

Supporting Information – How exfoliated Graphene Oxide nanosheets organize at water interface: evidences for a spontaneous bilayer self-assembly

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S.1 Relaxation isotherm

The relaxation of a GO film at the air-water interface is slow. Indeed, as can be seen on Figure SI 1, at high surface pressures (starting at about $\pi = 45 \text{ mN.m}^{-1}$), the surface pressure decreases by $\pi = 15 \text{ mN.m}^{-1}$ over a period of five hours. The film of GO is rather stable at the air-water interface, even at high surface pressures.

S.2 Fitting x-Ray Reflectivity spectra

The fitting was performed using the GenX software.

Let $r'_{j-1,j}$ be the Fresnel reflectivity in the absence of multiple reflections between the layers $j-1$ and j and $r_{j-1,j}$ be the reflectivity at the

rough interface between the layers $j-1$ and j :

$$r_{j-1,j} = \frac{r'_{j-1,j} + r_{j,j+1} e^{-2i\Delta_j q_{z,j}}}{1 + r'_{j-1,j} r_{j,j+1} e^{-2i\Delta_j q_{z,j}}} e^{-2q_{z,j-1} q_{z,j} \sigma_{j-1}^2}$$

$$\text{with } q_{z,j} = \sqrt{q_z - 16\pi r_e \rho_{e,j} - \frac{i32\pi^2 \beta_j}{\lambda^2}},$$

where r_e is the classical electron radius and β_j is the adsorption coefficient of the j layer.

The quality of the fits was evaluated using the Figure of Merit (FOM) provided by the software, which computes the difference between the logarithms of the experimental data and of the simulated data. The FOM are provided in the following sections.

During the adsorption

To have a rough idea of the expected density, we consider that a unit cell of graphene contains two carbon atoms on a surface of 5.2 \AA^2 . Furthermore, the expected thickness of a not

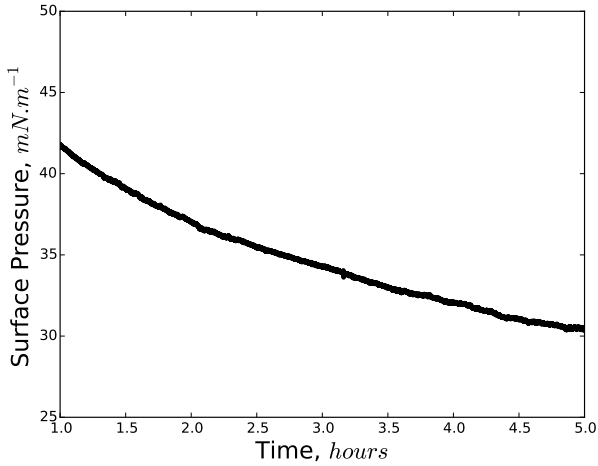


Figure SI 1: Evolution of the surface pressure with respect to time of a GO film at high surface pressures π .

hydrated GO sheet is of about 6 \AA as shown by Vorobiev and coworkers who studied the GO hydration by using neutron reflectivity¹. This cell contains about 2 atoms of carbons, 0.8 of oxygen, and 0.24 of hydrogen. Thus, the density ρ is of about:

$$\rho = \frac{2 * 12 + .8 * 16 + 0.24 * 1}{6.022 * 5.2 * .6} = 1.97 g.cm^{-3}$$

ρ is the highest density reachable in a dry environment. If we take into account the water molecules, we expect a thickness of about 10 \AA leading to a maximum density for GO sheets with water molecules is of about $1.99 g.cm^{-3}$. This is to be expected since the increase of the thickness of a GO sheet once hydrated is pretty significant, compensating the increase of electron carriers.

Reflectivity spectra shown on Figure SI 2 were recorded over a period of five hours after the spreading of GO to monitor the change of XRR signal during the adsorption of GO sheets at the air-water interface. The spectra were performed with completely open barriers and do not undergo huge change during this period of five hours. This could indicate either that nothing changed or that few things changed but were not statistically relevant enough to modify the detected intensity. Table SI 1 groups the fitting parameters for this model. One could expect that only one layer of GO sheets get inter-

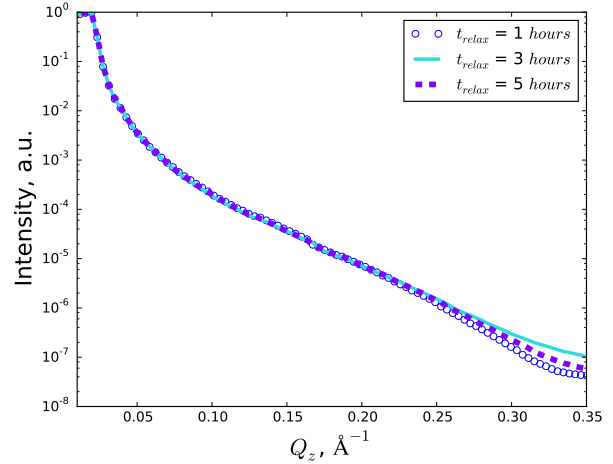


Figure SI 2: Reflectivity spectra of GO at the air-water interface at $\pi = 0 mN.m^{-1}$ with respect to relaxation time.

posed between the air and the water. However the fits lead to a 20 \AA thick layer. Using the two layers model, the two different layer parameters can not be differentiated at such a surface pressure. Thus, the model we proposed is made by two similar layers, as shown on Figure SI 3. Each of these two layers has a thickness of about 9.5 \AA , and a density of about $1.29 g.cm^{-3}$, in agreement with a diluted region. Such a thickness and vertical spacing of the sheets are coherent in highly humid conditions as expected at the air-water interface. Figure SI 4 shows the evolution of the fitting parameters over time at the air-water interface.

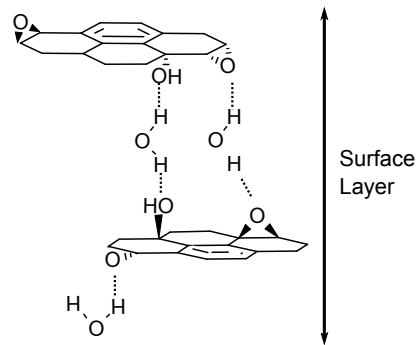


Figure SI 3: Schematic model of the double layer of GO at the air-water interface.

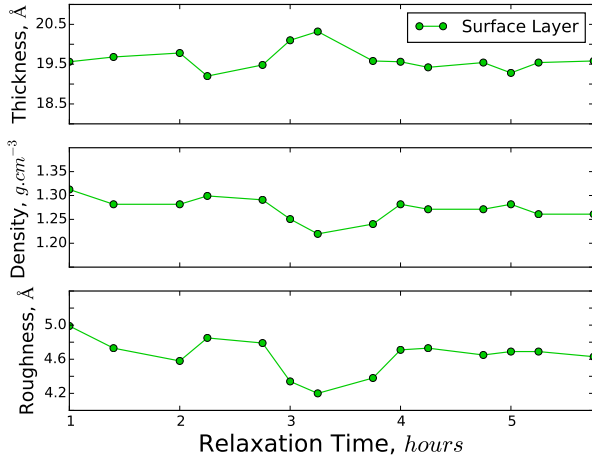


Figure SI 4: Evolution of (a) the thickness, (b) the density and (c) the roughness fitting parameters for the reflectivity spectra of GO at the air-water interface with respect to relaxation time.

Table SI 1: Fit parameters of XRR spectra of GO adsorption at the air-water interface.

Relaxation time (hours)	Thickness (Å)	Roughness (Å)	Density ($g.cm^3$)	FOM
1	19.4	5	1.31	0.028
3	20.2	4.3	1.25	0.024
5	19.2	4.7	1.28	0.024

During the compression

Figure SI 5 shows the different spectra and fit curves under compression. Table SI 2 details the fitting parameters for the two layers of GO sheets at the air-water interface.

Table SI 2: Fit parameters of XRR spectra of GO compression at the air-water interface (Layer 1 in contact with the air, Layer 2 in contact with the water for each surface pressure π).

π ($mN.m^{-1}$)	Layer	Thickness (Å)	Roughness (Å)	Density ($g.cm^3$)	FOM
0	1	10	5	1.3	0.026
	2	10	5	1.3	
5	1	10.6	5.2	1.1	0.018
	2	10.1	1.2	1.5	
20	1	12	6.4	1.2	0.020
	2	10	.8	1.5	

Conservation of quantity $\rho \times V$ for the two layers Let V_b , S_b , e_b and ρ_b be respec-

tively the volume, the surface (determined assuming a hexagonal network using GIXD experiments), the thickness and the density of the buried layer, V_u , S_u , e_u and ρ_u be respectively the volume, the surface, the thickness and the density of the upper layer (in contact with air).

If the matter quantities are equal,

$$\rho_b \times V_b = \rho_u \times V_u \iff \frac{\rho_u}{\rho_b} = \frac{V_b}{V_u}$$

At $\pi = 20 mN.m^{-1}$:

$$\frac{\rho_u}{\rho_b} = \frac{1.2}{1.5} = .80$$

$$\frac{V_b}{V_u} = \frac{S_b \times e_b}{S_u \times e_u} = \frac{(4.2)^2 \times 10}{(4.31)^2 \times 1.2} = 0.79$$

$$\text{i.e. } \rho_b \times V_b = \rho_u \times V_u$$

Thus, the matter quantities are equal between the two layers. The density of the upper layer is smaller because each sheet occupy a larger space than sheets of the buried layer.

S.3 AFM transfer

The transfer ratio of Langmuir films on solid surfaces is calculated as followed²:

$$\tau = \frac{A_{\text{substrate}}}{A_{\text{trough}}},$$

where A_{trough} is the area variation of the trough during the lifting of the substrate, and $A_{\text{substrate}}$ is the substrate surface. The transfer ratio describes the quality of a LB transfer. To maintain the surface pressure constant, the area of the trough has to be decreased during the transfer. If the surface decrease is equal to the surface pressure of the substrate, all the material lost at the water surface should have been transferred on the substrate, leading to a transfer ratio of about 1. For transfers of GO films performed at $\pi = 20 mN.m^{-1}$, we typically obtain a transfer ratio higher than 0.9, indicating that the transfers were efficient.

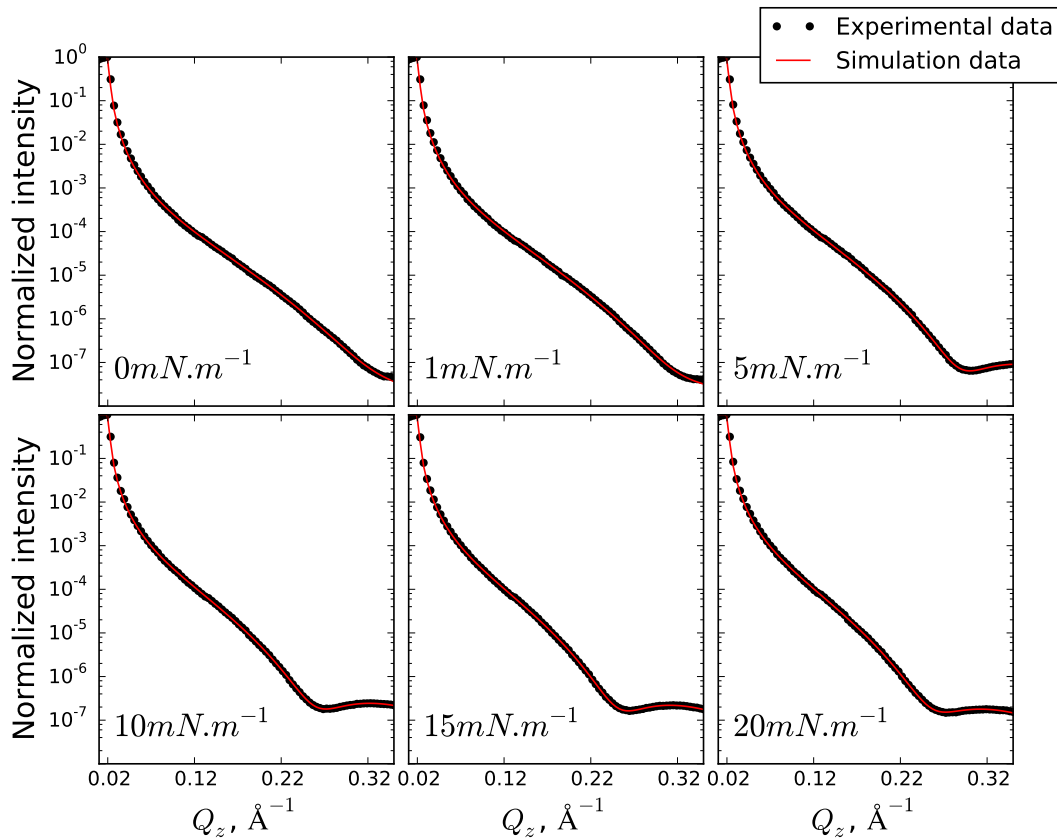


Figure SI 5: Fitted XRR spectra at different surface pressures π .

References

1. Vorobiev, A.; Dennison, A.; Chernyshov, D.; Skrypnichuk, V.; Barbero, D.; Talyzin, A. V. Graphene oxide hydration and solvation: An in situ neutron reflectivity study. *Nanoscale* **2014**, *6*, 12151–12156.
2. Gaines, G. L. *Insoluble monolayers at liquid-gas interfaces*; Interscience Publishers: New York, 1966.