

Probing the 2D confinement on hydrogen dynamics in water and ice adsorbed in graphene oxide sponges

Electronic Supplementary Information

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1 Experimental Methods

1.1 Sample Preparation

The graphene oxide (GO) is prepared by hydrothermal oxidation in a sealed autoclave. Typically, 50 mg graphene are cooled in a 50 ml autoclave at 4 C for 1 hour before experiment. The pre-cooled KMnO_4 (1 g) and concentrated sulfuric acid (20 ml) are slowly added into the autoclave under ice bath. The autoclave is tightly sealed and kept in the fridge for 2 hours before heating in oven at 150 C for 2 hours. The resulted GO are thoroughly washed with deionized water and dried in oven overnight (see Figure 2). To synthesize the graphene hydrogel, purified GO is dispersed in 20 ml water (2 mg/ml) and sealed in an autoclave (50 ml volume). The autoclave is heated in oven at 160 C for 12 hours. The cylinder-shaped hydrogel is thoroughly washed with water and freeze-dried for 2 days.

1.2 FTIR characterisation of dry GO

The FTIR spectrum of GO sponge, which was used for the DINS measurements, reported in Figure 1, shows the presence of hydroxyl, epoxide and carbonyl groups. No obvious peak for C-H band is observed. Therefore, the hydrogen amount in the GO sponge is very small.

1.3 Hydration Procedure

The freeze-dried cylindrical GO gel was put in a glass bottle and soaked in deionized water for 12 hour prior to the DINS experiment. The glass bottle was fully filled with water and properly capped to avoid water evaporation.

The GO sponge has a strong ability to absorb water. In the present experiment, the weight of dry GO was 0.168 g. The specific surface area of GO sponge varies 180 to 800 m^2/g , depending on different synthetic methods and the GO exfoliation degree. The GO sponge used in the DINS experiment was prepared with a method described in Ref.¹ with a reported surface area of 414 m^2/g . The sample with water fully absorbed in the GO sponge had a total weight of 1.340 g. Weights

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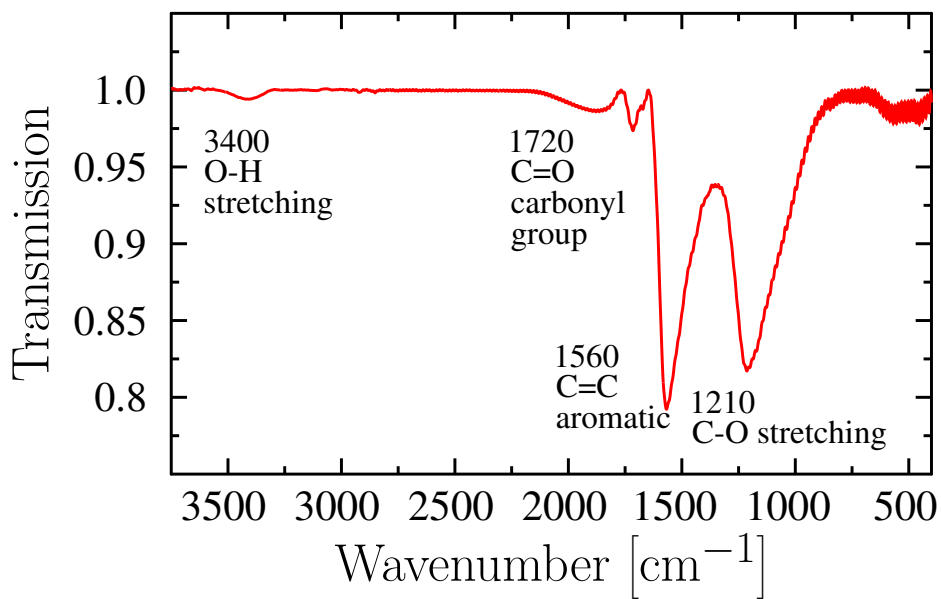


Fig. 1 FTIR spectrum of the dry GO sponge.

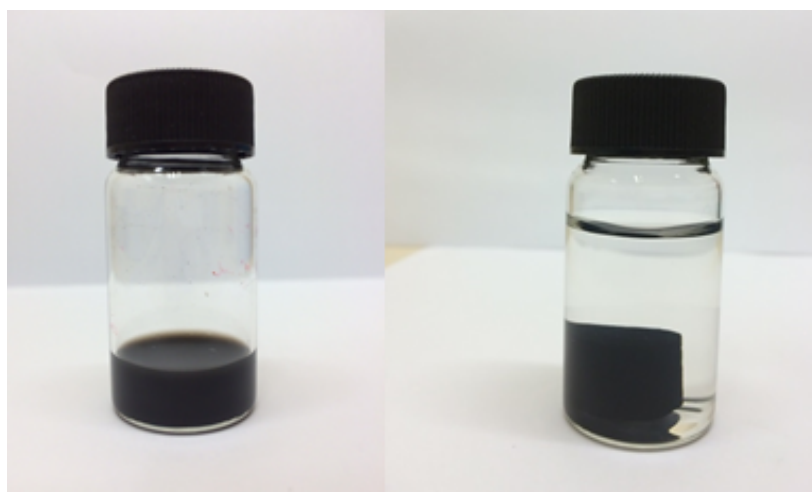


Fig. 2 GO solution (left) and GO hydrogel soaked in water (right).

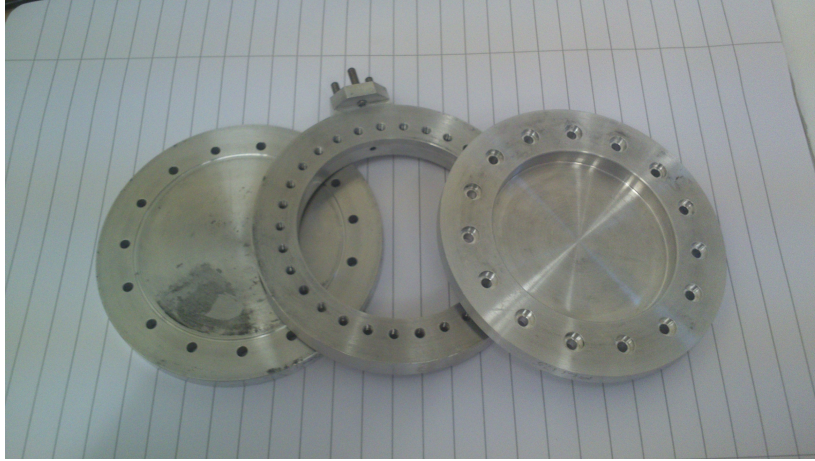


Fig. 3 Aluminium sample container used for their DINS measurements.

of the hydrated sample and the dry GO were 1.172 g and 0.168 g, respectively, corresponding to approximately 87 wt% of adsorbed water.

1.4 Sample transfer into the sample containers

The hydrated GO sponge sample consisted of three GO sponges (total masses 0.168 g of dry GO plus 1.172 g of water), which were located inside a square Al sachet (and placed in the centre of the Al sample container (see figure 3 below). The inner volume of the sample container was 1 cm width and 7 cm diameter. To maximise neutron signal from the sample the diagonal of the squared sachet was 7 cm, equal to diameter of sample container.

1.5 DINS measurements

VESUVIO is an inverse geometry spectrometer, *i.e.*, for each scattering angle, θ , the final energy of the scattered neutrons, E_1 , is selected using a Au resonance filter which absorbs neutrons in a narrow range of energies² with the scattering signal recorded by individual detectors. VESUVIO operates for DINS experiments in the IA regime where the incident neutron wavelengths are much less than the inter-atomic spacing and thus atoms scatter incoherently, with scattered intensity being the sum of intensities from individual atoms in the sample. The count rate as a function of the time of flight (t.o.f.) t yields:

$$C(t) = \sqrt{\frac{8E_0^3}{m_N L_0^2}} I(E_0) D(E_1) \left(\sum_M N_M \frac{d^2 \sigma_M}{d\Omega dE_1} \right) d\Omega \quad (1)$$

where $I(E_0)dE_0$ is the number of incident neutrons s^{-1} with energies between E_0 and $E_0 + dE_0$, $D(E_1)$ is the probability that a neutron of energy E_1 is detected, m_N is the neutron mass, L_0 is the moderator - sample distance, N_M is the number of atoms of mass M in the sample and $\frac{d^2 \sigma_M}{d\Omega dE_1}$ is the partial differential cross-section for the struck nucleide. In the forward direction scattered neutrons are detected by Yttrium Aluminum Perovskite (YAP) scintillators³, located at a distance L_1 , ranging between 0.5 m and 0.75 m from sample position, in the angular range 32.75° to 72.5° . In the backward direction scattered neutrons are detected by Li⁶ scintillators, located at a distance

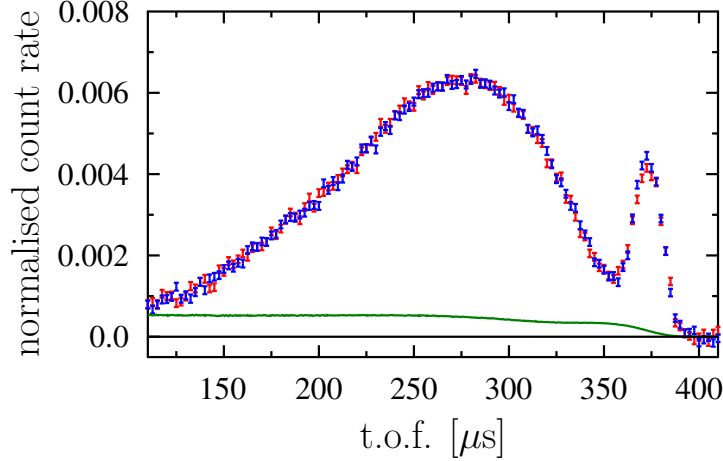


Fig. 4 Angle averaged of the raw *t.o.f.* spectra for water and ice adsorbed in GO sponges at $T = 293$ K (red line) and $T = 20$ K (blue line) and MS component (green line).

ranging between 0.46 m and 0.67 m from sample position, in the angular range 130° to 163° . At each scattering angle the energy of the scattered neutrons, E_1 , is selected by using Au analyzer foils ($E_1 = 4897$ meV). The instrument operates using the Foil Cycling (FC) technique, in forward scattering^{2,4}, and the Double Difference (DD) technique⁵, in backward scattering in the range of wave vector and energy transfers is $27 \text{ \AA}^{-1} \leq q \leq 230 \text{ \AA}^{-1}$ and $2.5 \text{ eV} \leq \hbar\omega \leq 65 \text{ eV}$, respectively and $10^{-3} \text{ eV} \leq \hbar\omega \leq 10^4 \text{ eV}$, respectively^{6,7}.

Multilayer stacked graphene oxide layers, in the range from 6 to 12 \AA , ensured ice formation in these layer by layer stacked layers as well as water trapping ability in 2D and the NCS signal strengths. The sample synthesis has been carried out to guarantee a number of more than 10^{21} water molecules trapped in the matrices, allowing a reliable counting statistics at both temperatures.

The integrated proton current for DINS data yielded $I = 4220 \text{ \mu Ah}$ for $T=293$ K, $I = 3960 \text{ \mu Ah}$ for $T=20$ K.

Raw *t.o.f.* data of individual detectors for water and ice in GO have been corrected by γ -background and multiple scattering (MS) and Al sample container contributions using a Monte Carlo simulation and the simulated signals subtracted from the experimental data. Angle averaged sum over all forward scattering detectors of *t.o.f.* data for water and ice adsorbed in GO are reported in Figure 4 together with MS contribution. From this figure one can see the hydrogen signal peaked between 250 – 300 μs and the Al signal peaked between 350 – 400 μs . An example of a *t.o.f.* corrected spectrum for water in GO sponges at $T = 293$ K, for an individual detector, $\theta = 35$ degrees, is reported in Figure 5. Averaged raw experimental hydrogen NCP and corrected NCP are reported in Figure 6 and Figure 7, respectively. Figure 8 reports the raw data for hydrated and dry GO in y space, respectively; this latter figure shows that the contribution of hydrogen signal from the dry GO is negligible in comparison with the signal from the hydrated sample.

The partial differential cross-section from Eq. (1) can be expressed as a function of the NCP, $J(y)$ as follows:

$$\frac{d^2\sigma_M}{d\Omega dE_1} = b^2 \left(\frac{E_1}{E_0} \right)^{1/2} \frac{M}{\hbar q} J(y). \quad (2)$$

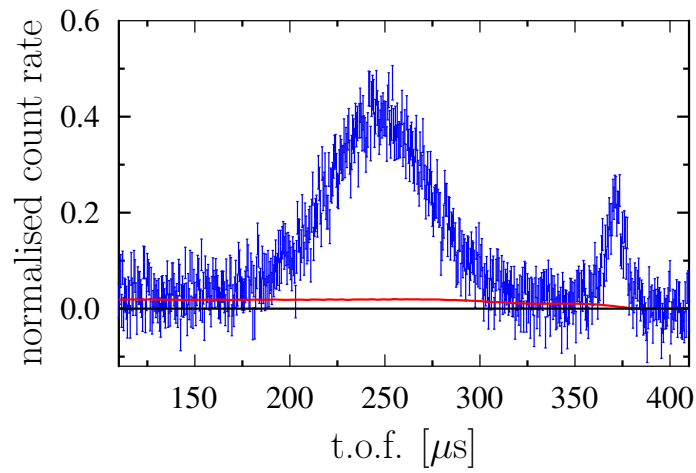


Fig. 5 Individual DINS spectrum in t.o.f. for water in GO sponges at $T = 293$ K (blue line), $\theta = 35$ degrees, corrected for γ -background and multiple scattering (MS) and Al sample container contributions. The MS contribution is plotted in red line.

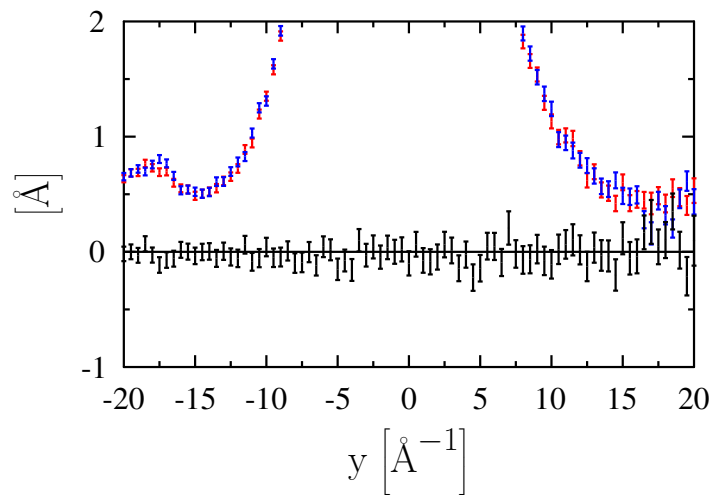


Fig. 6 Angle averaged raw hydrogen NCP for water and ice in GO sponges at $T = 293$ K (red square with error bars) and $T = 20$ K (blue square with error bars) and the difference signal.

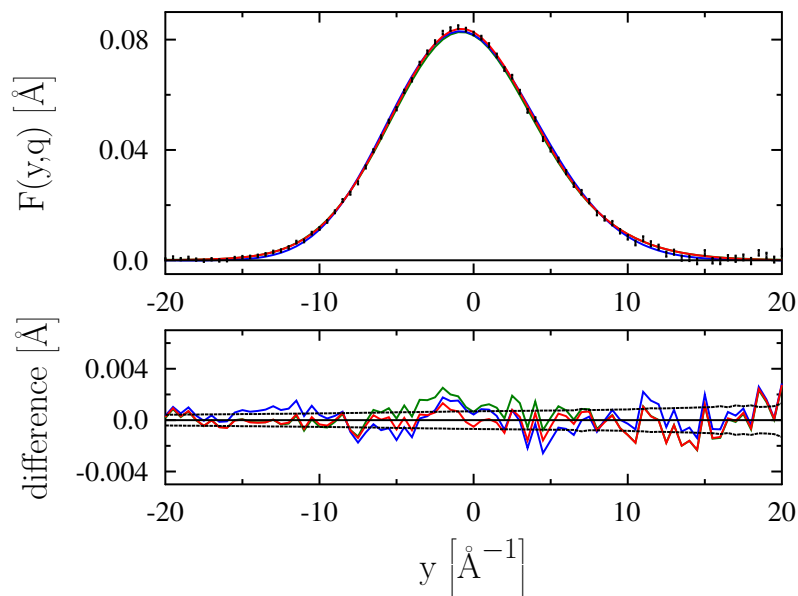


Fig. 7 Averaged experimental response function, $F(y, q)$, (black dots with error bars) at $T = 293$ K and line shapes resulting from fit using model M1, M2 and simple Gaussian lineshape. Upper panel: multivariate-Gaussian model (M2) is reported as a (green line). Lower panel: difference between lineshape resulting from model M2 and $F(y, q)$. Similar comparison is reported for Gauss-Hermite model (M1) up to the first polynomial (red line) and the with no polynomials (blue line).

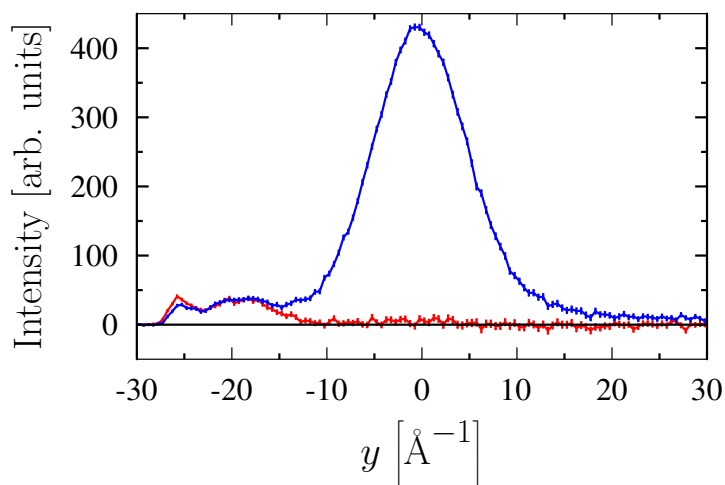


Fig. 8 Raw data for hydrated (blue line and dots with error bars) and dry (red line and dots with error bars) GO in y -space.

Due to the finite q values in the scattering process the NCP at each detector retains the q dependence, expressed by the function $F(y, q)$. The latter includes a further broadening due to experimental resolution function, $R(y, q)$. The $F(y, q)$ function is related to the count rate via the expression:

$$F(y, q) = \frac{BM}{E_0 I(E_0)} q C(t) \quad (3)$$

where B is a constant taking into account: the detector solid angle, its efficiency at $E = E_1$, the time-energy Jacobian, the free-atom neutron cross section and the number of particles hit by the neutron beam. DINS data sets at all temperatures have been y -scaled according to Eq. (3).

In order to derive the $n(p)$, a line-shape analysis of $F(y, q)$ has been performed using models M1 and M2. The defining equations for the NCP related to a Gauss-Laguerre momentum distribution has the form of a Gauss-Hermite expansion

$$J_{M1}(y) = \frac{e^{-\frac{y^2}{2\sigma^2}}}{\sqrt{2\pi}\sigma} \left[1 + \sum_{n=2}^{\infty} \frac{c_{2n}}{2^{2n}n!} H_{2n} \left(\frac{y}{\sqrt{2}\sigma} \right) \right] \quad (4)$$

and the NCP in the case of the multivariate Gaussian distribution has the form

$$J_{M2}(y) = \frac{1}{\sqrt{2\pi}\sigma_x\sigma_y\sigma_z} \int_{\Omega} \frac{d\Omega}{4\pi} \exp \left[-\frac{y^2}{2S^2(\theta, \phi)} \right] S^2(\theta, \phi) \quad (5)$$

with

$$\frac{1}{S^2(\theta, \phi)} = \sin^2 \theta \left(\frac{\cos^2 \phi}{\sigma_x^2} + \frac{\sin^2 \phi}{\sigma_y^2} \right) + \frac{\cos^2 \theta}{\sigma_z^2} \quad (6)$$

For both the models, the correction to the Impulse Approximation (IA) due to the Final State Effects (FSE) has been taken into account as an additive contribution of the form

$$J(y, q) = J_{IA}(y) + \Delta J(y, q) = \left(1 - A_3(q) \frac{\partial^3}{\partial y^3} \right) J_{IA}(y) \quad (7)$$

where $A_3(q) = \frac{\sigma^4}{9q}$.

The model fitting function has been obtained taking a numerical convolution of $J(y, q)$ with the experimental resolution $R(y, q)$, obtaining $F^{th}(y, q) = J(y, q) \star R(y, q)$. Individual detectors have been fitted simultaneously via the $F^{th}(y, q)$ line-shape in order to obtain the values of σ and c_4 in the case of M1, and σ_x , σ_y and σ_z in the case of M2. The fitting parameters have been deduced by minimization the value:

$$\chi^2 = \sum_l \sum_i \frac{\left(F_l^{th}(y_i, q_i) - F_l^{exp}(y_i, q_i) \right)^2}{\epsilon_{l,i}^2} \quad (8)$$

where l labels the considered detector.

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