REUNIÓN ANUAL CLUB ESPAÑOL DE MAGNETISMO- CÁDIZ NOVIEMBRE 2022

Magnetic Force Microscopy for **Biomaterials**

MIRIAM JAAFAR miriam.jaafar@uam.es











Thank you...





Agustina Asenjo



Manuel Vázquez



Rafael Pérez del Real



Oksana Fesenko



Eider Berganza



Magnetic Force Microscopy for Biomaterials

Scope

- Introduction
- Co- Virus like particles
- MFM in liquids
- Special MFM probes
- Some applications
- Conclusions





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Motivation: Magnetism & Biology



The importance of characterization

Significant advances in science require the development of new theories, new fabrication techniques, but also accurate characterization methods.



•High spatial resolution

•High sensitivity

Complementary information

How can SFM help in the characterization of biomaterials?



Motivation: Scanning Force Microscopy & Biology

IMAGING and MANIPULATING nanostructures in physiological conditions on a single molecule level.



STUDY MECHANICAL PROPERTIES

A.P.Perrino and R. García







VISUALIZE THE STRUCTURE DYNAMICS AND DYNAMIC **PROCESSES**

Kodera et al. Nature, 2010 Annu. Rev. Biophys. 2013

1,174 ms 1,320 ms 1,467 ms













Current Opinion in Virology 2016



Scanning Force Microscopy





Motivation: SFM in magnetism

MAGNETIC FORCE MICROSCOPY

Appl. Phys. Lett. **50**, 1455 (1987) J. Appl. Phys. **62**, 4293 (1987)





- •Low cost technique.
 - •Lateral resolution better than 20nm
- •Additional information (3D topo,...)
- •To study individual elements
- Magnetization reversal process



Topography Elect

Electrostatic properties

Magnetic properties

M. Jaafar et al. Beilstein J. Nanotechnol. 2011, 2, 552–560







Magnetic Force Microscopy: Dynamic modes

DYNAMIC MODES



ທ_{ູ sp} ພູ Driving frequency

MFM signal = frequency shift



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 $F_{magnetic} = m_{tip} \bullet VH_{sample}$

ω/ω_

1,5

Magnetic Force Microscopy: Dynamic modes

DYNAMIC MODES



¹⁰⁰ nm Long range
 ¹⁰ nm Medium range
 ¹ nm Short range



Second pass: MFM



First pass: Topography

Motivation: MFM from magnetism to biomagnetism

Classical ferromagnetic samples

Ferromagnetic domains- Domain Wall movement

Frontiers of magnetic force microscopy O. Kazakova et al. J. Appl. Phys. 125, 060901 (2019) hin filme

ures→ CHALLENGES.... Data storage -Antiferromagnets -Spin-caloritronics -Topological insulators Ono et al. Science 2000 -2D materials **Nanoparticles** -Biomaterials $u \cdot H = 0 mT$ (HZ) 8f S. P. Pa Science 32 Resolution C. Moya et al. Nanoscale, 2015.7. 17764-17770 **Molecular magnets** ons Sensitivity DOI: 10.102 13) Nano Le Low-Temperature Magnetic Force Microscopy $20 \, \text{m}$ Magnet-Based Microarrays Different environments

Quantitative information

PROBE-ENGINEERING

Customized probes are used to perform very specific tasks and push the limits of commercial MFM systems \rightarrow

- ✓ to achieve a higher resolution
- ✓ to reduce/increase probe—sample interaction → High sensitivity but without disturbing the magnetic structure of the samples
- ✓ to be able to combine different scanning modes.
- ✓ Working in different environments (liquids)



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NON STANDARD OPERATION MODES

- ✓ to achieve a higher resolution: measure as close as possible
- \checkmark to be able to combine different scanning modes \rightarrow Complementary information
- ✓ Working in different environments (liquids)



Imaging biological samples under physiological conditions by Magnetic Force Microscopy





Imaging biological samples under physiological conditions by Magnetic Force Microscopy



Experiments in liquids (*Low Q*)

Biological conditions

For certain samples, measuring in physiological media will be critical



C. Carrasco et al., PNAS. 2009

Desiccation effects on ϕ 29 viruses



nanoreactor Aljabali, A. A. A.; Sainsbury, F.; Lomonossoff, G. P.; Evans, D. J.. Small 2010, 6 (7), 818-821.

To move closer toward the development of virus like particles (VLPs) for such applications as magnetic hyperthermia treatments, it is essential to investigate the magnetic moment of individual particles because they are required to be easily manipulated by magnetic fields.

Virus

suggested as

nanometric-sized



In collaboration withc Prof. David Evans, Dr. P.J. de Pablo



Is it possible to analyze the metallic cluster grown inside the virus capsid with MFM?

capsids have been

templates for building up

promising

magnetic



- Electron microscopy imaging provides a comparison between empty (eVLPs) and loaded viruses (Co-VLPs) by the different contrast inside the particles
- Unmodified particles were invisible under transmission electron microscopy (TEM).
- The TEM data suggested that the virus cages are completely filled with metallic cobalt



M. JAAFAR et al., ACS Appl. Mater. Interfaces. 6, pp. 20936 – 20942 (2014).



Magnetic nanoparticles



Control Experiment: CoNps are of similar size \rightarrow we expected to find similar magnetization values in the case of solid filling of Co-VLPs.

Co-Virus like particles:





Variable Field Magnetic Force Microscopy Measurements

M. JAAFAR et al., ACS Appl. Mater. Interfaces. 6, pp. 20936 – 20942 (2014).



Magnetic nanoparticles





Q(air)~200 Q(vacuum)~ 10000



Co-Virus like particles:

Co-VLP signal is ~8 times lower than that of the commercial CoNP, indicating that the amount of the magnetic Co inside virus particles is less than expected. -Co-VLPs have about 8 times less Co than commercial Co-Nps??.







Biological specimens can dramatically change their properties when studied far away of physiological conditions→ it is important of being able to develop MFM measurements in liquid media

- Protein shells are severely affected by dehydration.
- In particular, virus structures are prone to collapse
 - The difference between heights observed for
 collapsed Co-VLP and eVLP (~9 nm) establishes a
 top limit for the size of the cobalt cluster inside the viruses.



M. JAAFAR et al., ACS Appl. Mater. Interfaces. 6, pp. 20936 – 20942 (2014).



MFM in liquids



- The difficulty in developing MFM for detecting magnetic interactions in liquids as a consequence of the high damping forces on the cantilever, which are several times greater than in air.
- This is the origin of the low quality factor Q of the cantilever resonance characteristic of liquid measurements.
- This low Q results in a significant loss of sensitivity in the MFM signal.

P. Ares, **M. Jaafar**, A. Gil, J. Gómez-Herrero and A. Asenjo, **Small** 11 (36) 4731-6 (2015)



MFM in liquids



Tip sample distance

HV signals are the cleanest ones, whereas the liquid signals are the noisiest.

But... it can be observed that in both vacuum and liquid, where the attractive forces are much lower than in air, the <u>magnetic signal can be detected</u> <u>with the tip very close to the sample (tip sample distances <10 nm), in contrast to air conditions</u>

P. Ares, **M. Jaafar**, A. Gil, J. Gómez-Herrero and A. Asenjo, **Small** 11 (36) 4731-6 (2015)





MFM in liquids. Fe₃O₄ nanoparticles



Small 11 (36) 4731-6 (2015)

Cubic NPs, 30 nm side, courtesy of P. Morales, ICMM-CSIC

Volume (nm³)

To improve the sensitivity we need specific cantilevers, NOT OFFERED by the companies

$$\delta \omega = -\frac{1}{2} \frac{\omega_0}{k} \frac{\partial F}{\partial z}$$
Higher sensitivity
requires ω_0 / k as high

R. García and R. Pérez, Surface Science Reports (2002)

 a_{2} μ_{0}

The noise increases for softer cantilevers

$$\sqrt{\frac{1}{kQ}}$$

The adhesion of the magnetic coating to the AFM probe is and additional handicap



29/7 ~ 4



Custom made MFM probes

Different trends can be identified:

(i) customized *magnetic coatings*, where the magnetic properties of the material are varied

(ii) probes with magnetic *adhered structures*, such as Fe-filled carbon nanotubes (CNTs) or magnetic beads

(iii) MFM probes with *fabricated nanostructures*

Wolny et al., J. Appl. Phys. 108, 1 (2010)

Belova et al., Rev. Sci. Instrum. 83, 93711 (2012).

Corte-León et al., J. Magn. Magn. Mater. **400**, 225–229 (2016)

O. Iglesias – Freire, et al .Beilstein J. Nanotechnol., 7, 1068–1074 (2016)

Puttock et al., IEEE Trans. Magn. 53, 1–5 (2017)







Magnetic nanorods growth by Focused Electron Beam Induced Deposition onto non magnetic probes





De Teresa et al. J. Phys. D: Appl. Phys. 49 (2016) 243003









J.M. de Teresa, C. Magén, J.P. Navarro

3D nanorods have been fabricated using commercial Helios Nanolab 600 and 650 Dual Beam systems

Precursor gases: Co2(CO)8 and Fe2(CO)9 Electron beam voltage in the range of 3 to 30 kV.

Range of current: 50-100 pA (Co) and 43-86 pA (Fe)



Magnetic nanorods growth by Focused Electron Beam Induced Deposition onto non magnetic probes



Material Geometrical parameters Different cantilevers









J.M. de Teresa, C. Magén, J.P. Navarro







Custom made **BIOLEVER MFM probe**

Fe Nanorods



M. Jaafar et al. Nanoscale, 2020, 12, 10090



Custom made **BIOLEVER MFM probe**

Fe Nanorods



CEMAG Club Español de Magnetiano

Custom made BIOLEVER MFM probe

Core-Shell Nanorods





Minimizing the degradation of the magnetic properties due to surface oxidation

> **M. Jaafar** et al. Nanoscale, 2020, 12, 10090



High aspecto ratio: advantages

INCREASING THE COERCIVE FIELD \rightarrow

The high-aspect ratio achievable in FEBID nanorod tips makes them magnetically harder than the commercial ones, reaching coercive fields higher than 900 Oe.

Magnetic Field (Oe)

LOWER VAN DER WAALS INTERACTION \rightarrow

It allows measuring the magnetic properties of the sample **much closer to its surface**



CONFINED MAGNETIC STRAY FIELD→

The shape of the nanorods produces a very confined magnetic stray field, whose interaction with the sample is extremely localized and perpendicular to the surface, with negligible in-plane components.



0

M. Jaafar et al. Nanoscale, 2020, 12, 10090



FePd multilayer REFERENCE SAMPLE

The frequency shift is proportional to the magnetic moment of the tip.



CUSTOMIZATION OF THE TIP STRAY FIELD



Some challenges in MFM: Biomaterials

Sub-100 nm diameter nanodots (magneto-mechanical actuators)

In collaboration with M Goiriena-Goikoetxea, A García Arribas, M.L. Fdez- Gubieda





M Goiriena-Goikoetxea, et al. Applied Physics Reviews 7 (1), 011306 (2020)



Nanoscale, 2017,9, 11269-11278 Nanoscale, 2020, 12, 18646-18653 Magnetic Nanoheaters (Multishell Nanoarchitecture)

In collaboration with

G. Singh, C. Tejera, S. Gallego, D. Martínez – Martín



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M Goiriena-Goikoetxea, et al. Applied Physics Reviews 7 (1), 011306 (2020)



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In collaboration with

M. Goiriena – Goikoetxea, A. García – Arribas, K. Y. Guslienko. M.L. Fdz- Gubieda.



Permalloy (Py) sub-100 nm diameter particles (nanodots) with *no uniaxial* magnetic anisotropy or DMI

The nanodots possess a domed shape



Fabrication: Hole Mask Colloidal Lithography



6. Oxygen plasma etching 7. Permalloy sputtering

8. PMMA removal



M. Goiriena-Goikoetxea, ..., **M. Jaafar**...et al. Nanoscale,9, 11269-11278 (**2017**)









E. Berganza, **M. Jaafar** et al. Nanoscale, 2020, **12**, 18646-18653



VORTEX vs SKYRMIO











E. Berganza , M. Jaafar et al. Nanoscale, 12, 18646-18653 (2020)
E. Berganza, J.A. Fdz- Roldán, M. Jaafar et al. Sci. Rep. 12, (2022) 3426





CEMAG Club Español de Magnetismo

- Non-chiral hedgehog skyrmions are induced and further stabilized by the magnetic field coming out from the MFM probe in soft magnetic nanodots in absence of DMI and perpendicular anisotropy. High resolution MFM imaging and VF-MFM are used to characterize them.
- Analytical calculations and micromagnetic simulations confirmed the existence of metastable Néel skyrmions in permalloy nanodots even without external stimuli in a certain size range.





E. Berganza , M. Jaafar et al. Nanoscale, 12, 18646-18653 (2020)
E. Berganza, J.A. Fdz- Roldán, M. Jaafar et al. Sci. Rep. 12, (2022) 3426



Some challenges in MFM: BIOMATERIALS

Non standard operation modes

Multifrequency: Bimodal MFM

Magnetic Dissipation Force Microscopy



Gisbert V.G., C. Amo, **M. Jaafar** et al. Nanoscale 13 , 2026-2033 (2021)

M. Jaafar, A. Asenjo. Appl. Sci. 2021, 11, 10507.



M. Jaafar et al. Nanoscale, 2016, 8, 16989–16994

BIMODAL MFM

Quantitative imaging in MFM

Bimodal MFM has recently been used for **quantitative imaging** with high-spatial resolution

Gisbert V.G., Amo C.A., **Jaafar M**., Asenjo A., Garcia R. Nanoscale 13 , 2026- 2033 (2021)

Sub -Surface magnetic contrast









MAGNETIC PROPERTIES



Non Magnetic material

800



Bimodal MFM: Sub-Surface contrast





This contrast seem to be a nanomechanical effect that enable the identification of the magnetic properties of the particles (similar than C. Dietz et al, Nanotechnology 22 (2011) 125708)



Work in progress

In collaboration with of M. L. Fernández-Gubieda's group. UPV

MAGNETIC DISSIPATION FORCE MICROSCOPY

•Magnetic dissipation Force Microscopy studies tip-induced magnetization changes in the sample.





Conclusions

Non standard MFM imaging is a useful technique to study emerging Bio magnetic materials and structures (often extremely demanding in terms of resolution, sensitivity, and physical environment).

We have studied magnetic **nanoparticles in liquid**. We can distinguish the magnetic domains in this kind of samples.

Custom made bio-MFM probes are the best option to **improve the quality** of the magnetic signal in liquid.

All these examples demonstrate why MFM remains a powerful characterization tool.



MFM in liquids Small 11 (36) 4731-6 (2015)



Custom made MFM probes: Nanoscale, 12, 10090 (2020)



Nanoscale,8, 16989-16994 (2016) Nanoscale,9, 11269-11278 (2017) Nanoscale, 12, 18646 (2020) Nanoscale 13, 2026- 2033 (2021) Sci. Rep. 12, 3426(2022)



In collaboration with



Dr. Agustina Asenjo Dr. Eider Berganza

Prof. M Vázquez Dr. Rafael P. del Real Dr. Oksana Fesenko















Prof. J. Gómez-Herrero Dr. P. Ares

MAT2016-76824-C3-1-R



MDM-2014-0377



Prof. J. M. de Teresa Dr. C. Magén Dr. J.P. Navarro







THANK YOU FOR YOUR ATTENTION

miriam.jaafar@uam.es



