost perfect 2d Brownian diffusion was observed, e.g., for flat lying benzene molecules adsorbed on exfoliated graphite [2, 5]. Other researchers have looked at hydrocarbon 2d melting [7] or the intra-molecular diffusion in long-chain alkanes [3]. Graphite is an ideal base because most molecules only form weak van der Waals bonds with this surface. For aromatic molecules only quadrupole or higher order interactions exist, which means that super-lubricity can form between aromatic hydrocarbons and graphite [8]. Graphite is very accessible for neutron scattering experiments in the form of chemically exfoliated graphite. This material has a high specific surface density of about 30 m^2 per gram, but can be produced with a rather low defect density.

In this experiment we wanted to advance our study of 2d Brownian diffusion and bring it one crucial step further: in the theory of Brownian diffusion we expected to find ballistic diffusive behaviour if we regard the molecular motion at distances that are smaller than the mean free path, i.e., we expected undisturbed diffusion between molecular collisions. In a recently published study we have observed hints that such a ballistic motion might be found for benzene/graphite [2]. However, up to the described experiment the evidence was not yet very strong as the mean free path in an 0.1 monolayer (ML) benzene/graphite system corresponds to Q values where strong signal from the graphite substrate is found and where the rotational signal starts to play a dominating role. The mean free path at equal relative coverage can be reduced by studying larger aromatic molecules. In addition, friction force microscope measurements suggest that the substrate friction can be reduced by increasing the number of aromatic rings [8]. Hence, it was plausible that we could see the transition from Brownian to ballistic diffusion if we investigated larger molecules such as pyrene. This is what we aimed to do.

Previous and preliminary results

In recent test experiments we have been able to study the diffusion of an 0.5 ML film of pyrene adsorbed on exfoliated graphite both on IN6 and on the neutron spin echo spectrometer IN11 (Fig. 1). The experiments have shown that the long range diffusion of pyrene, is in the IN6 dynamic window, that it is clearly visible in the sub-monolayer regime and that the diffusion can be observed over a huge temperature range of between 50 and 400 K. However, the coverage of 0.5 ML was too high to show the expected ballistic motion as the mean free path is as big as the mean free path that we have achieved with our benzene experiments. It was highly interesting to decrease the coverage to the limit of the technical feasibility of IN6 and go to 0.1 and 0.2 ML for a further detailed measurement.

Experimental Results

The incoming neutron wavelength was set to 5.12 Å with an energy resolution at full width half maximum of 70 μeV. The neutron scattering signal of the adsorbed pyrene molecules was enhanced by using Papyex exfoliated graphite substrates (grade N998, > 99.8 % C, Carbone Lorraine), which have a high specific surface area of the order of 23 m^2g^{-1} and a preferential orientation of the graphite crystallites with their basal plane parallel to the scattering plane (in—plane scattering geometry). The specific surface area of the samples had been verified by Brunauer−Emmett−Teller (BET) nitrogen adsorption isotherms. Papyex exfoliated graphite disks of 2.5 cm diameter were heated under vacuum in a pyrolytic furnace for 20 hours at 623 K. Afterwards, the discs were deposited in a cylindrical aluminum sample holder. The amount of powder pyrene (Merck 99.7 %), required to reach 0.1 and 0.2 ML coverage, respectively, was weighed using a fine balance and then added to the graphite disks. Finally, the aluminum sample holder was hermetically sealed using a lid with a steel knife-edge. The sample was heated in a furnace at 550 K for one hour to sublimate the pyrene and promote its adsorption in the whole volume of the sample.

We used the orange cryostat as sample environment to control the temperature within the range of 1.7-350 K. We have performed measurements of 0.1 and 0.2 monolayers (ML) of pyrene as proposed. The upper thermal limit of the pyrene measurement was taken to be the cryostat thermal limit. In addition, we also measured the scattering function of the clean graphite substrate (before adsorption) in order to have a reference for the substrate contribution to the scattering function. Finally, the resolution function containing the elastic contribution of the instrument was measured using a sample of vanadium with the same geometry as the actual sample.

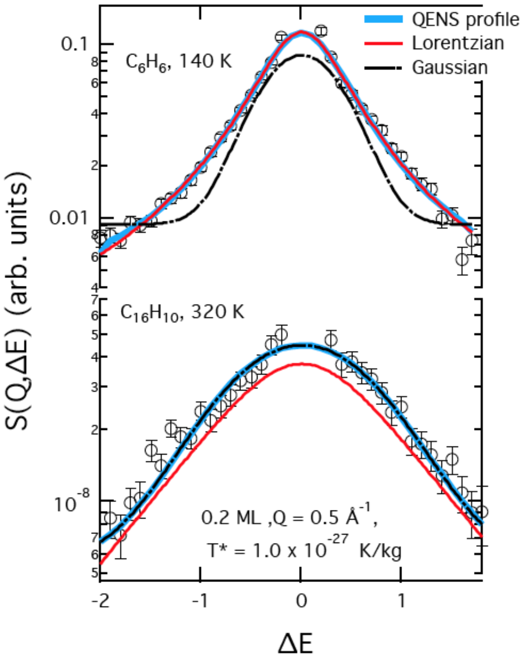

Figure 1: Comparison of a spectrum of 0.2 ML benzene/graphite from an earlier IN6 experiment (upper graph) with a spectrum of 0.2 ML pyrene/graphite from the present experiment (lower panel).

The data taken in this experiment were of very good quality and a publication is in preparation. Fig. 1 shows a comparison of a ToF spectrum of an 0.2 ML sample of pyrene/graphite with an 0.2 ML sample of benzene/graphite taken in our prior experiments on IN6. The spectra show a strong indication of ballistic diffusion for pyrene/graphite (Gaussian profile) and a Brownian diffusion for benzene/graphite at the tested Q value. A more detailed analysis of the data is required to substantiate our assumption and DFT as well as molecular dynamics calculations are under way to support the argument.

References

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