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# Benzene diffusion on graphite described by a rough hard disk model

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## ARTICLE INFO

## ABSTRACT

New insight into the nature of diffusion and the origin of friction of a prototype system for weak physisorption – benzene molecules, $C_6H_6$, adsorbed on the basal plane (0001) of graphite – has been obtained with quasi-elastic neutron scattering (QENS). Spectra were measured at relative adsorbate coverages between 0.1 and 1.0 monolayers (ML) and at sample temperatures between 60 K and 140 K. Our experimental observations require a substantial modification of the model of interaction between benzene molecules and graphite surfaces: in contrast to recent studies we find only weak kinetic surface friction, but a substantial dissipative interaction during inter-molecular collisions. At coverages of up to 0.5 ML the molecular dynamics are successfully modeled by a rough hard disk model, which we derive from a three-dimensional rough hard sphere model. At the full monolayer, three body and higher order collisions are dominant and the rough hard disk model breaks down, as expected.

## 1. Introduction

Carbon and hydrocarbon systems play a central role as models in fundamental friction research as well as in the search for low-friction building blocks in nanotechnology [1–9]. Although substantial progress has been made it is still extremely difficult to pinpoint friction processes under thermodynamically interesting conditions. An exciting recent finding in the class of carbon surface systems has been the observation of super-lubricity (negligible *static* friction or friction force, $F_x$) between graphene sheets and graphite surfaces using scan-

ning force microscopy [4,5]. Super-diffusion was also observed in molecular dynamics simulations of gold nano-clusters adsorbed on graphene [10]. On the other hand, a spectroscopic measurement based on $^3$He spin-echo (HeSE) and neutron spin-echo (NSE) spectroscopy studied the *kinetic* friction, $\eta$, of benzene molecules on graphite substrates [11,12], where $\eta$ is defined by the Einstein equation of diffusion [13] as used in the fluctuation–dissipation theorem by Kubo [14]:

$$D = \frac{k_B T}{m\eta}. \tag{1}$$

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Here, $m$ is the mass of the diffusing particles, $k_B$ is the Boltzmann constant, $T$ is the temperature and $D$ is the self-diffusion coefficient (in a strict sense the HeSE and $C_6D_6$ NSE experiments obtained the transport-diffusion coefficient, see below). $\eta$ can also be expressed by the kinematic viscosity, $v$, as employed in the Stokes–Einstein equation: $\eta = 2\pi d v/m$ with $d$ being the molecular diameter [15]. In the measurements reported in Ref. [11] a high friction of about 2.2 ps$^{-1}$ was obtained. The friction was mainly attributed to a dynamical coupling of the benzene molecules to the phonon bath of the graphite surface since no dependence on coverage was observed within the limited experimental range. The collisional friction was assumed to be of the order of 0.55 ps$^{-1}$ based on theoretical considerations.

Here, we present new neutron scattering data of benzene, $C_6H_6$, on graphite, which allow us to study the diffusive regime in substantially extended coverage and temperature ranges in comparison to the HeSE studies [11]. The data yield a novel picture of the origin of the kinetic friction in this system, which might lead to a change in the design of nano motors based on weakly physisorbed systems [16]. $C_6H_6$ is a powerful *incoherent* neutron scatterer and the present experiments, hence, yield the *self*-correlation function of the moving molecules as well as the self- or tracer-diffusion coefficient (as used in Eq. (1)) [14,17,18]. This is in contrast to the *coherent* scattering observed in HeSE and $C_6D_6$ NSE measurements [11], which provide the total scattering function and, thus, the collective or transport diffusion coefficient (see [17,19,20] for a detailed discussion of the differences). Whereas the self-diffusion framework gives a thermodynamic treatment of the motion of tagged particles, and thus allows us to extract the molecular friction, the collective diffusion framework considers the correlations between centers of mass and describes mass transport. In the limit of small coverage and weak correlations self- and collective diffusion can be assumed to be similar, but our present incoherent scattering study circumvents the use of approximations as it directly measures the self-diffusion. To exclude instrumental artifacts, we have used a range of neutron time-of-flight (TOF), spin-echo (NSE) and backscattering (BS) spectrometers.

## 2. Experimental

### 2.1. Instrument details

We have performed measurements using the TOF spectrometer IN6 and the NSE spectrometer IN11 at the Institut Laue-Langevin (ILL) as well as the BS spectrometer OSIRIS at the ISIS neutron source. The incoming neutron wavelengths were set to 5.12, 5.50 and 6.66 Å, respectively, at the IN6, IN11 and OSIRIS spectrometers with respective energy resolutions at full width, half maximum of 70 μeV (IN6), 1 μeV (IN11), and 24 μeV (OSIRIS). The IN11 spectrometer was used in the high signal set-up IN11C. We used liquid He cryostats as sample environment with an accessible temperature range of 1.7–350 K. The resolution function containing the elastic contribution of the sample was measured at 2 K for each coverage. The upper practical thermal limit for our dynamical study was the benzene desorption temperature of 150 K [21].

### 2.2. Sample preparation

The neutron scattering signal of the adsorbate molecules was enhanced by using Papyex exfoliated graphite substrates (grade N998, > 99.8% C, Carbone Lorraine), which have a specific surface area of the order of 23 m$^2$ g$^{-1}$ [22] and a preferential orientation of the graphite crystallites with their basal plane parallel to the scattering plane (in-plane scattering geometry) [22,23]. The specific surface area of the samples was verified by BET (BrunauerEmmettTeller) nitrogen adsorption isotherms. The exfoliated graphite disks of 2.5 cm diameter were heated under vacuum in a pyrolytic furnace for 20 h at 623 K. Afterwards, the disks were deposited in a cylindrical aluminum sample holder and the amount of liquid benzene (Merck 99.7%), which is required to obtain a desired coverage, was dosed as liquid with a micro-pipette. Finally, the aluminum sample holder was hermetically sealed using a lid with a steel knife edge. We prepared four different samples following the same protocol with relative coverages of 0.1 ML, 0.2 ML, 0.5 ML, and 1.0 ML, respectively.

### 2.3. MD calculation procedure

To improve the understanding of the physics behind the measured spectra, we have performed additional molecular dynamics (MD) simulations. The molecular trajectories were calculated with the CERIUS$^2$ program package (Accelrys, Inc.), Version 4.8, following the procedure described in Ref. [12]: we used NVE (constant particle number, volume and total energy) dynamics. This statistical ensemble was chosen because of a better stability of the calculations compared to NVT (constant particle number, volume and temperature). The calculational time step was 1 fs time, which allowed us to include the fast hydrogen dynamics, and the atomic positions were written into the trajectory files every 200 fs. The trajectories were given 50 ps for equilibration before data was used for evaluation and analysis. The COMPASS forcefield [24] was used with automatic atom typing and no amended parameters. The van der Waals cut-off distance was chosen to be 20 Å. Atom charges were calculated by charge equilibration at the beginning of each dynamics run and were kept constant throughout the runs. For comparison with the experimental results, scattering functions were extracted from the MD trajectories using the nMoldyn 3 software package [25].

## 3. Results and discussion

Fig. 1 displays typical neutron TOF scattering functions $S(Q, \Delta E)$ at a sample temperature of 140 K and at coverages from 0.1 ML up to 1 ML together with a spectrum extracted from MD simulations of a single adsorbed molecule for reference. The energy transfer, $\Delta E = E_f - E_i$, is drawn on the ordinate and the momentum transfer for all spectra is $Q = |\vec{Q}| = |\vec{k}_f - \vec{k}_i| = 0.4$ Å$^{-1}$. As a general feature we find in all scattering functions an intense elastic scattering region around $\Delta E = 0$ meV that is mostly generated by the scattering from the graphite substrate. The broader feature surrounding the elastic band is the so-called quasi-elastic broadening. The quasi-elastic signal disappears if no adsorbate is present and,