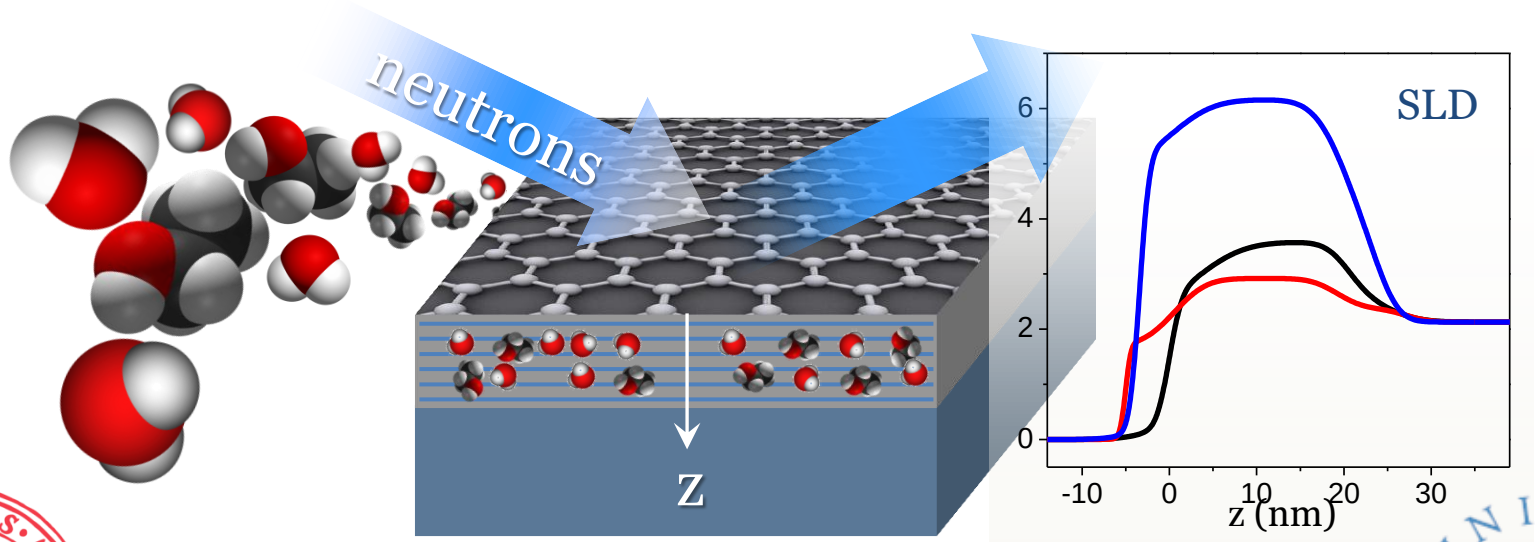
Спирт или вода?
Проблема проницаемости оксид-графеновой мембраны с точки зрения рефлектометриста



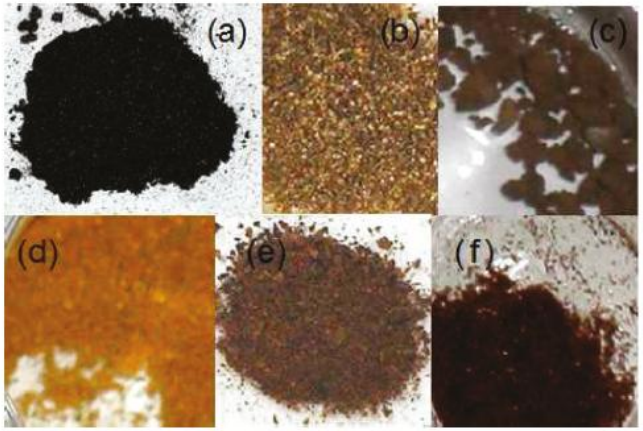
Алексей Воробьев
Факультет физики и астрономии, Университет Уппсала
Александр Талызин
Факультет физики, Университет Умеа
Дмитрий Чернышов
SNBL at ESRF

Graphite oxide and graphen oxide

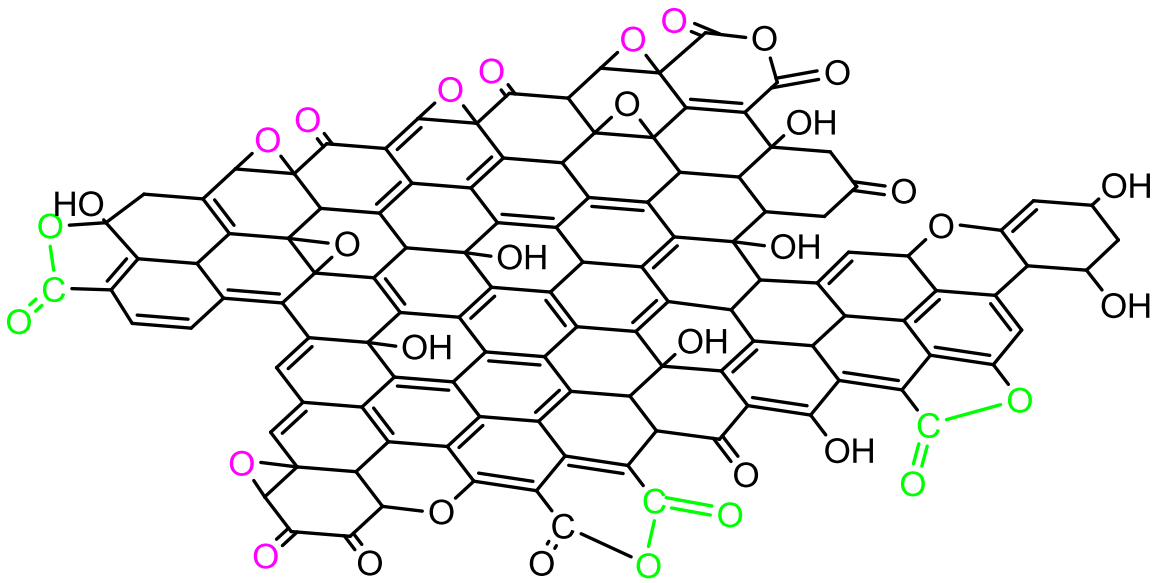
Brodie's method: oxidation of graphite by $NaClO_3$ and HNO_3 .
Known since 1859!

Hummers method: H_2SO_4, $NaNO_3$, $KMnO_4$
....

Graphite oxides are different

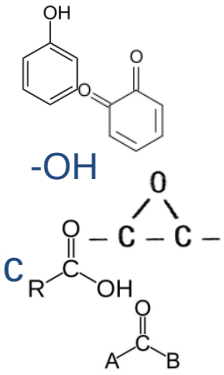


Graphite oxide can be dispersed on ***graphene oxide*** in solvents



The oxidation procedure incorporates various functional groups:

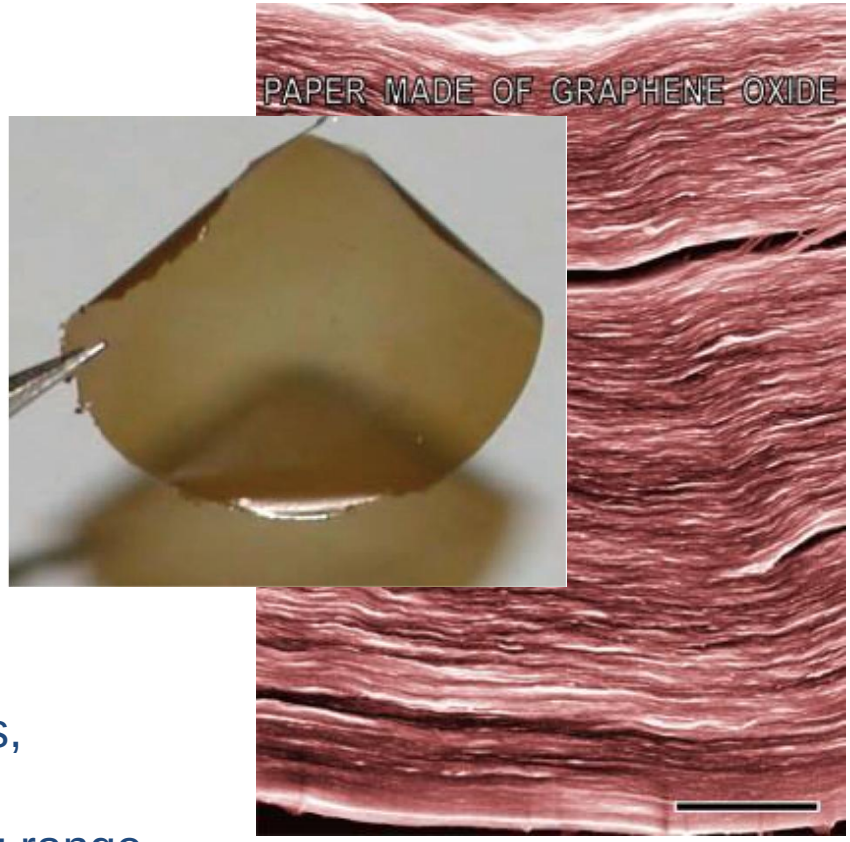
- phenolic
- quinone
- hydroxyl -OH
- epoxy
- carboxylic
- carbonyl



Graphene oxide is strongly hydrophilic

Graphene oxide paper/ membrane

Graphene oxide flakes can be precipitated from water solution to make membranes.



Combination of excellent mechanical properties and chemical tunability.

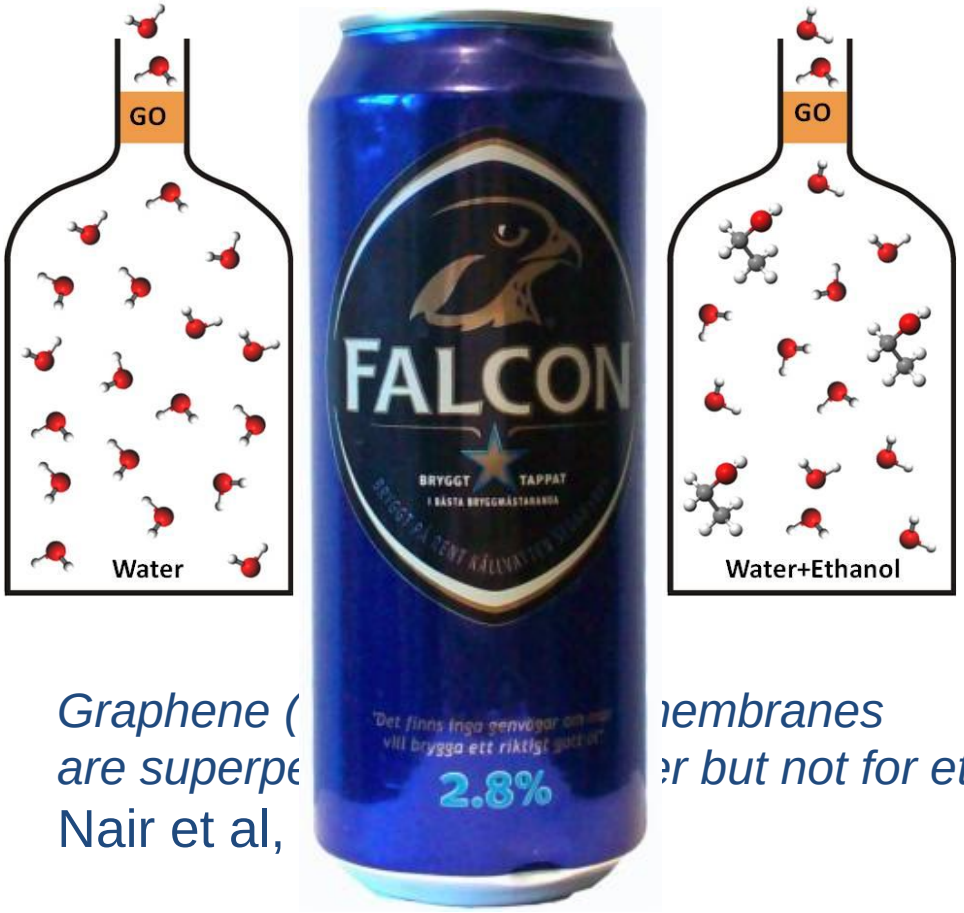
D. A. Dikin et al, Nature, 2007

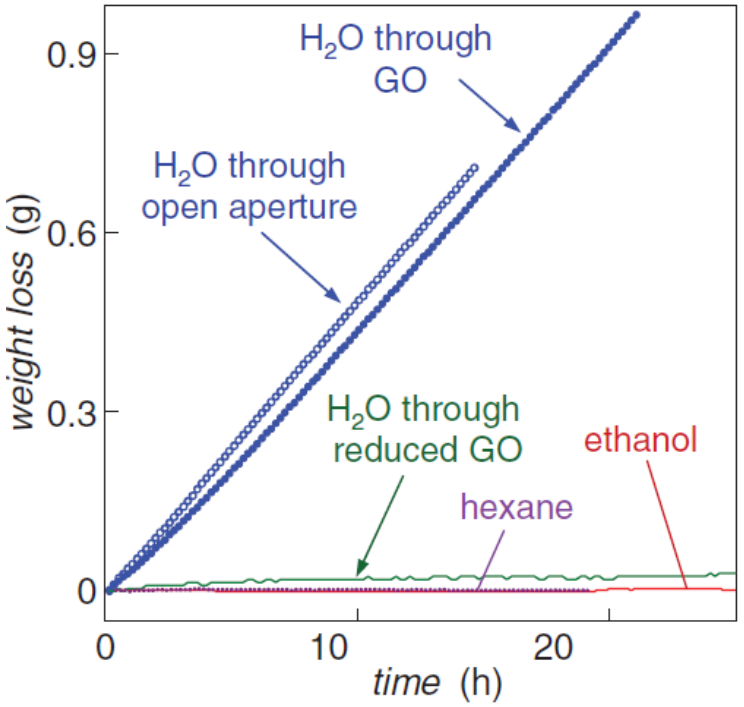
Possible applications:

- protective layers, chemical filters,
- supercapacitors, electronic components,
- molecular storage
- nanoelectrochemical resonators in MHz range
- electrode materials
- membranes with unusual permeability

.....

Graphene oxide membranes



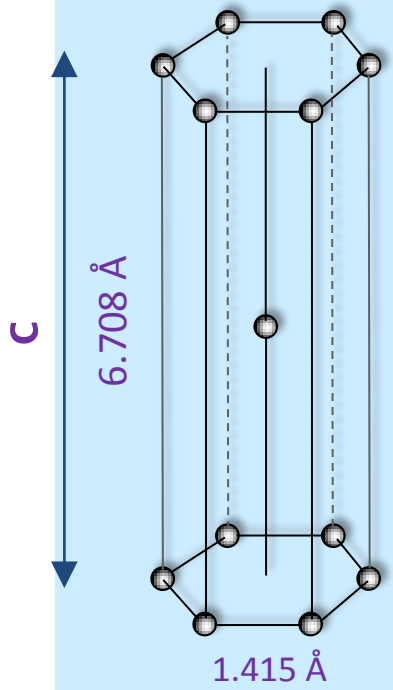


Graphene (…embranes
are superpe… …er but not for ethanol and even for helium.
Nair et al,

WHAT STRUCTURAL FEATURES ARE BEHIND?

Graphite vs. GO membrane

Graphite
formula unit C_4

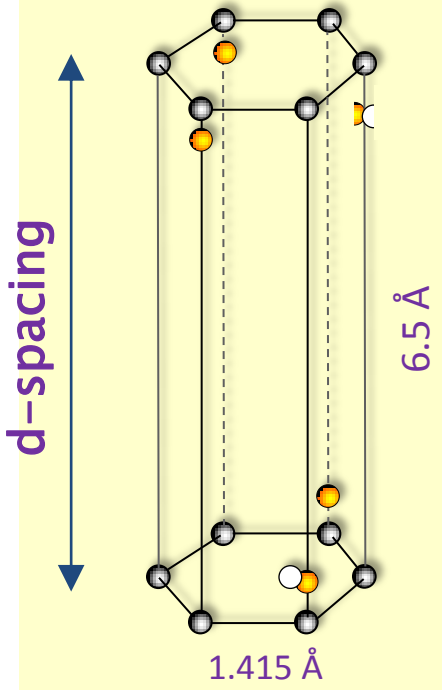


Graphite
c-centered hexagonal
C6/mmc
lattice parameters
a=2.4612 Å, c=6.708 Å

cell volume V_0=35.189 Å^3

density 2.267 g/cm^3

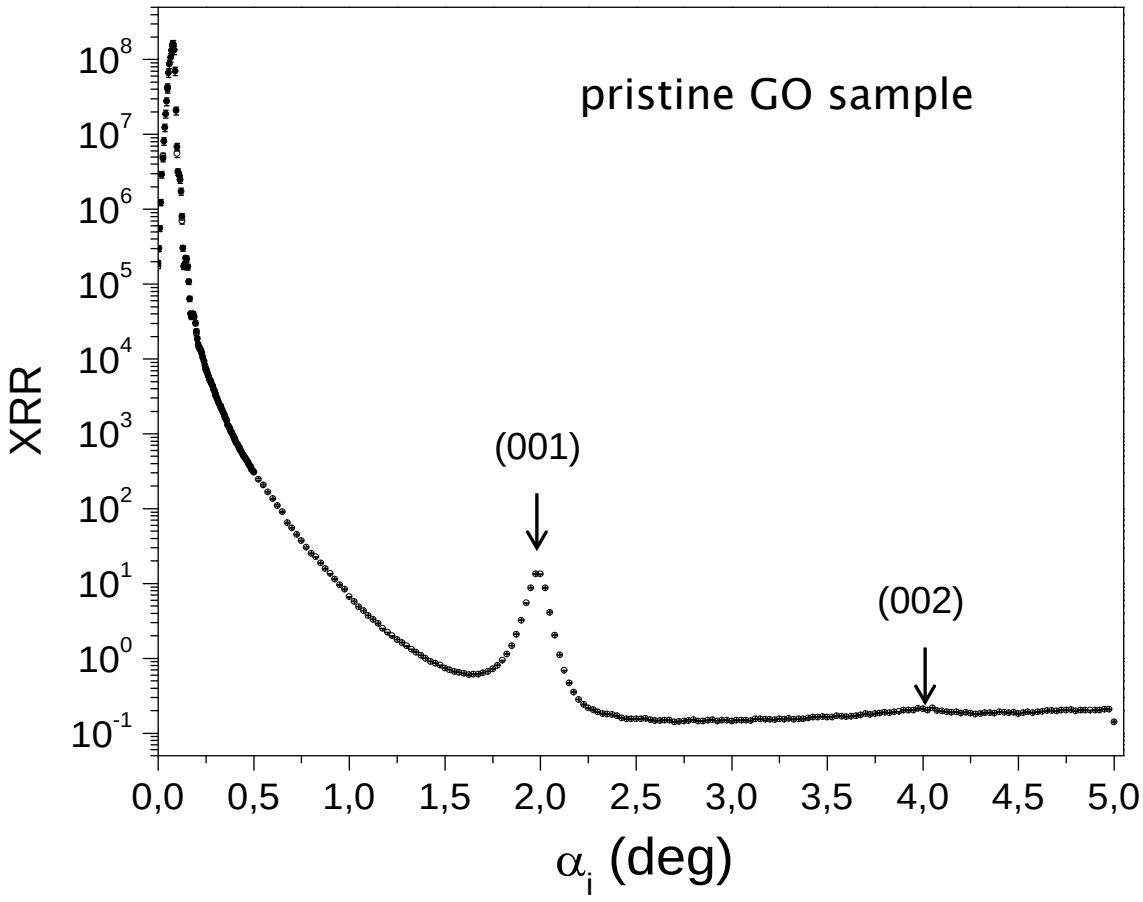
Graphene oxide membrane
formula unit $C_2O_{0.76}H_{0.24}$



Carbon
Oxygen
Hydrogen

in dehydrated GO film
d-spacing is 6.5 Å

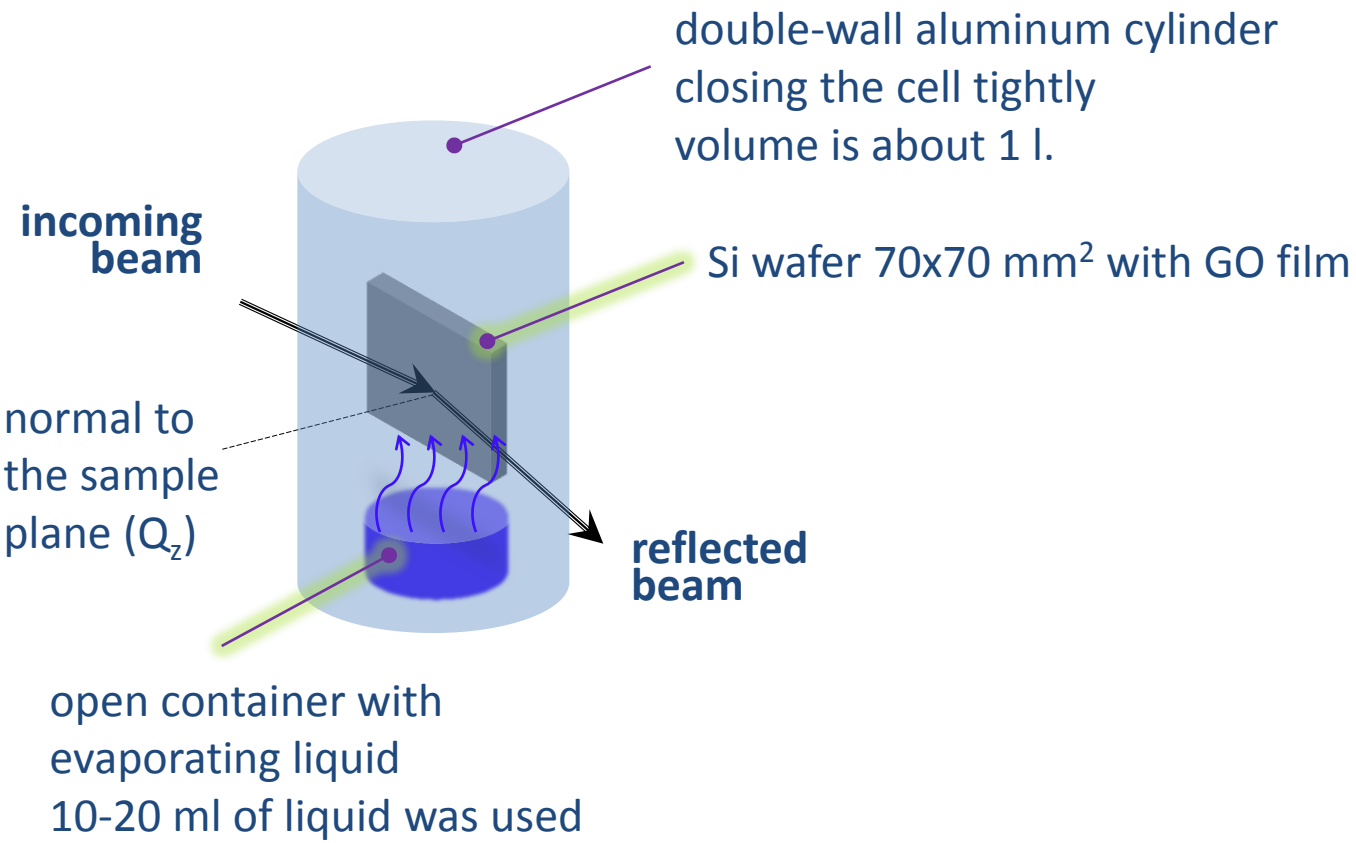
X-ray (synchrotron) reflectivity data



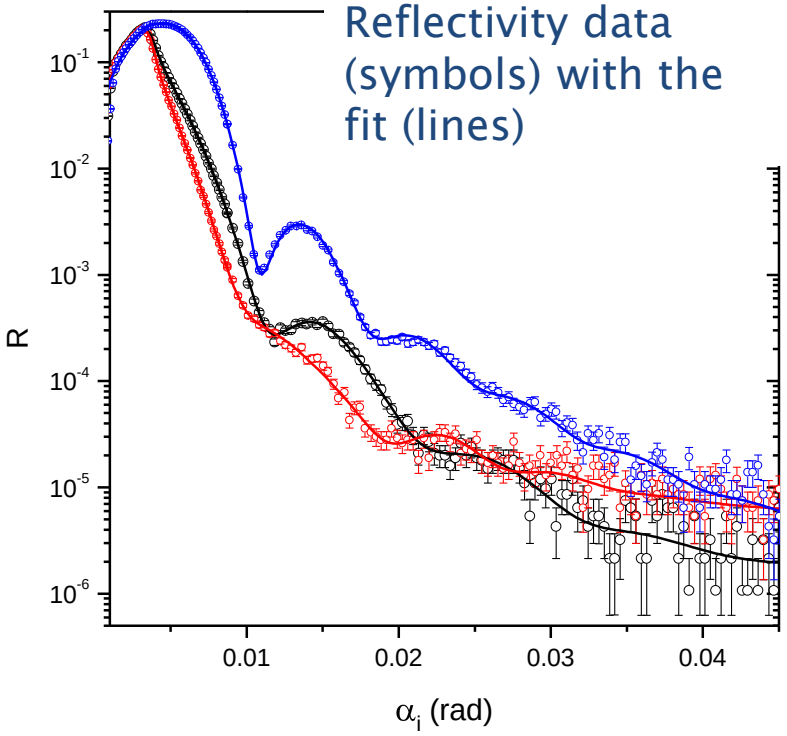
in dehydrated GO film
d-spacing is 6.5 Å

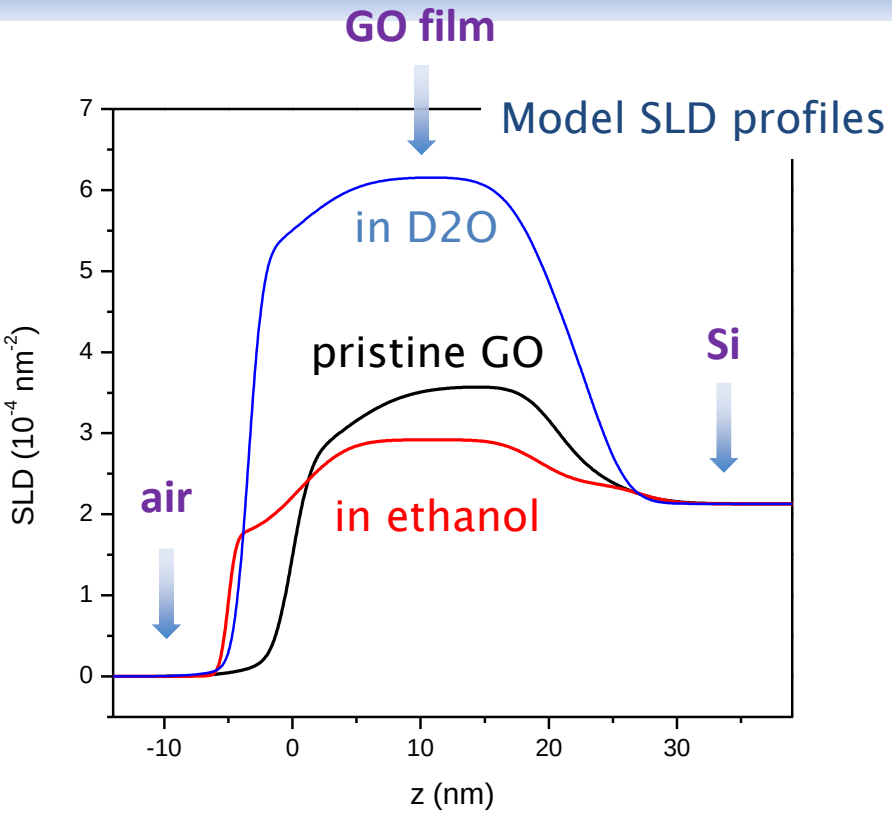
in real pristine sample
d-spacing is 8.3 Å

Sketch of the neutron experiment



Examples of neutron reflectivity data





Output of reflectivity experiment – parameters of the film: thickness, roughness, scattering length density (SLD).

Thickness of dry film 26.7 nm and d-spacing 8.3 Å (from X-rays) imply that sample consists of 32 GO monolayers.

⇨

At any thickness of the film one can deduce d-spacing and consequently cell volume V.

SLD parameter ρ

b – neutron scattering length (NSL) specific for every isotope (see Table)

$B = \sum b_i$ – total NSL of molecules or crystal unit cells consisting of several atoms with corresponding individual b_i ;

V – volume of the GO unit cell.

$$\rho_0 = B_0 / V_0$$

$$\rho_1 = (B_0 + B_x)/ V_1$$

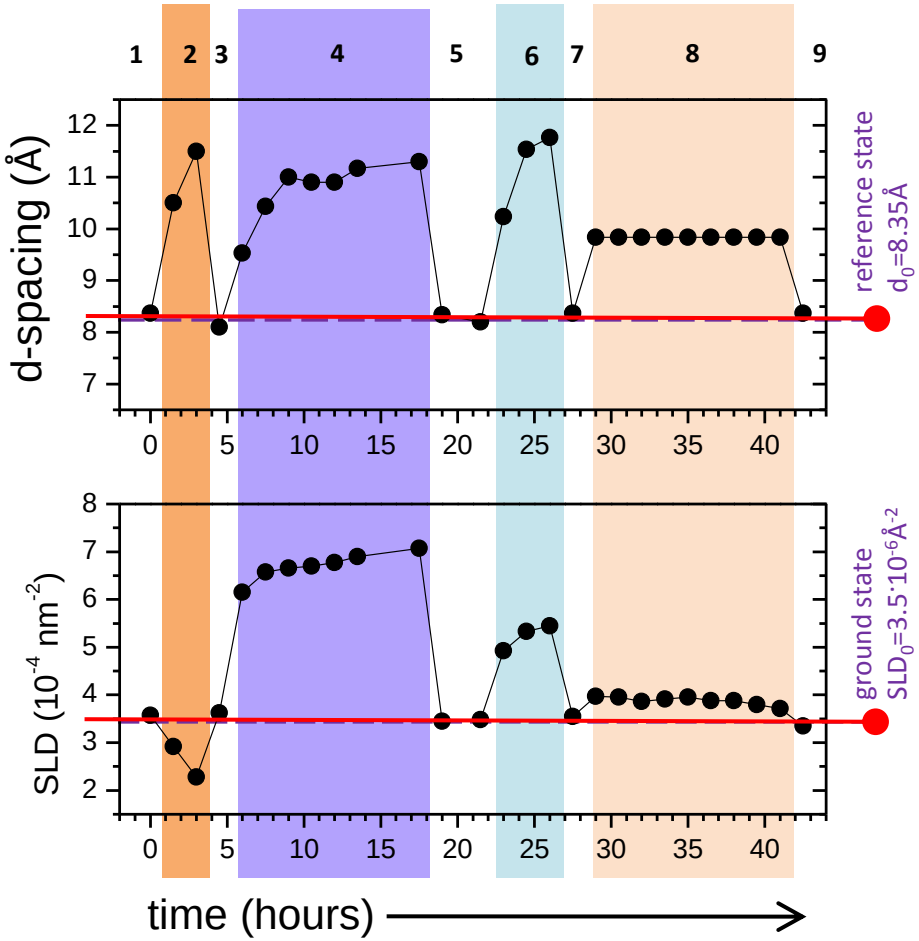
$$B_x = \left(\frac{V_1\rho_1}{V_0\rho_0} - 1\right)B_0 = \left(\frac{L_1\rho_1}{L_0\rho_0} - 1\right)B_0$$

compound	chemical formula	B (10^{-4} Å)
carbon	C	0.6648
oxygen	O	0.5805
hydrogen	H	-0.3740
deuterium	D	0.6674
light water	H_2O	-0.1675
heavy water	D_2O	1.9150
	OH	0.2068
ethanol	C_2H_6O	-0.3339

Values of neutron scattering length $B = \sum b_i$ of relevant atoms and molecules. Compounds with negative B are highlighted.

1. Adsorption of H_2O and ethanol decrease SLD.
2. Adsorption of D_2O increase SLD.
3. Adsorption of D_2O or ethanol increase d-spacing (V).

Experiment-1: ground state



compound	chemical formula	B (10^{-4} Å)
carbon	C	0.6648
oxygen	O	0.5805
hydrogen	H	-0.3740
deuterium	D	0.6674
light water	H_2O	-0.1675
heavy water	D_2O	1.9150
	OH	0.2068
ethanol	C_2H_6O	-0.3339

Values of neutron scattering length B = $\sum b_i$ of relevant atoms and molecules. Compounds with negative B are highlighted.

$\rho_0 = 4.96 \cdot 10^{-6}$ Å^{-2} (dehydrated GO)

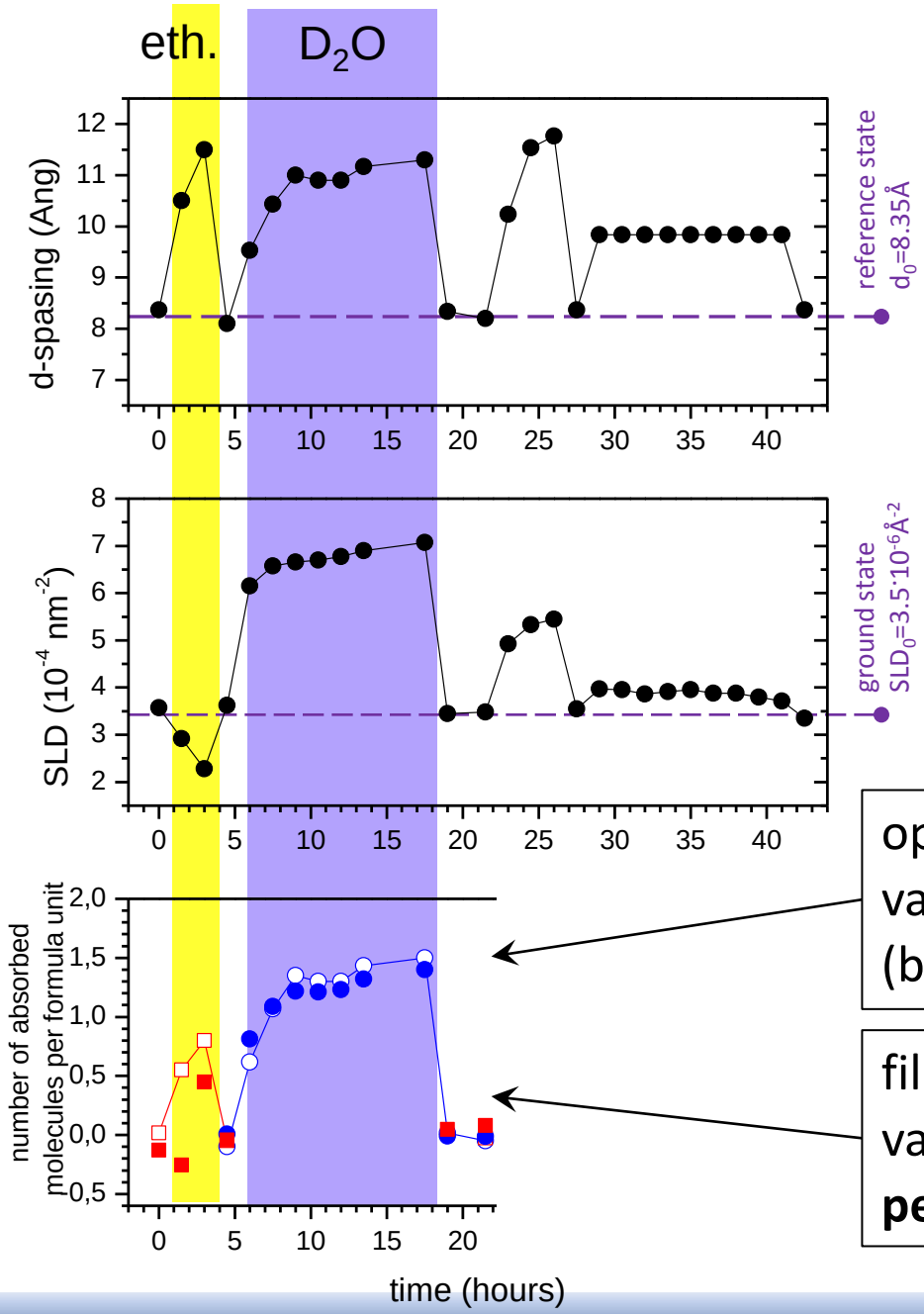
$\rho_{exp} = 3.50 \cdot 10^{-6}$ Å^{-2}

$B_x = -0.142 \cdot 10^{-4}$ Å = 0.85 H_2O

$C_2O_{0.8}H_{0.24} + (H_2O)_{0.85}$

explains increased d-spacing: 8.3 Å instead 6.5 Å

Experiment–2: pure solvents



open symbols – interpretation of d-spacing variation in terms of adsorbed **monolayers** (based on the size of molecules)

filled symbols – interpretation SLD variation in terms of **adsorbed molecules per unit cell** (based on NSL and V)

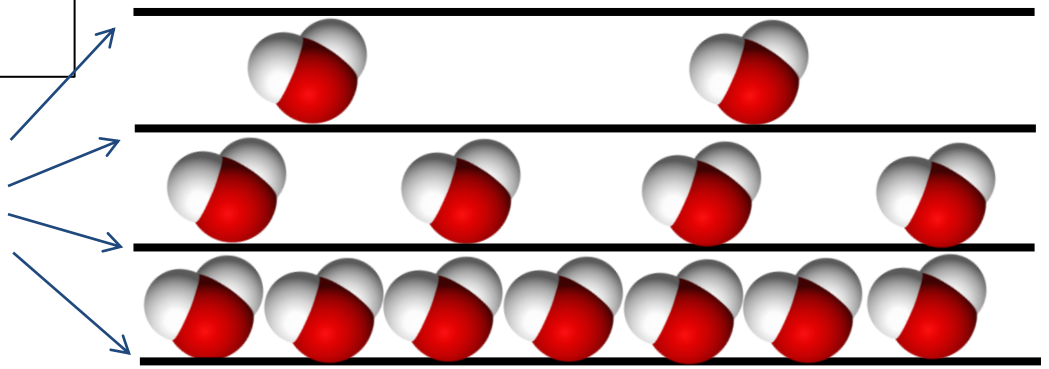
Interpretation

interpretation of d-spacing variation in terms of adsorbed **monolayers**
(based on the size of molecules)
conventional way used to treat XRD data

if d-spacing increased by 2 Å we say that 1 monolayer is intercalated

but what is 1 monolayer?

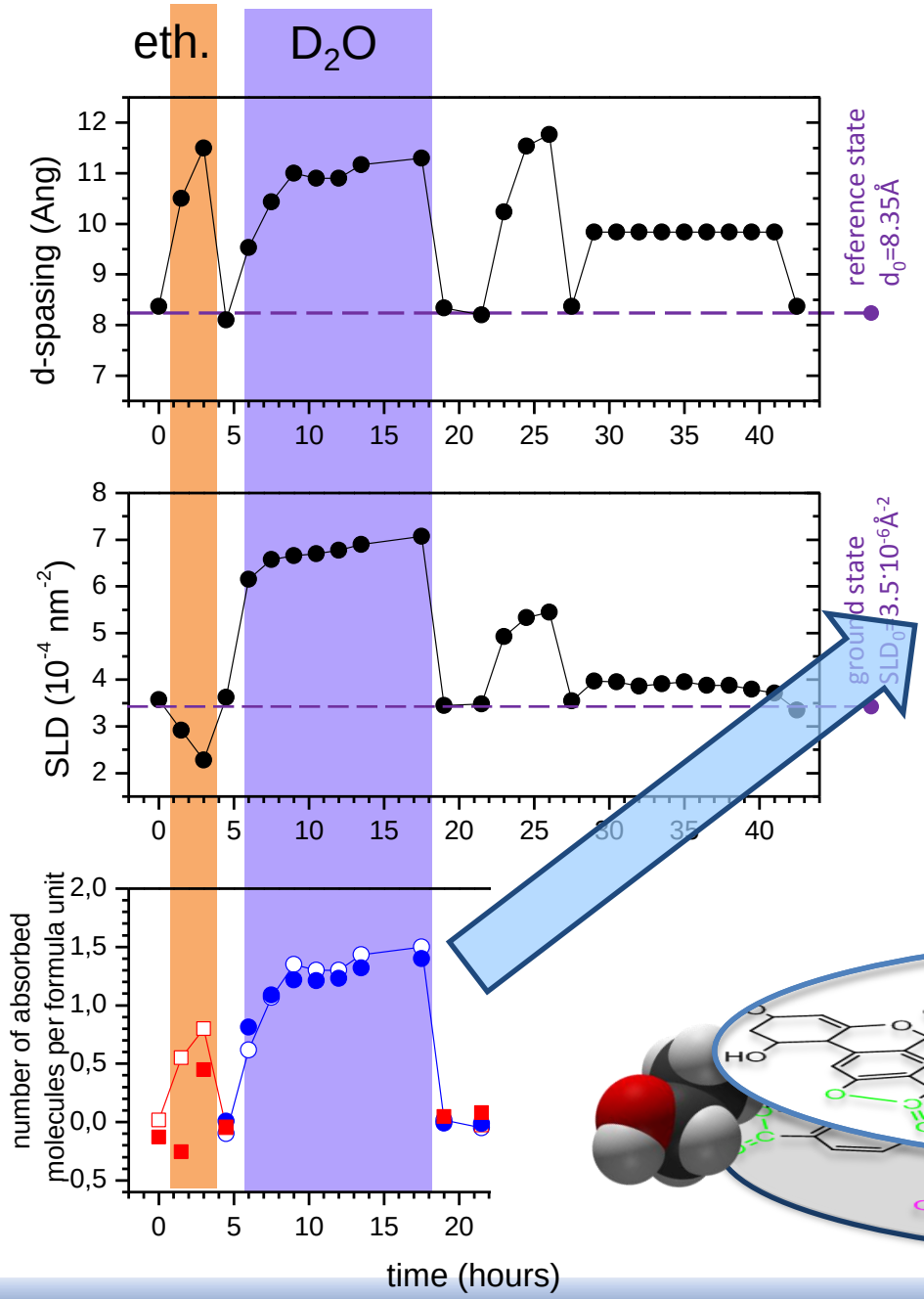
GO flakes



completely lost in case of binary or more complex solvents

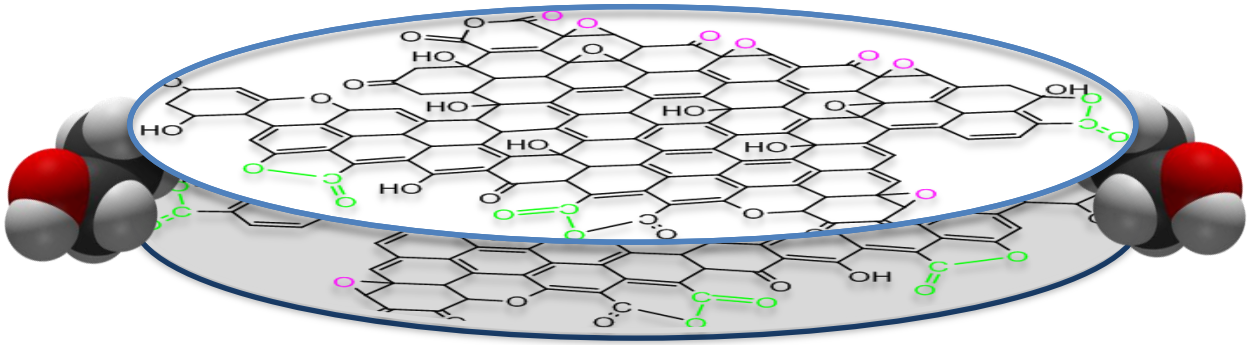
interpretation of SLD variation in terms of **number and type of adsorbed molecules per unit cell,** (based on NSL and V)
advantage of neutron reflectometry

Experiment–2: pure solvents

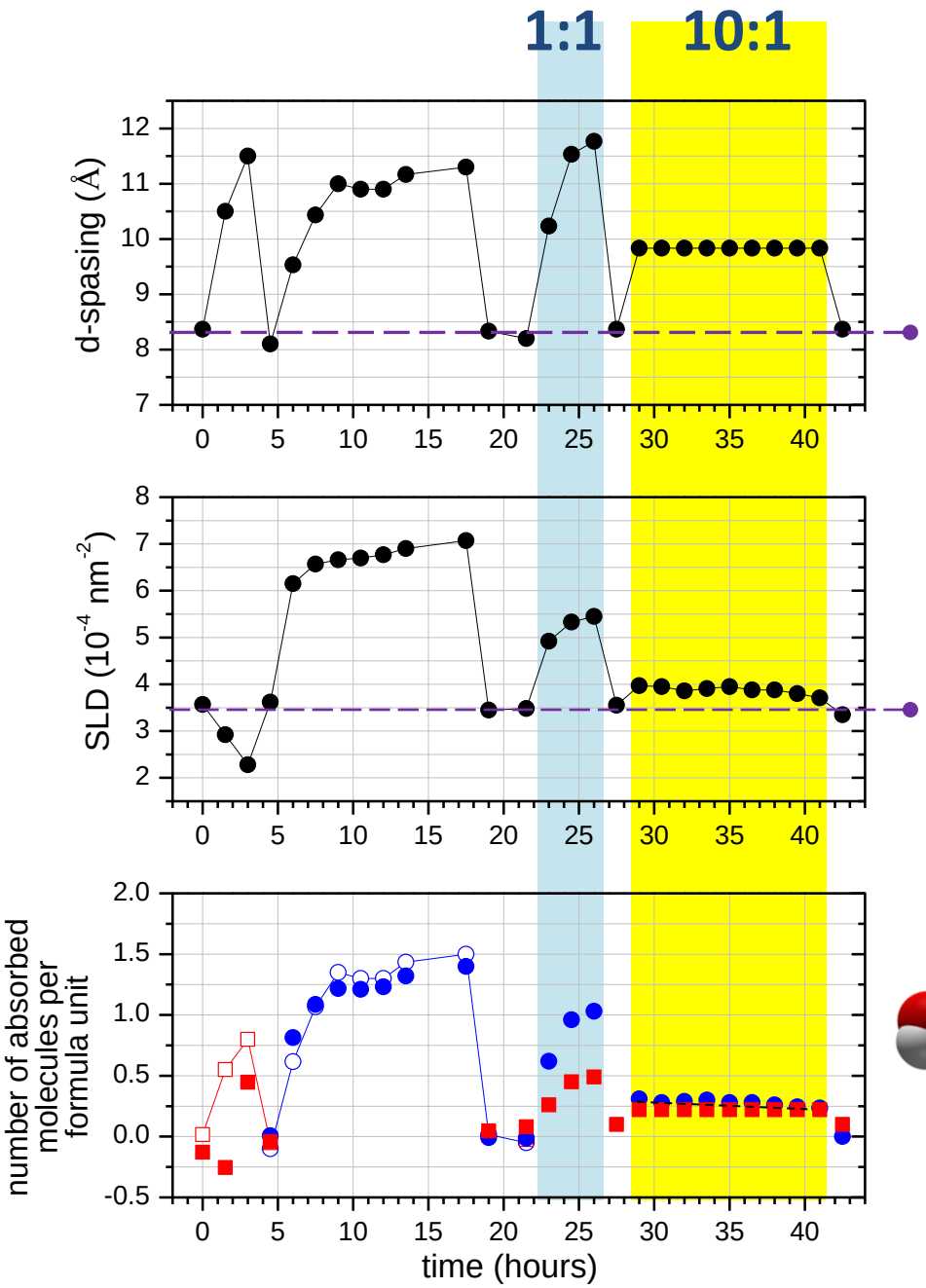


Results:

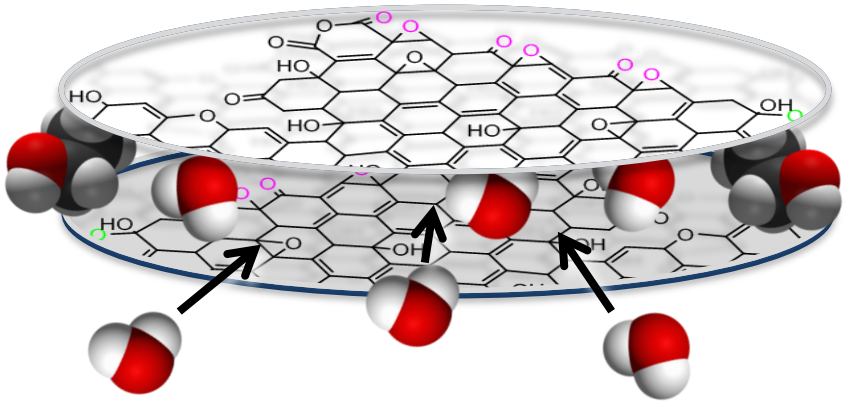
- both solvents penetrate into GO
- lateral density of complete D_2O monolayer (2 Å thick) is 1 molecule per 1 carbon hexagon
- after 4 hours of exposure lateral density of 0.56 ethanol monolayer (4 Å thick) is 1 molecule per 1 carbon hexagon
- in the first 2 hours it is much less



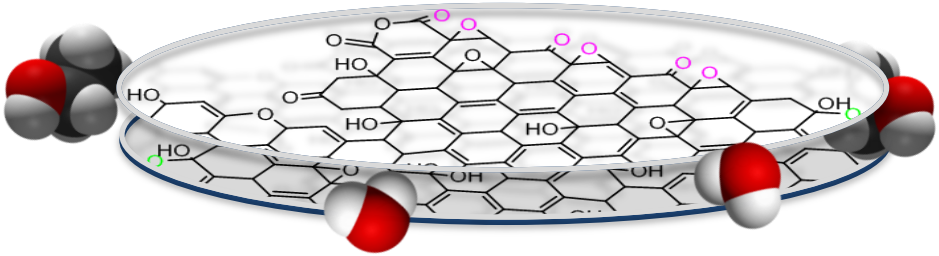
Experiment-3: binary mixtures ethanol:D_2O



1:1



10:1



Summary

Ground state of the GO film:

* 0.85 layer H_2O absorbed at ambient humidity after synthesis;
* this layer remains unchanged even after multiple flashing with D_2O/ethanol vapor

Pure solvents:

* both D_2O and ethanol intercalate into the GO membrane (on top H_2O ground layer)
* lateral density of complete D_2O monolayer is **1** molecule per 1 carbon hexagon; that of ethanol is **0.55** molecule per hexagon
* release and insertion of both molecules are fast processes

Vapor 1:1 **ethanol:D_2O**

Inside GO **0.56:1.01** molecules per formula unit after 6 hours

Vapor 10:1 **ethanol:D_2O**

***** Inside GO **0.2:0.3** after 2 hours and **0.25:0.25** after 10 hours;
* d-spacing is constant

To be continued

Nanoscale, 2014, **6**, 12151

Welcome to Super-Adam at ILL !

Swedish CRG

~ 150 days of beam-time per year are distributed between our internal users.

Proposals: https://userclub.ill.eu/cvng/

Алексей Воробьев: avorobiev@ill.eu