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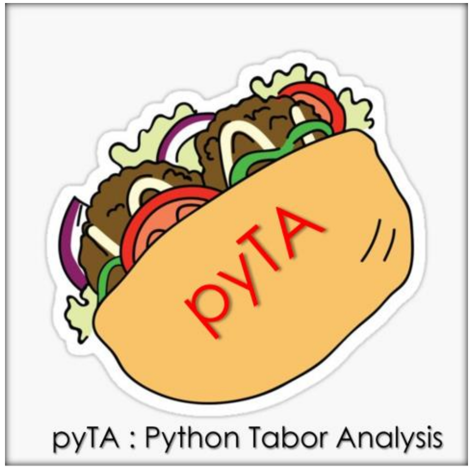
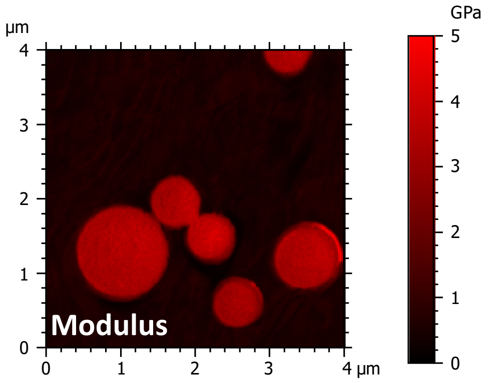
Study of the mechanical and viscoelastic properties of complex heterogeneous polymeric systems at the nanoscale and automated population identification

Pierre Nickmilder

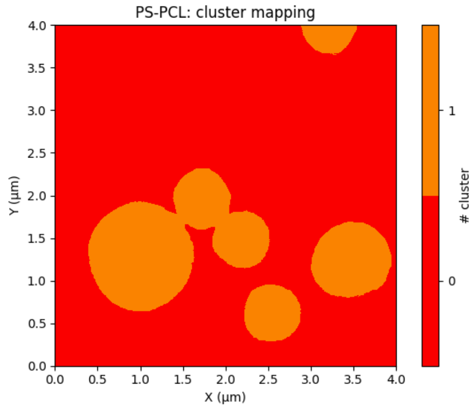
Forum des microscopies à sonde locale 2023 - 04-07 avril - Obernai

One year ago …

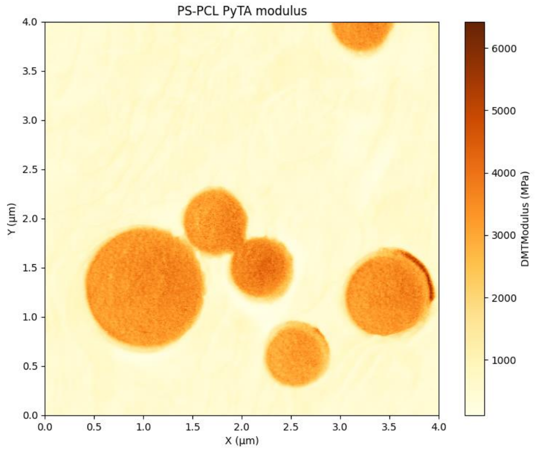




Sorting of the data
Unsupervised



Tabor

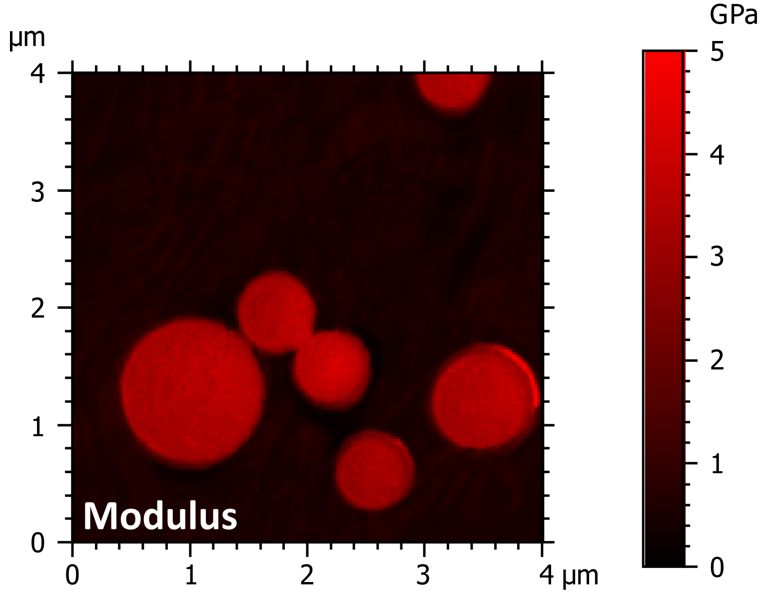


No data type limitation

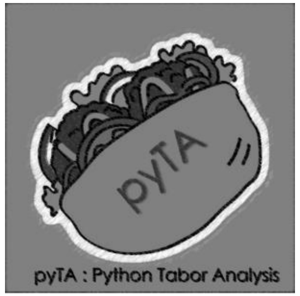
Today …

Aim

- Automatised multidimensional analysis
- Machine Learning
  - Clustering of the data (Kmeans, GMM)
  - Force curve analysis (Tabor, R^2)



« **Py**thon Code for Approach and Retract force curve analysis of Organic and hybrid Soft materials »



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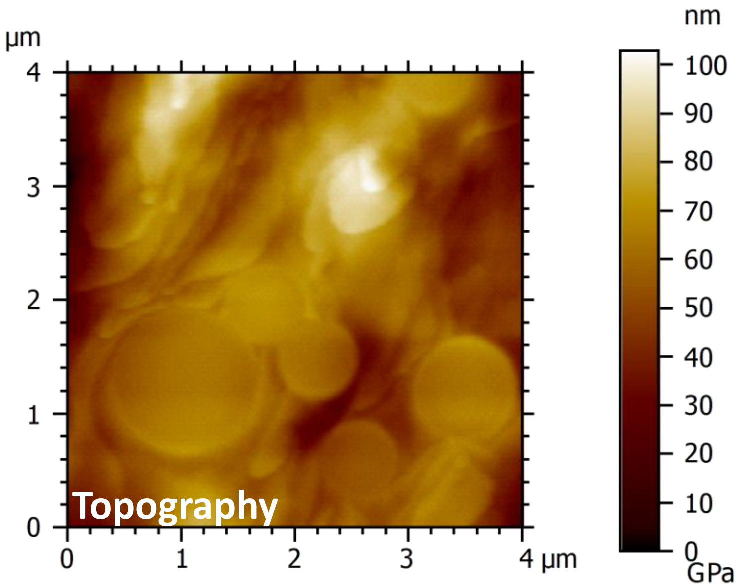
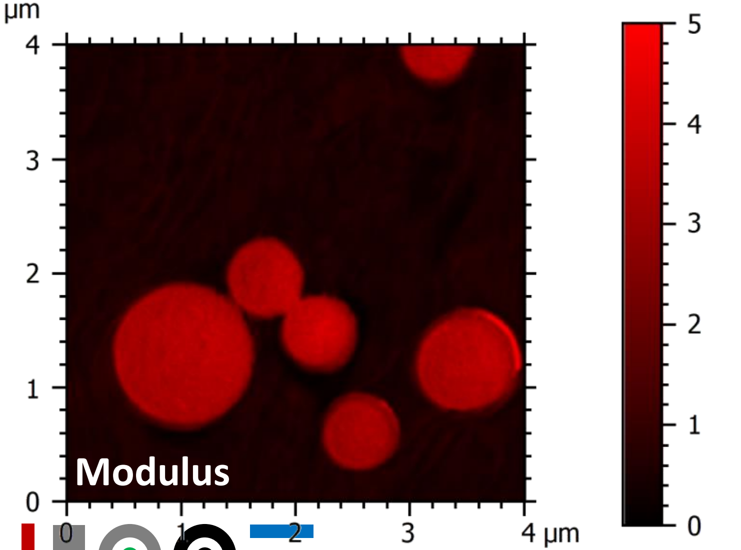
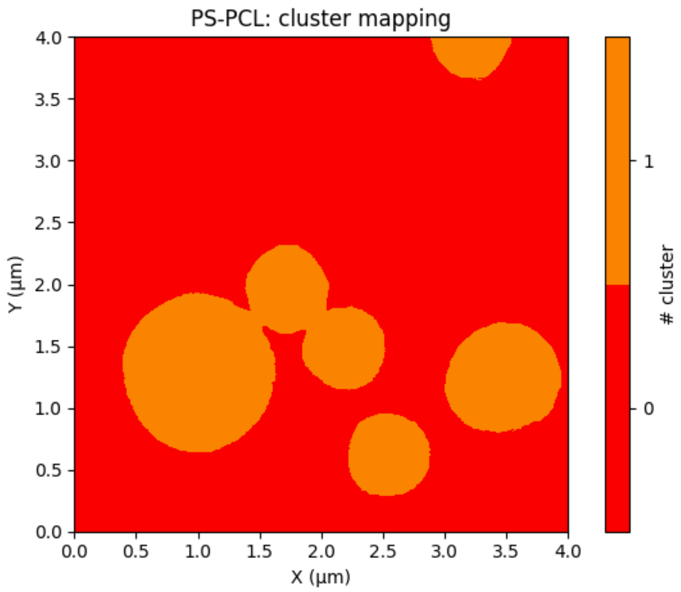
Test sample PS-PCL

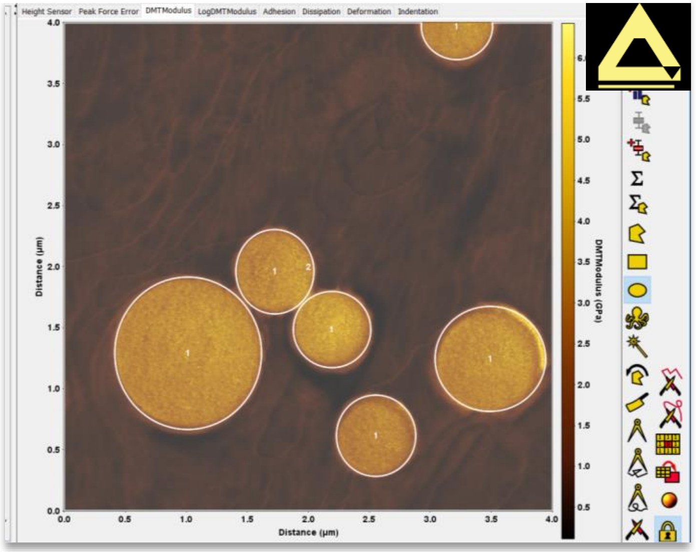




ROI selection



Automatized Analysis



« by hand » analysis

What happens on a more complex sample?

High Impact Polypropylene (HiPP)

Industrial nanocomposite samples, used in the manufacture of bumpers

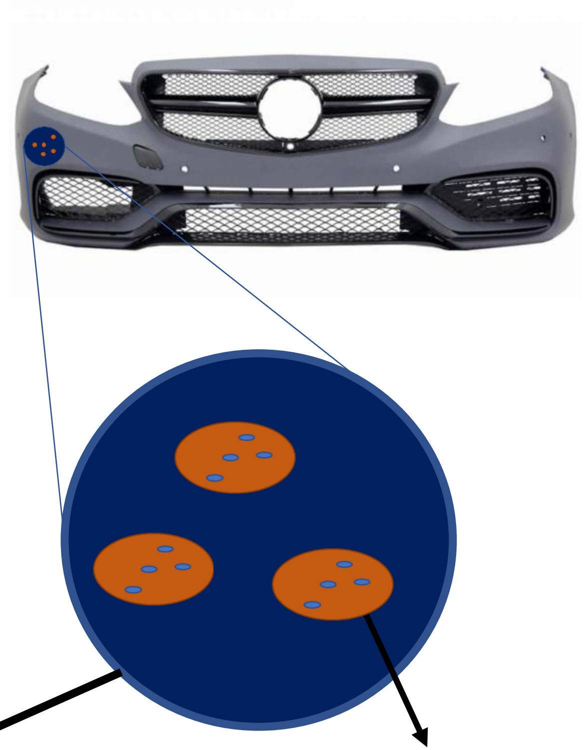
Inclusions **dissipate energy**

Importance of the **morphology**
Importance of the **charge crystallinity control**

Mechanical and viscoelastic nanoscale analysis

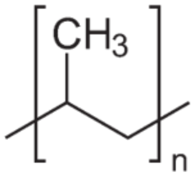
PFT

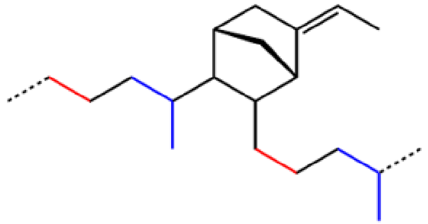
nDMA



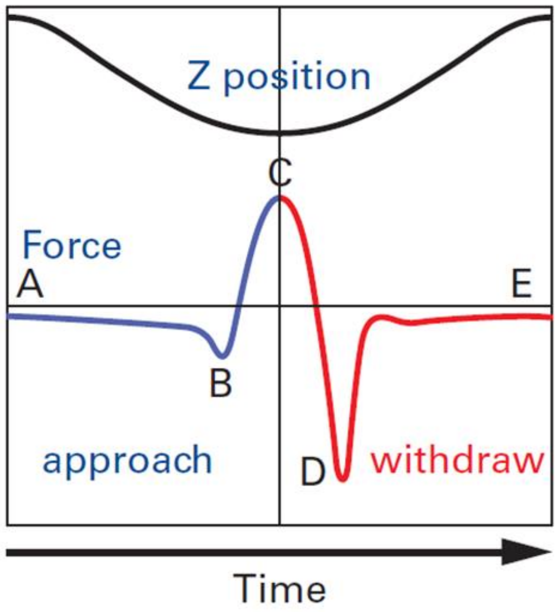
PP Matrix

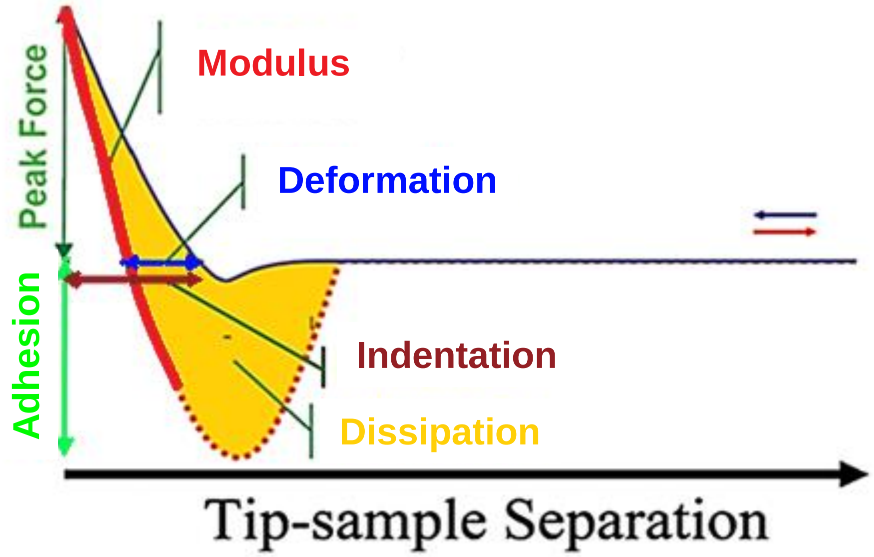
PER Inclusion





Mechanical properties: Peak Force Tapping (PFT)

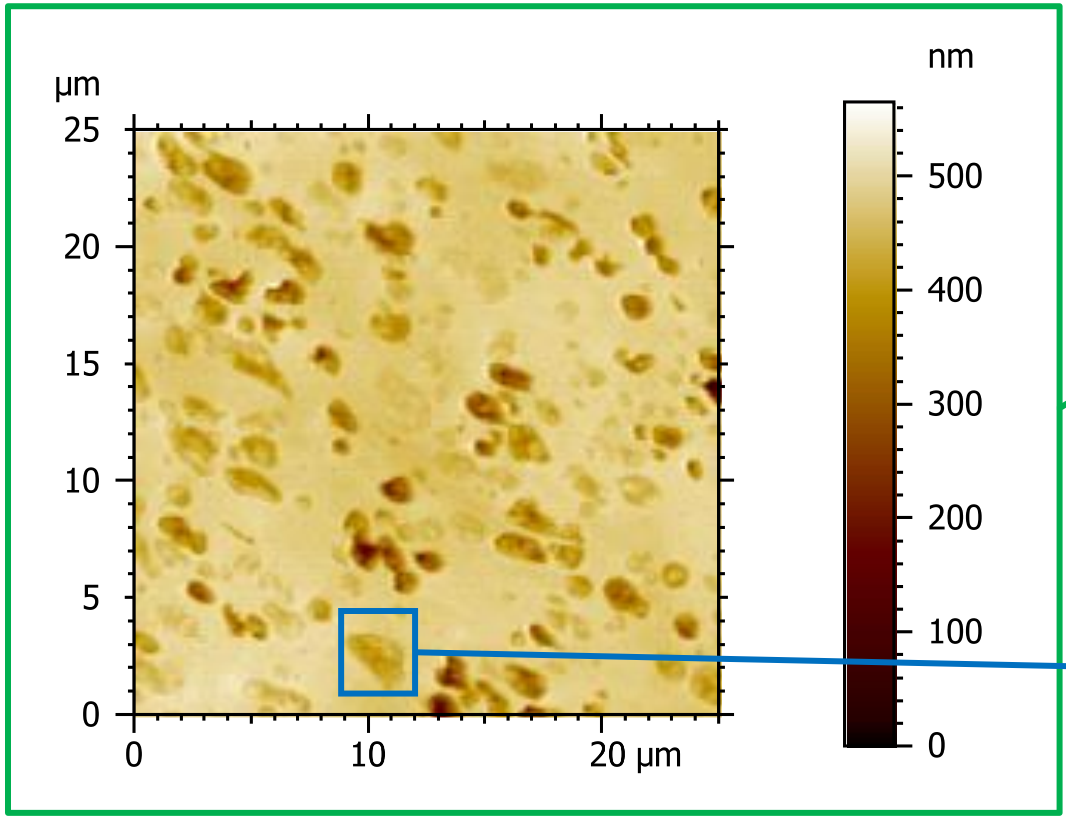


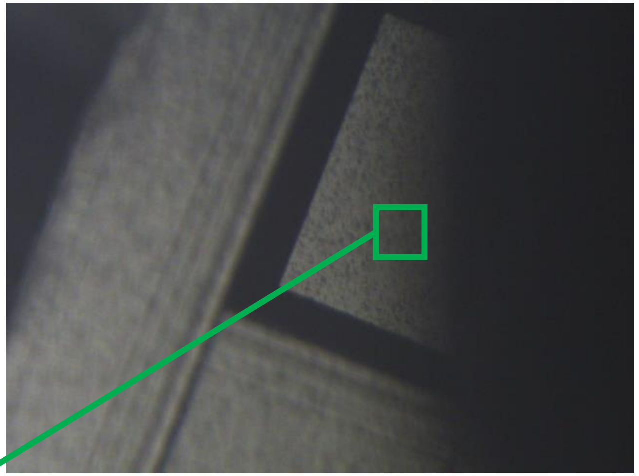


A. Approach VDW forces (attraction)
B. Snap-in
C. Contact Coulomb forces (repulsion)
D. Snap-out Capillary forces (attraction)
E. Retract

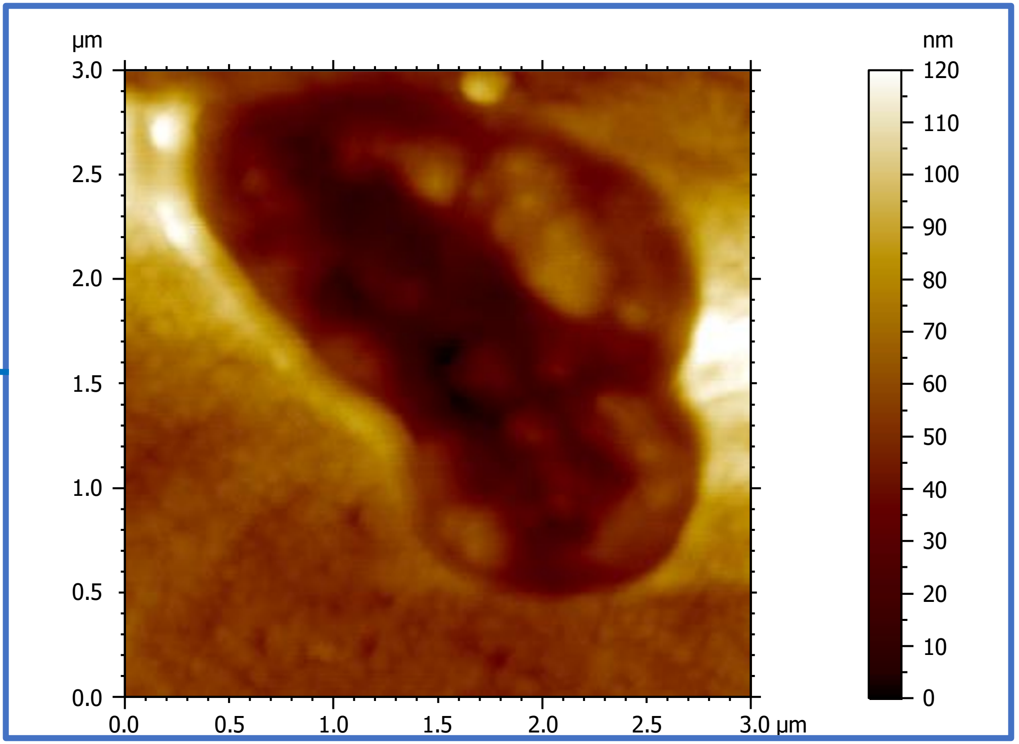
Cartography of mechanical properties
1 force curve for each pixel (.pfc)

HiPP

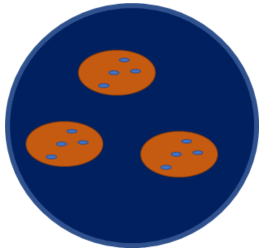




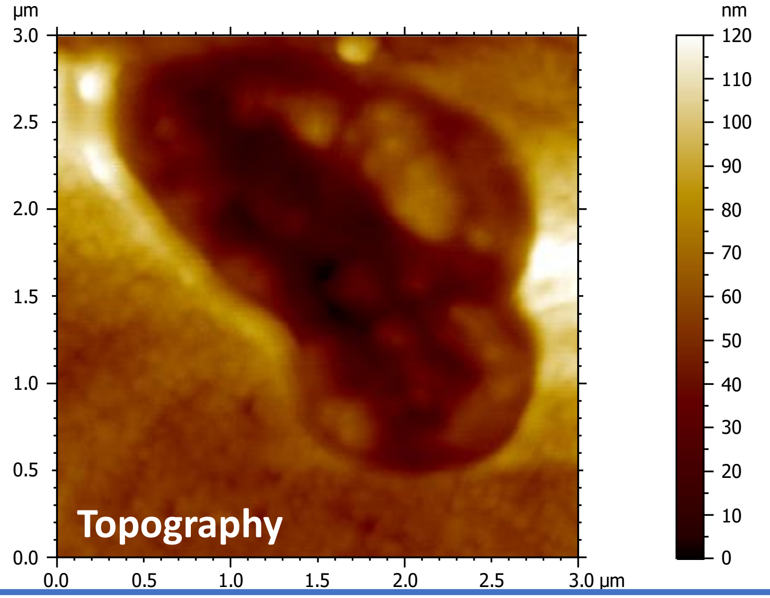
Cryomicrotomed sample

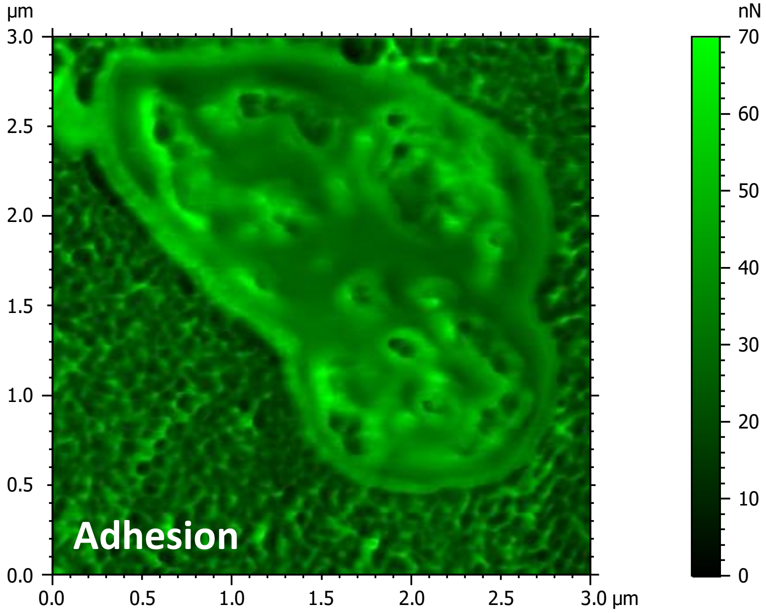


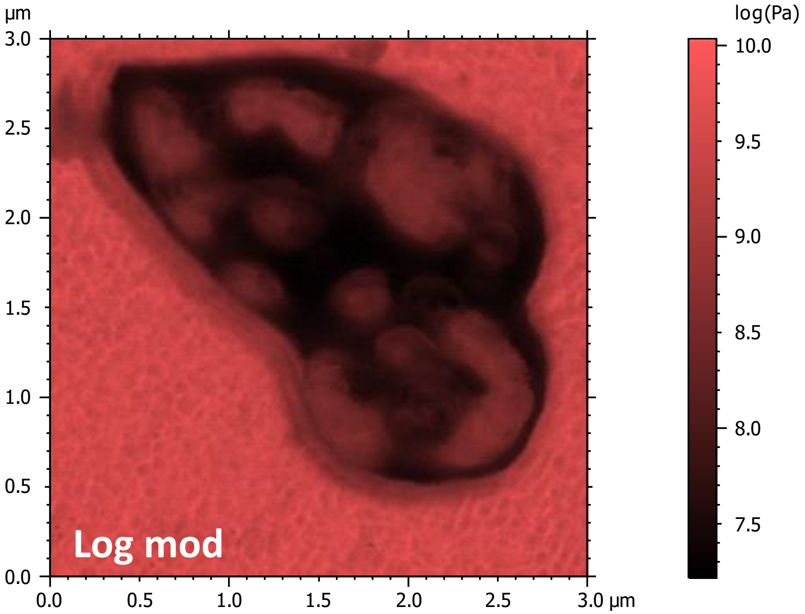
Good charge dispersion

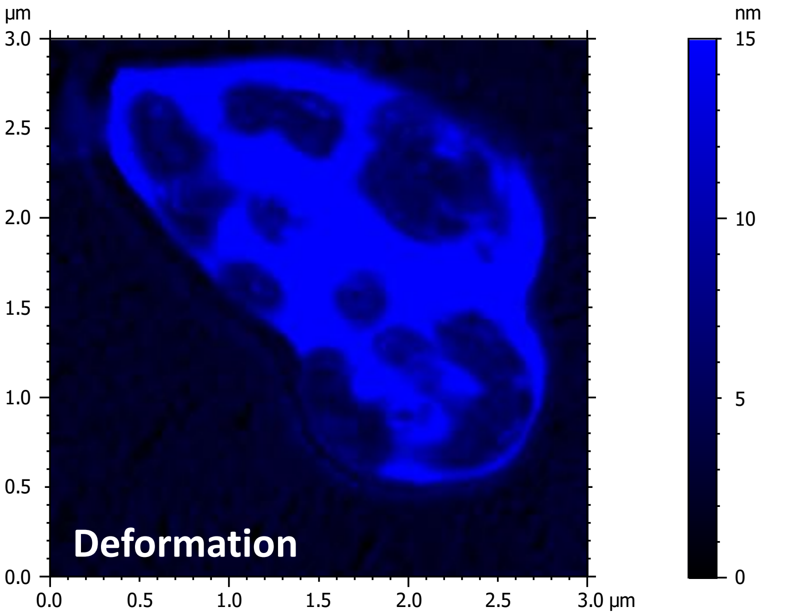


Peak Force Tapping



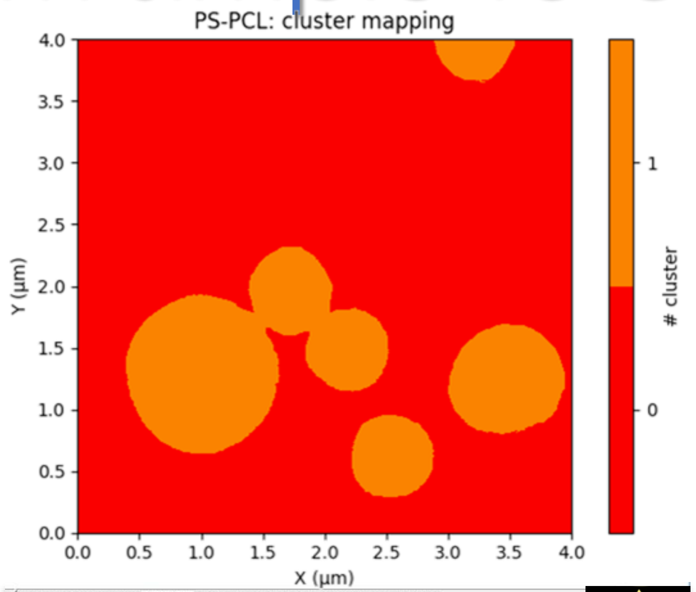


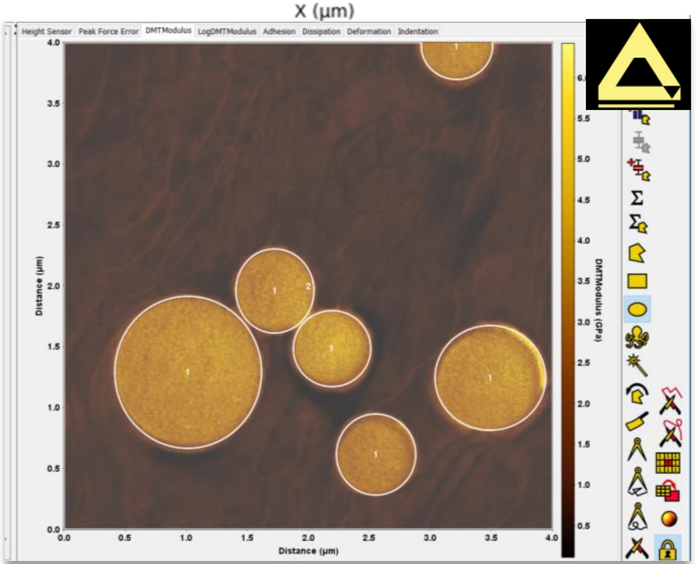


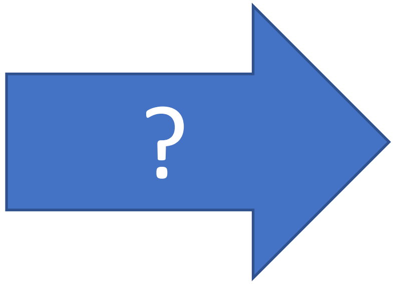


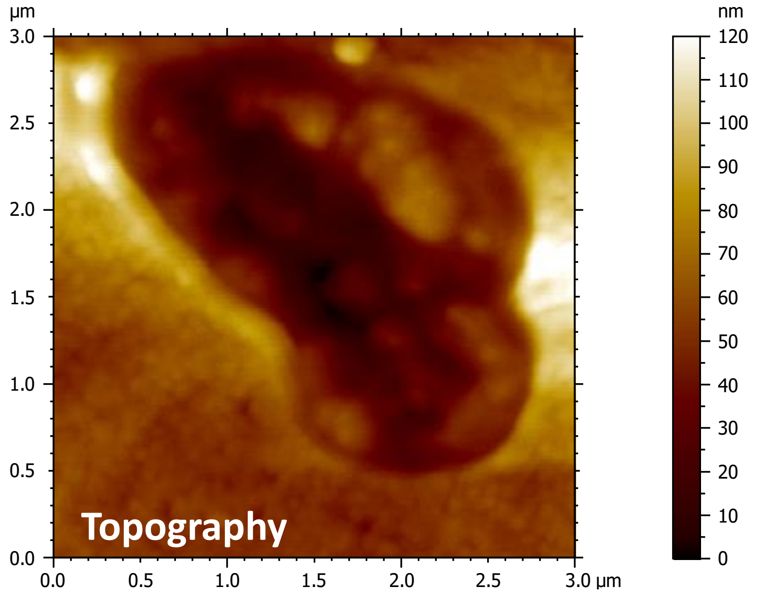
8 available channels

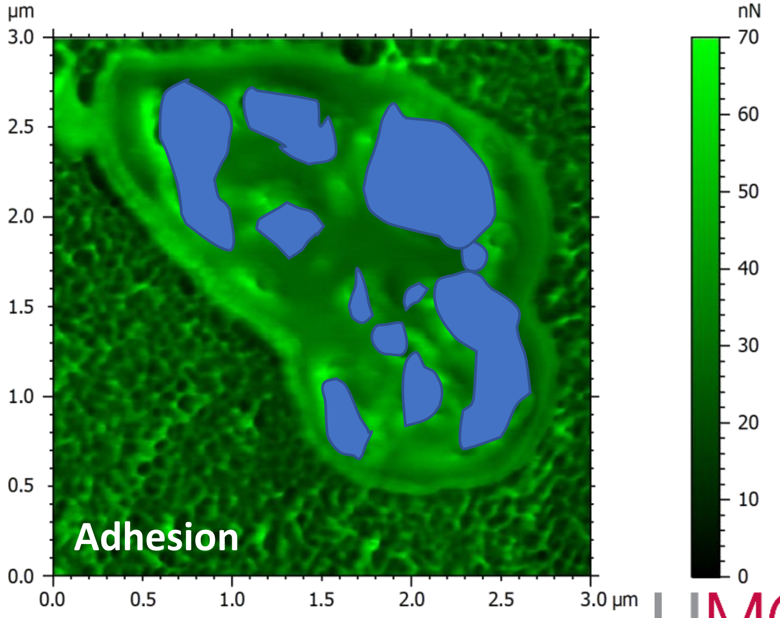
From simple to complex











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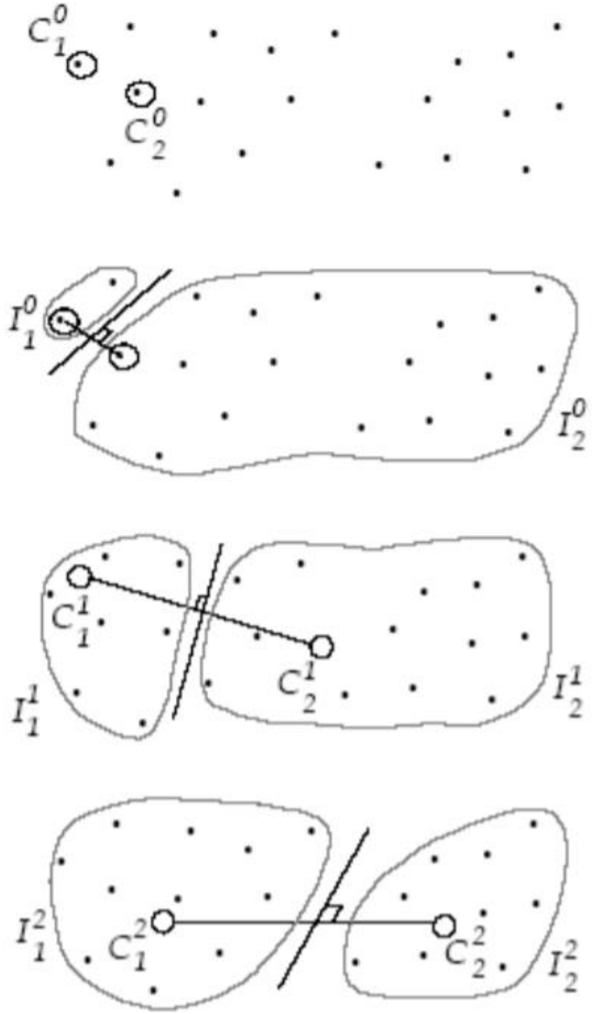
PyCAROS clustering algorithm: KMeans, GMM



Random centroids

C_1^0 et C_2^0

Centroids define classes

I_1^0 et I_2^0

Classes define new centroids

C_1^1 et C_2^1

New classes

I_1^1 et I_2^1

C_1^2 et C_2^2

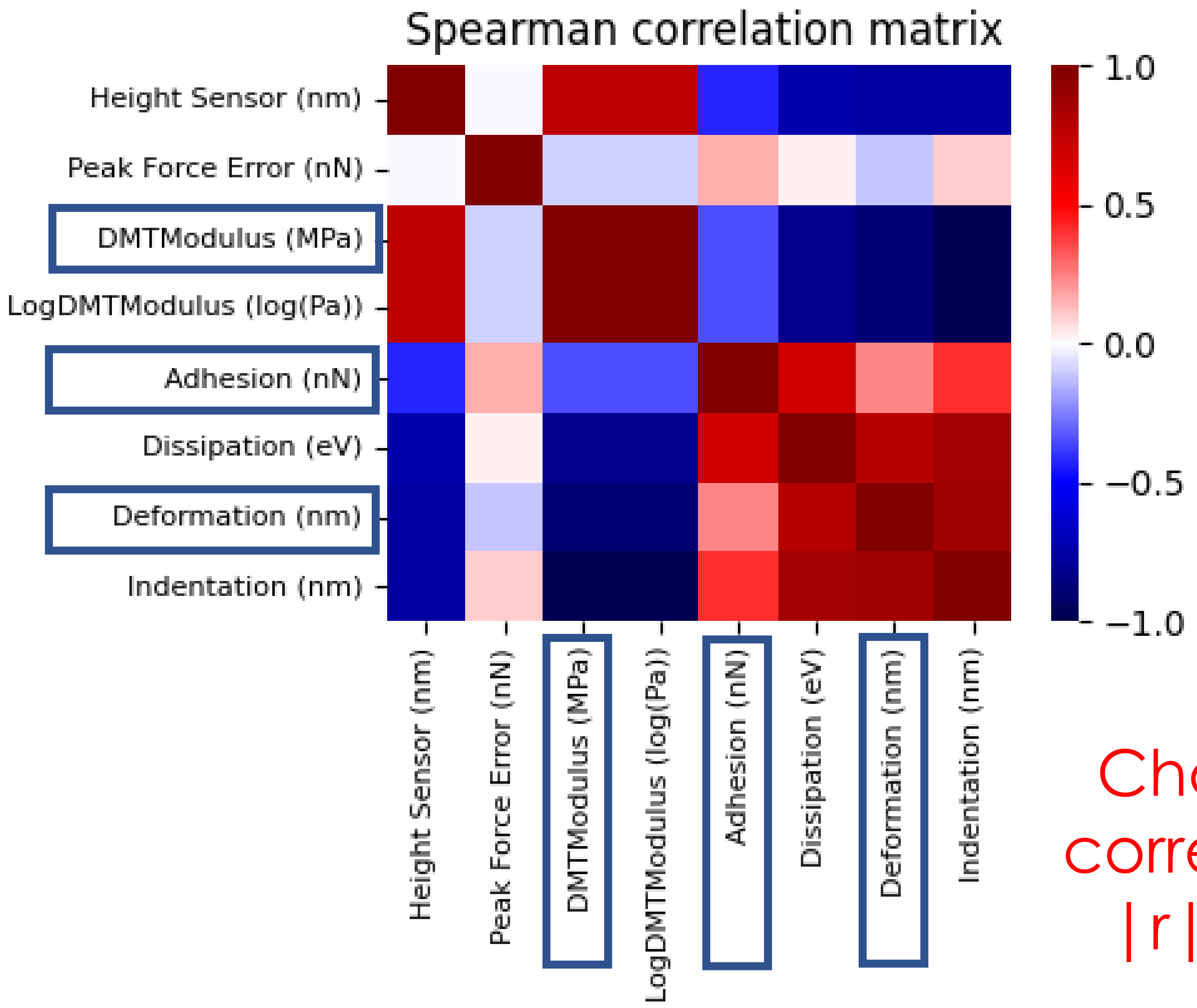
Iteration

I_1^2 et I_2^2

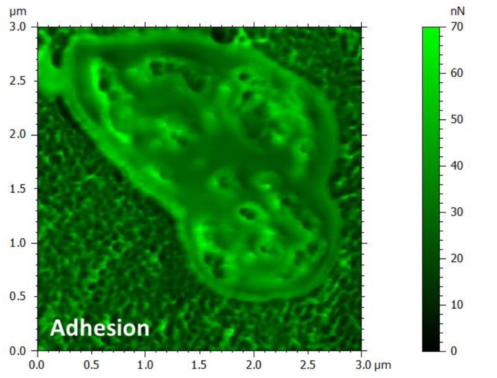
Optimized cluster inertia

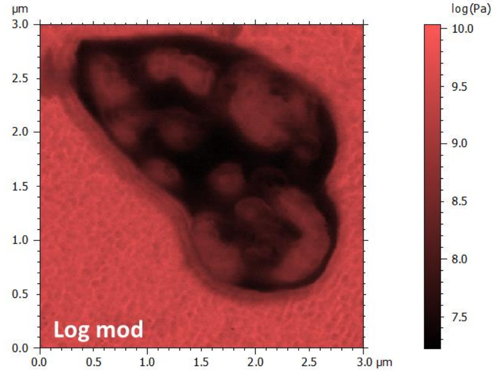
Clustering of multiple channels

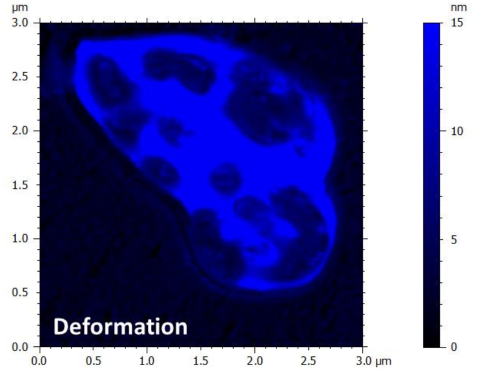
Channel selection: how to do it?



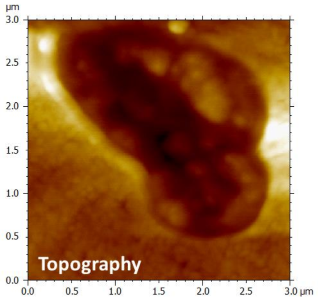
Channel correlation
|r|≥ 0.7

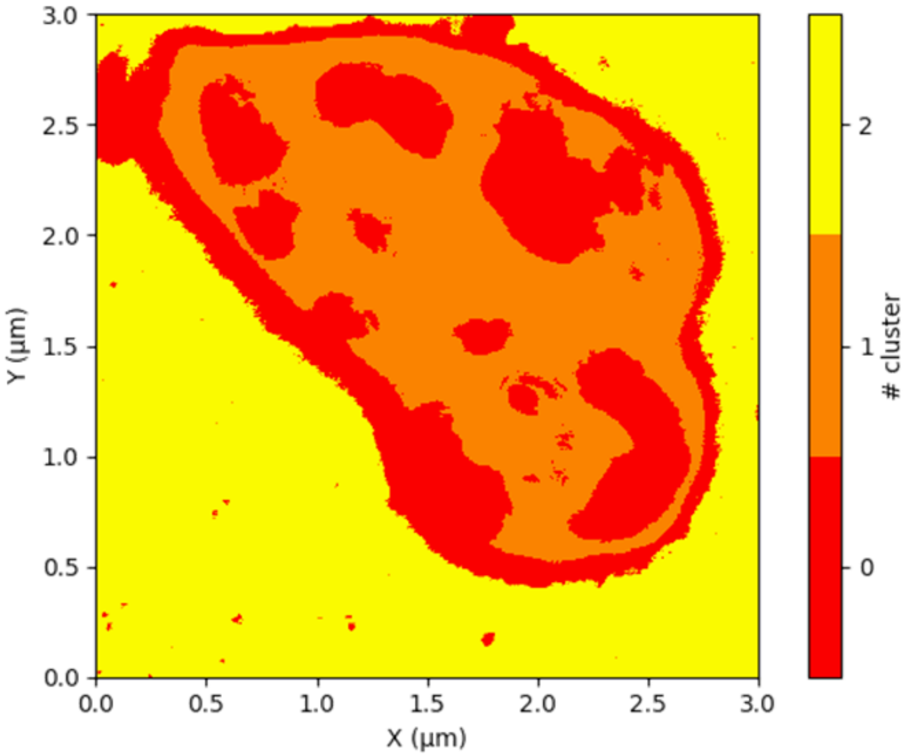






Peak Force Tapping: the clustering

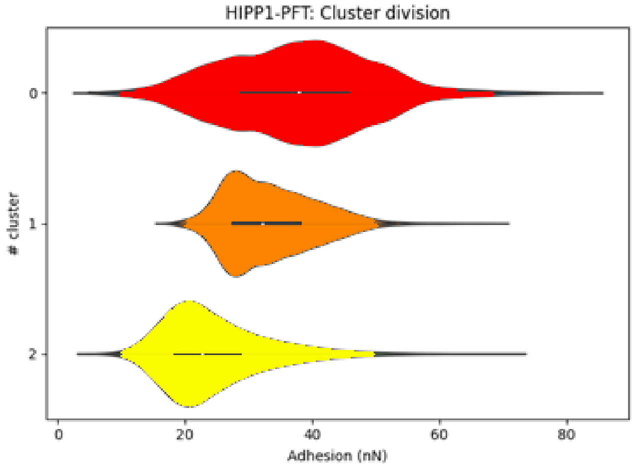


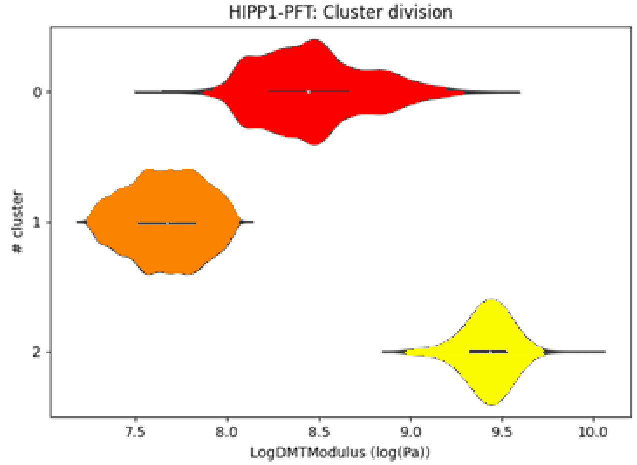


PP matrix

Rubber

PE crystalline phase
+ Interphase





Cluster	Modulus (MPa)	adhesion (nN)	dissipation (eV)	deformation (nm)
0	378.1 ± 1.8	37.65 ± 0.10	4530 ± 18	5.12 ± 0.02
1	50.8 ± 0.2	33.29 ± 0.05	8859 ± 11	15.40 ± 0.05
2	2789 ± 5	24.45 ± 0.05	793 ± 2	2.11 ± 0.02

- Raw Data (.txt)
- Statistics on population
- Histogram
- Violin plot

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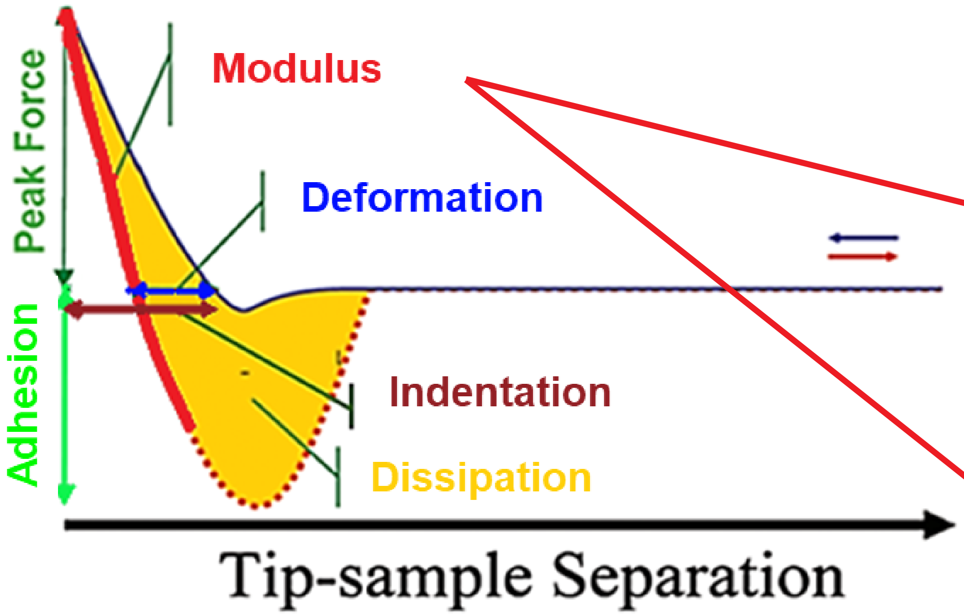
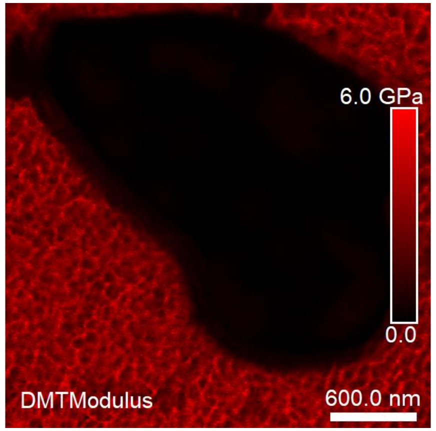
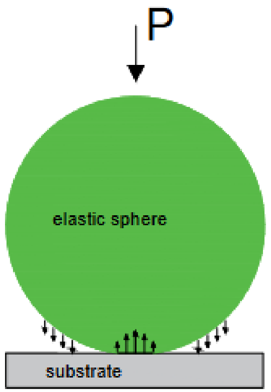
Rigidity modulus fit



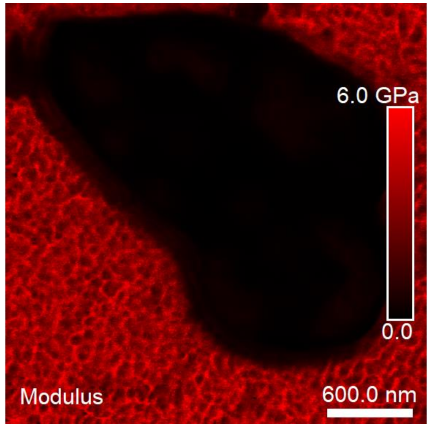
Different in the consideration of the adhesion forces and viscoelasticity

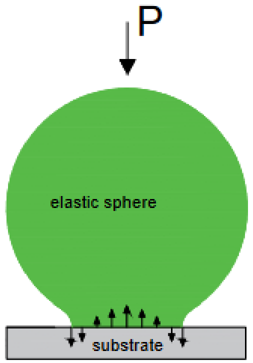
DMT

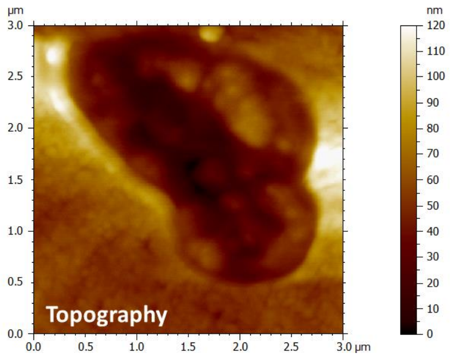




JKR



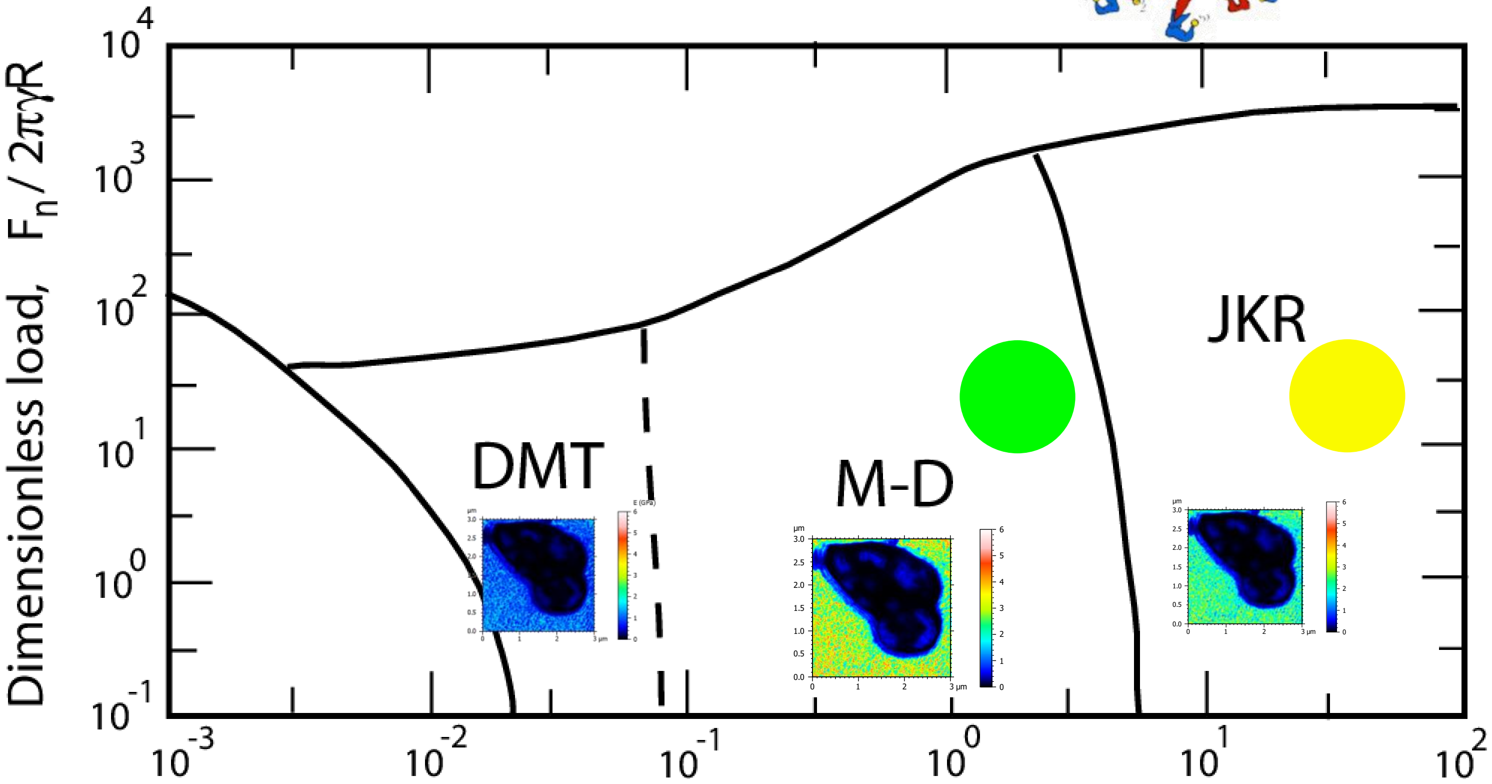


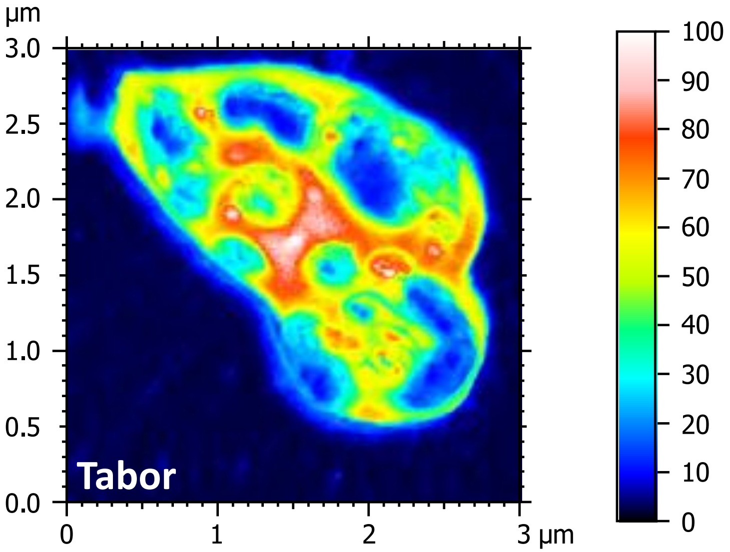


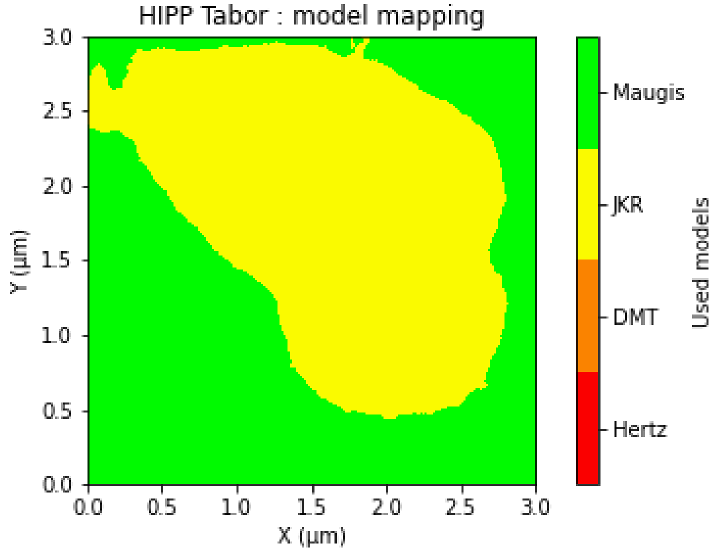
How to chose the good one?

Contact mechanics: Models

Tabor coefficient λ_M



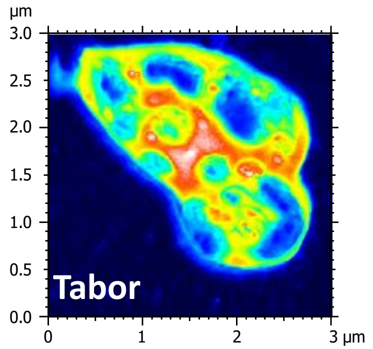


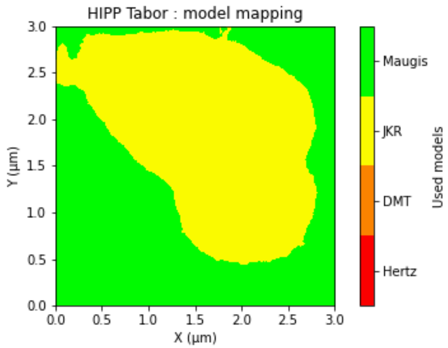


$$\lambda_M = 1.16\ \lambda_T = 1,16 * \left(\frac{R\Delta\gamma^2}{E_R^2 z_0^3}\right)^{1/3}$$

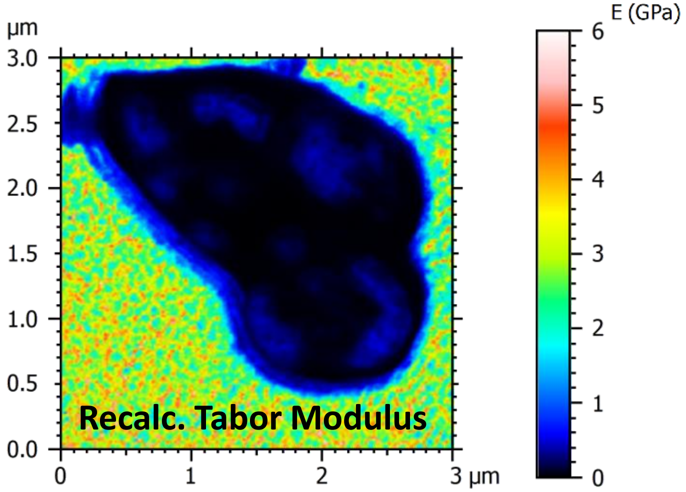
Johnson, Greenwood, J. Colloid Interface Sci., 1997, 192, 326.

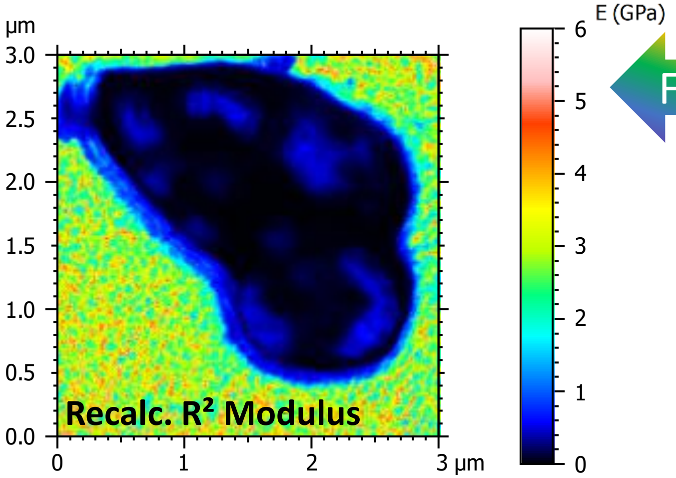
Modulus mapping



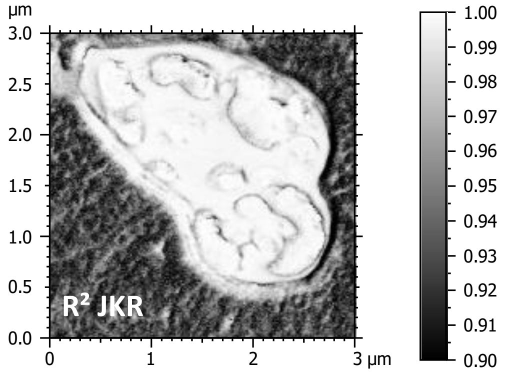


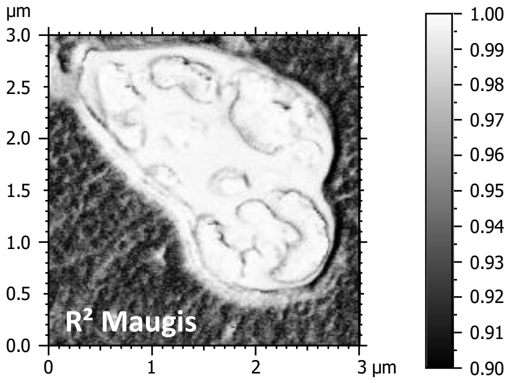
From Tabor map





From R² map

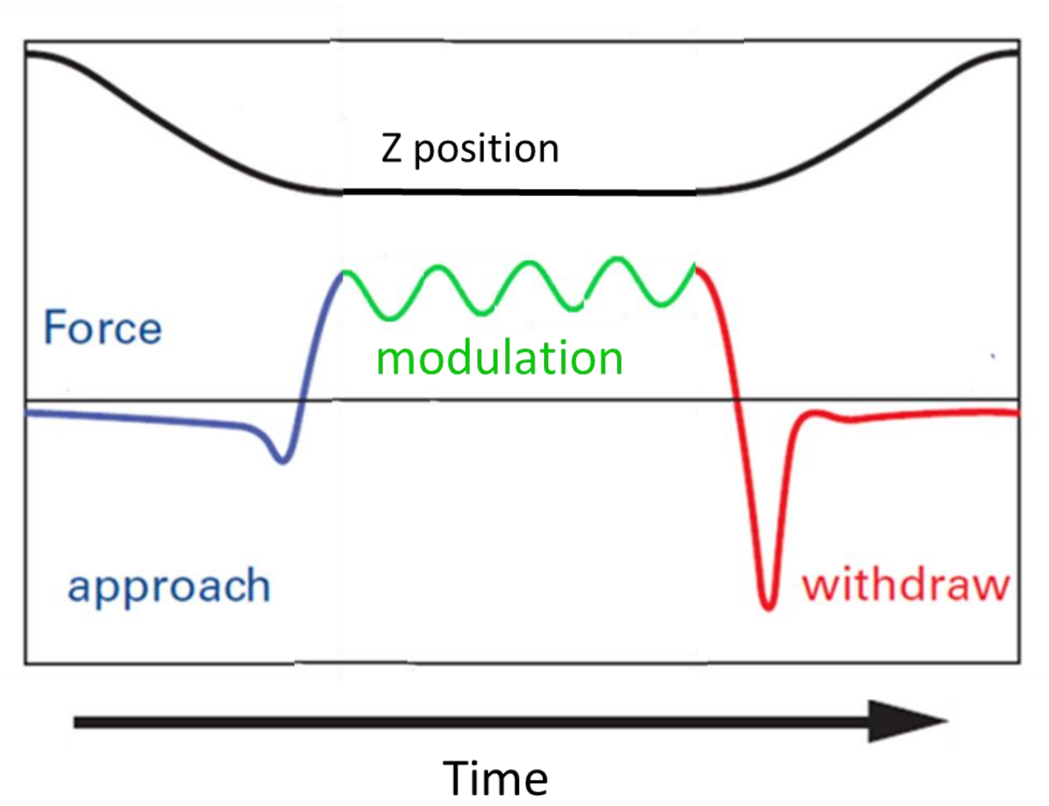




JKR, DMT … or any available mechanical model

Viscoelastic properties: nano-DMA

Frequency modulation when the tip is in contact with the surface



FFV = **single** frequency

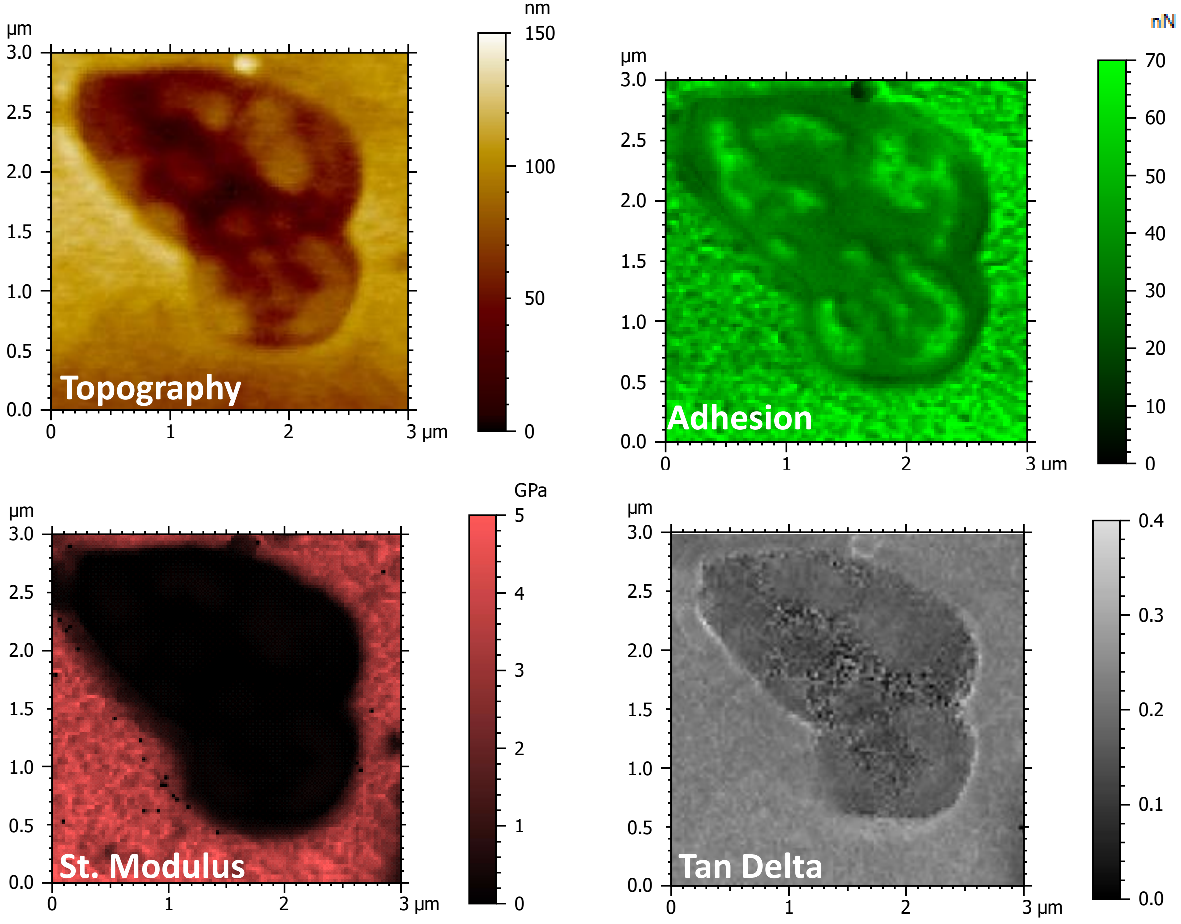
- cartography

nano-DMA = frequency **rampscript**

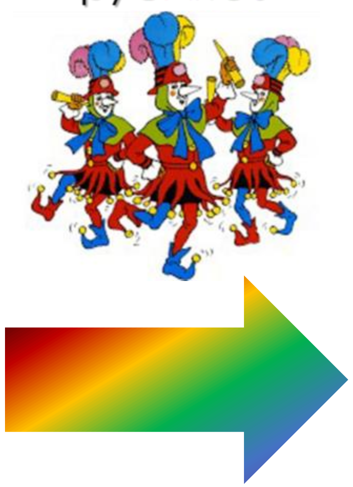
- spectroscopy

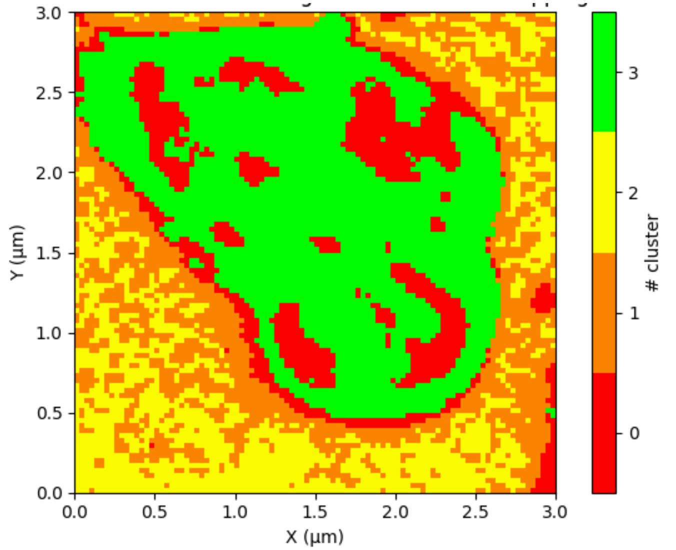
- Storage modulus (E')
- Loss modulus (E'')
- Tan delta (E''/E')
- … 15 channels available !

Nano-DMA: Clustering



pyCAROS





Cluster	Modulus (MPa)	adhesion (nN)	Sto. Modulus (MPa)	Loss Modulus (MPa)	Tan. Delta
0	502 ± 30	45.8 ± 0.3	409 ± 25	86 ± 6	0.181 ± 0.03
1	3678 ± 35	46.3 ± 0.3	2657 ± 21	593 ± 6	0.223 ± 0.02
2	5677 ± 42	58.0 ± 0.4	3759 ± 22	860 ± 6	0.230 ± 0.01
3	127 ± 7	31.4 ± 0.1	126 ± 9	27 ± 2	0.181 ± 0.05

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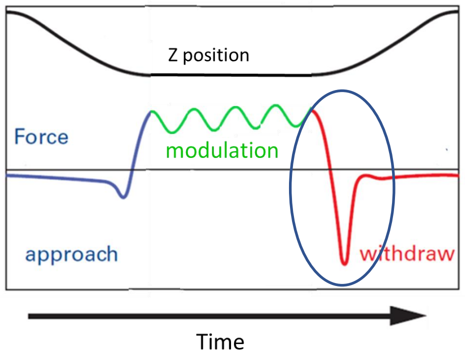
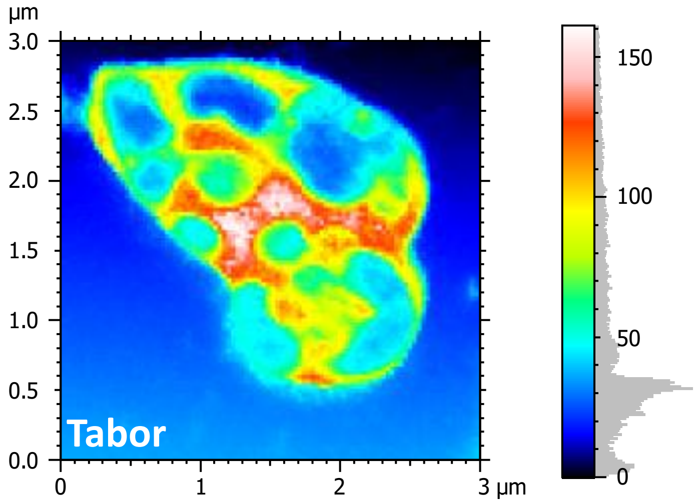
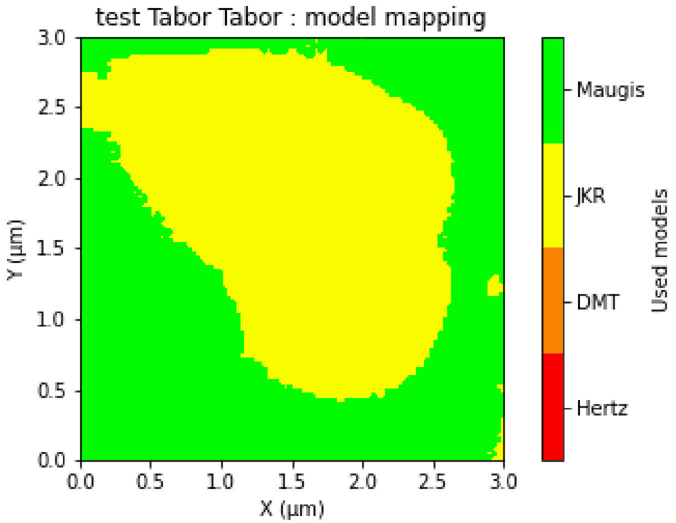
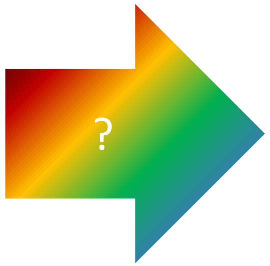
Nano-DMA: Clustering

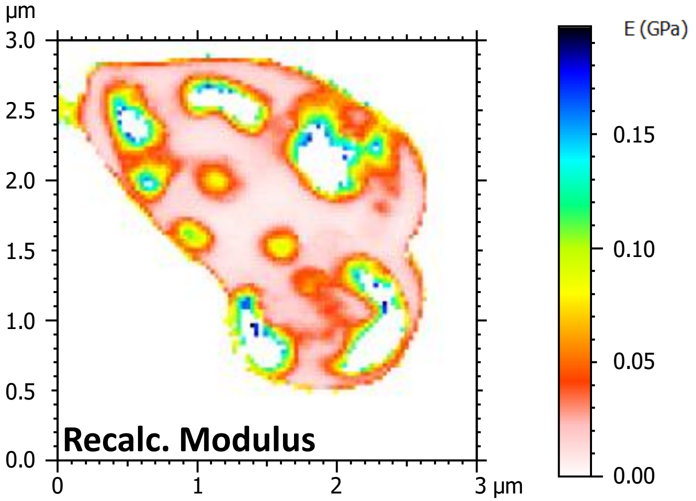
Force curve Fit (JKR)

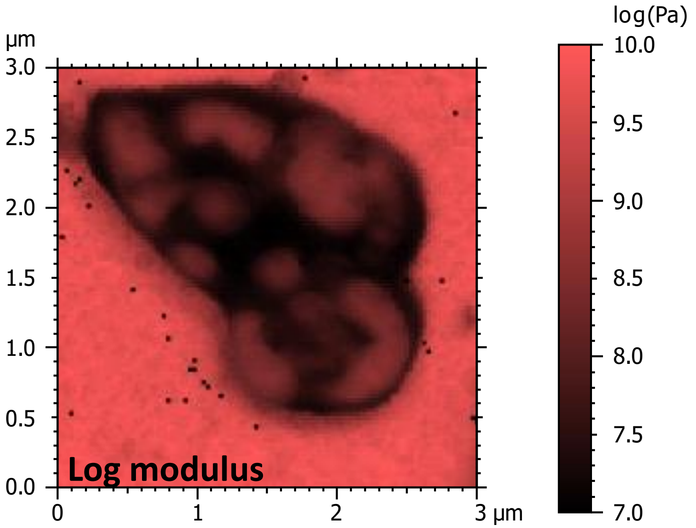












NanoScope Analysis 2.0

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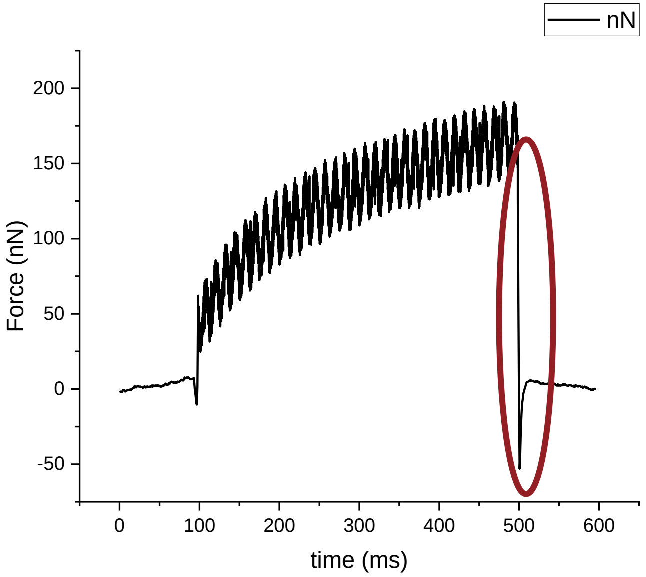
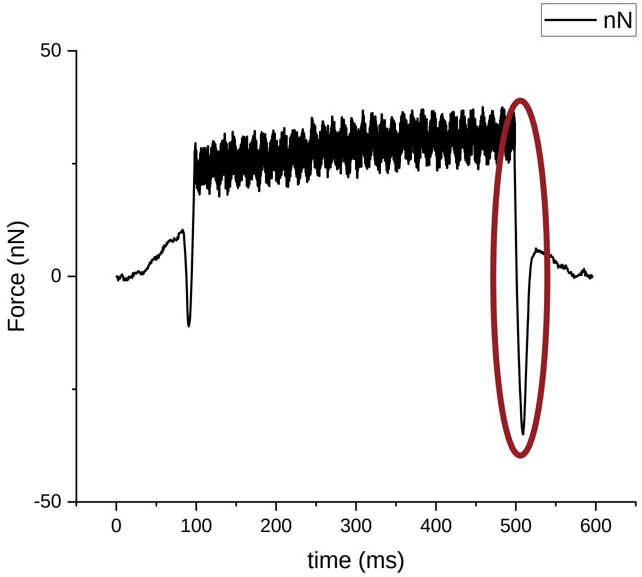
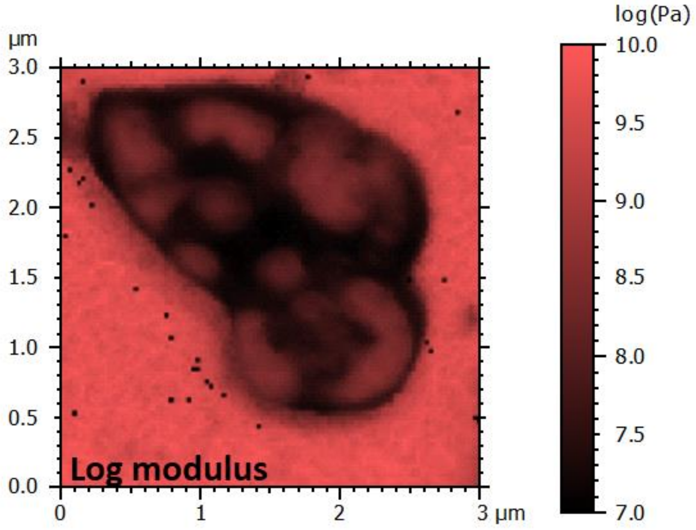
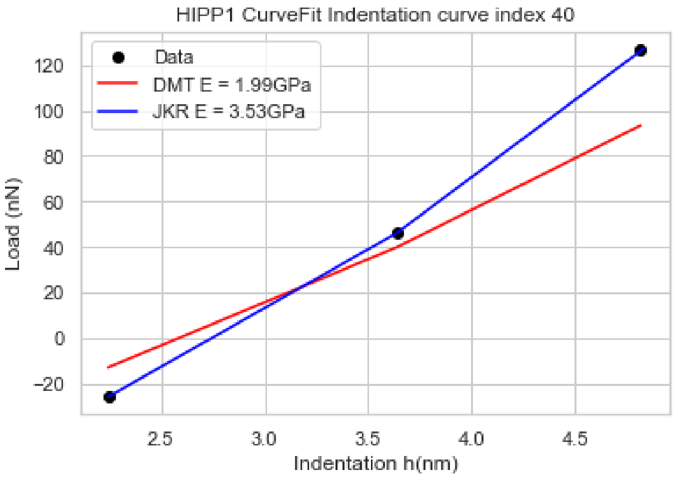
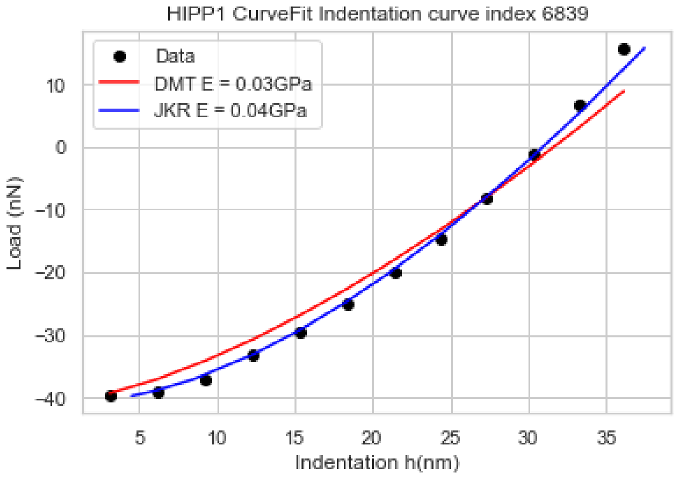
nanoDMA fit





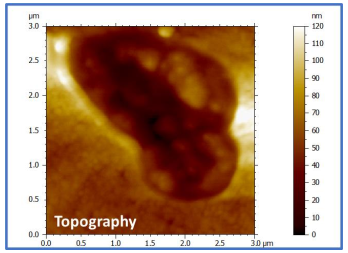




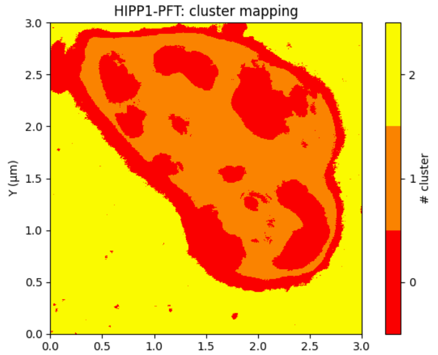


Number of data for the fit too small …
But still mapped in Nanoscope Analysis!

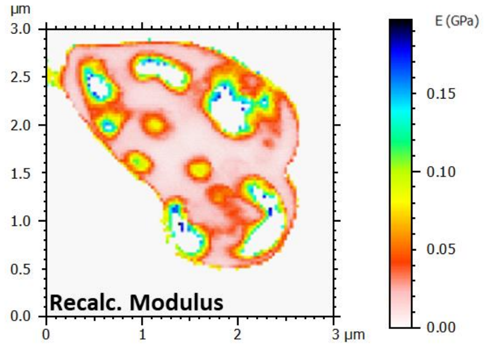
Conclusions



We illustred the power of pyCAROS on an complex (industrial) sample

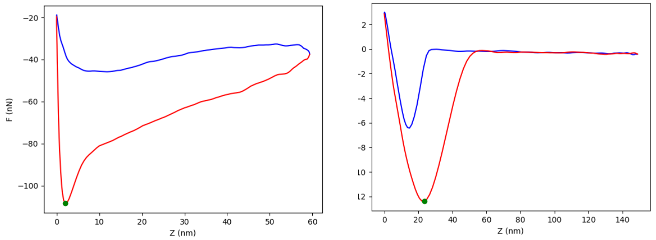


Clustering-multidimensional analysis



Force curve analysis

Force curve quality analysis by « deep » learning (see Thomas' Poster)



Aknowledgement

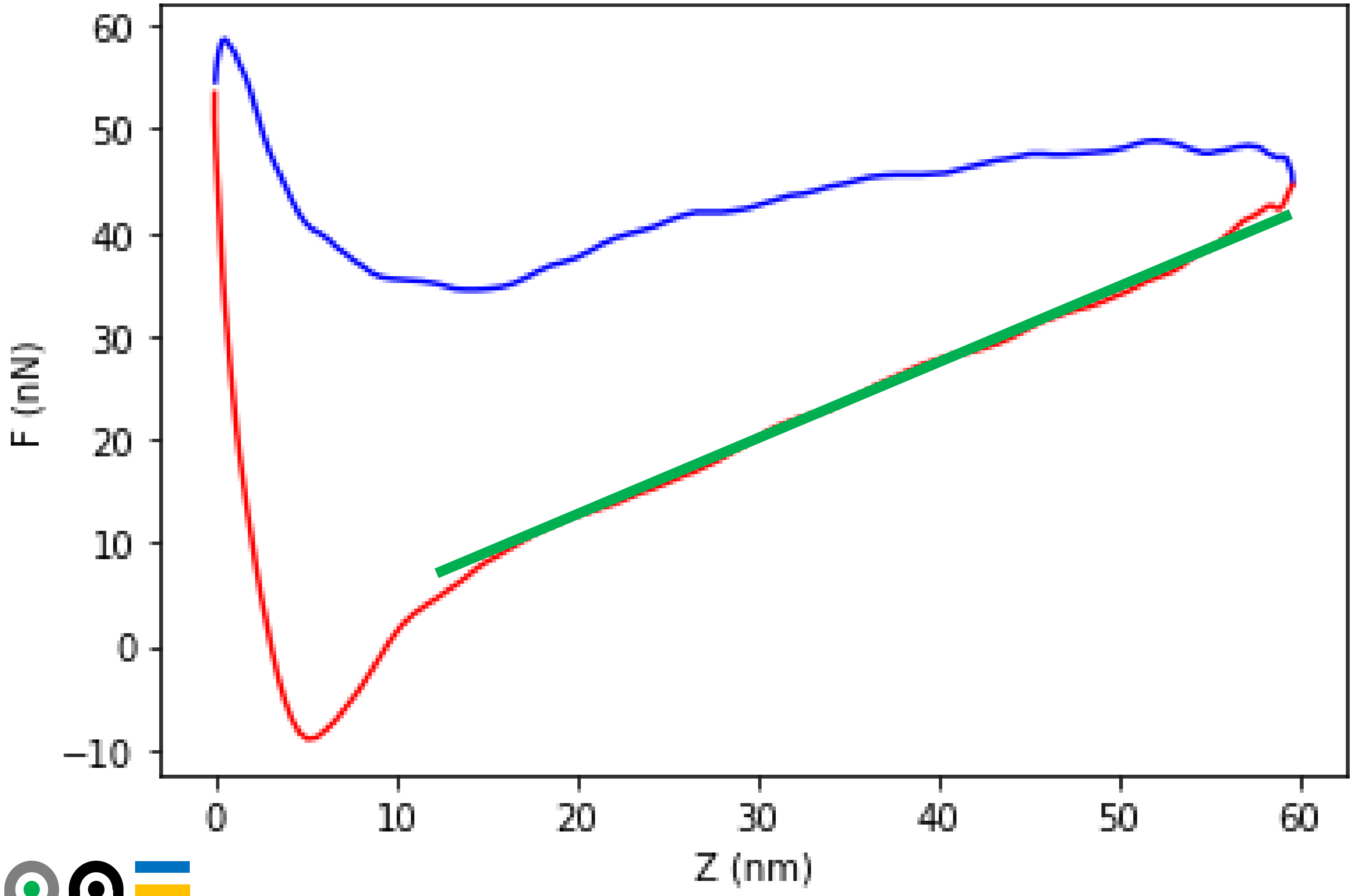
Lanti Yang

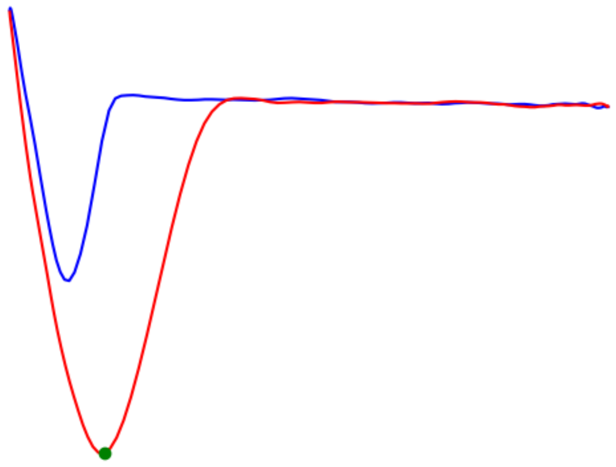
Philippe Leclere
Thomas De Muijlder

LPNE


thank you
danke
謝謝
ngiyabonga
teşekkür ederim
tapadh leat
спасибо
dank je
gracias
mauruuru
hvala
bedankt
dziękuję
mochchakkeram
go raibh maith agat
sagolun
sukriya
kop khun krap
obrigado
grazie
arigatô
takk
dakujem
мерси
terima kasih
ευχαριστώ
merci
감사합니다

Machine Learning: Feature selection

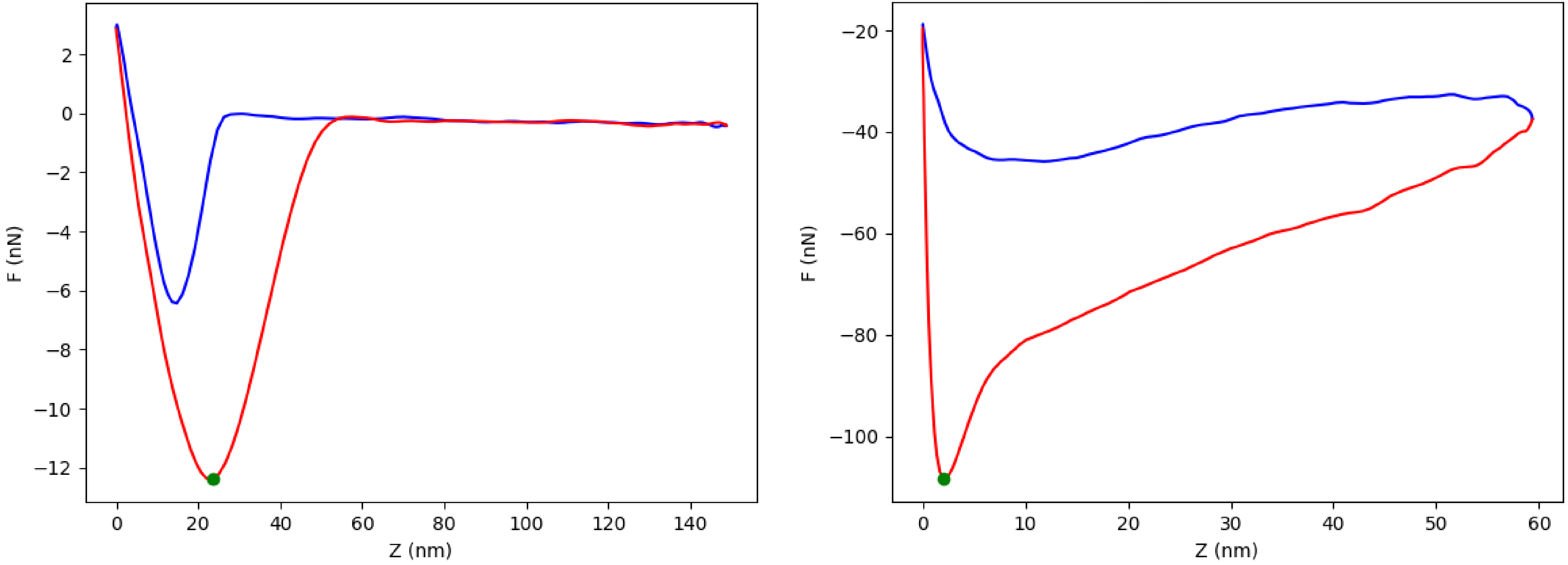




Baseline slope

Quality of the acquisition

512x512 = 26214
force curves



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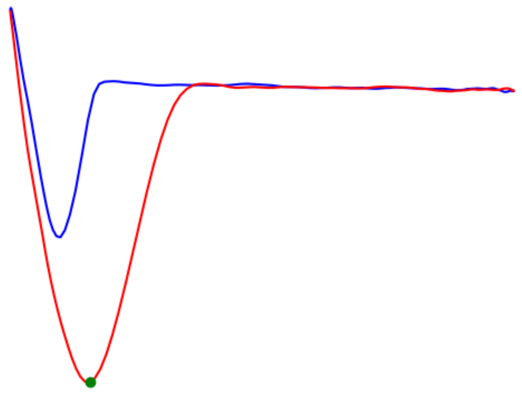
Supervised Machine Learning



	Feature 1	F2	…	F15
Curve 1				
Curve 2				
…				
C 250 000				

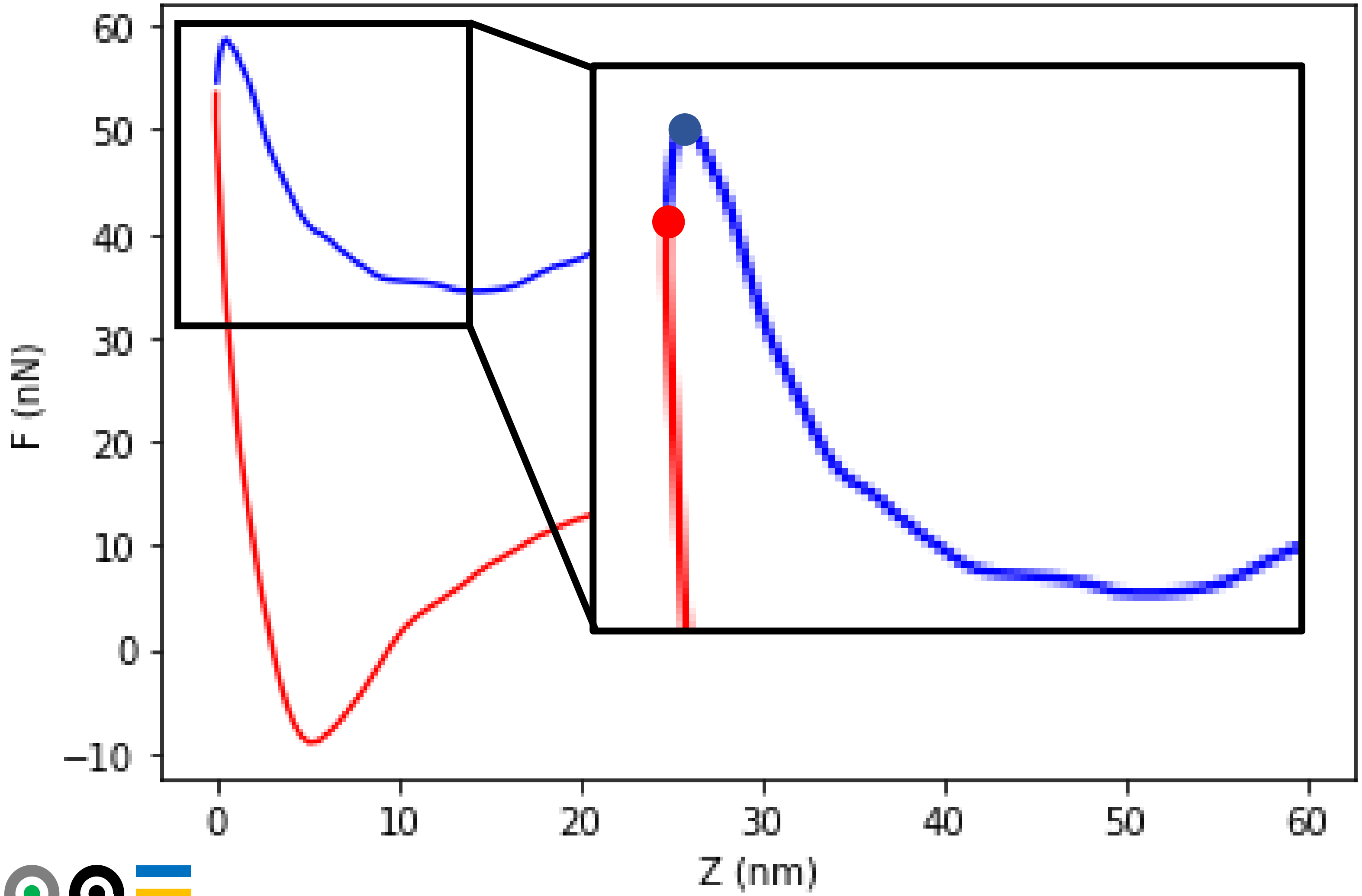
Description

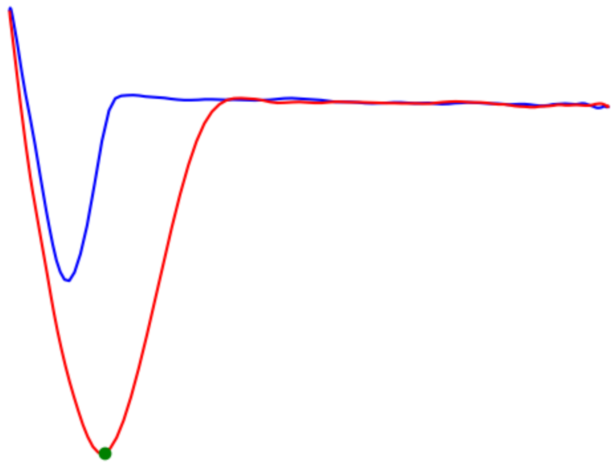
TARGETS

0. Unusable
1. Noisy
2. Usable
3. Good

Evaluation

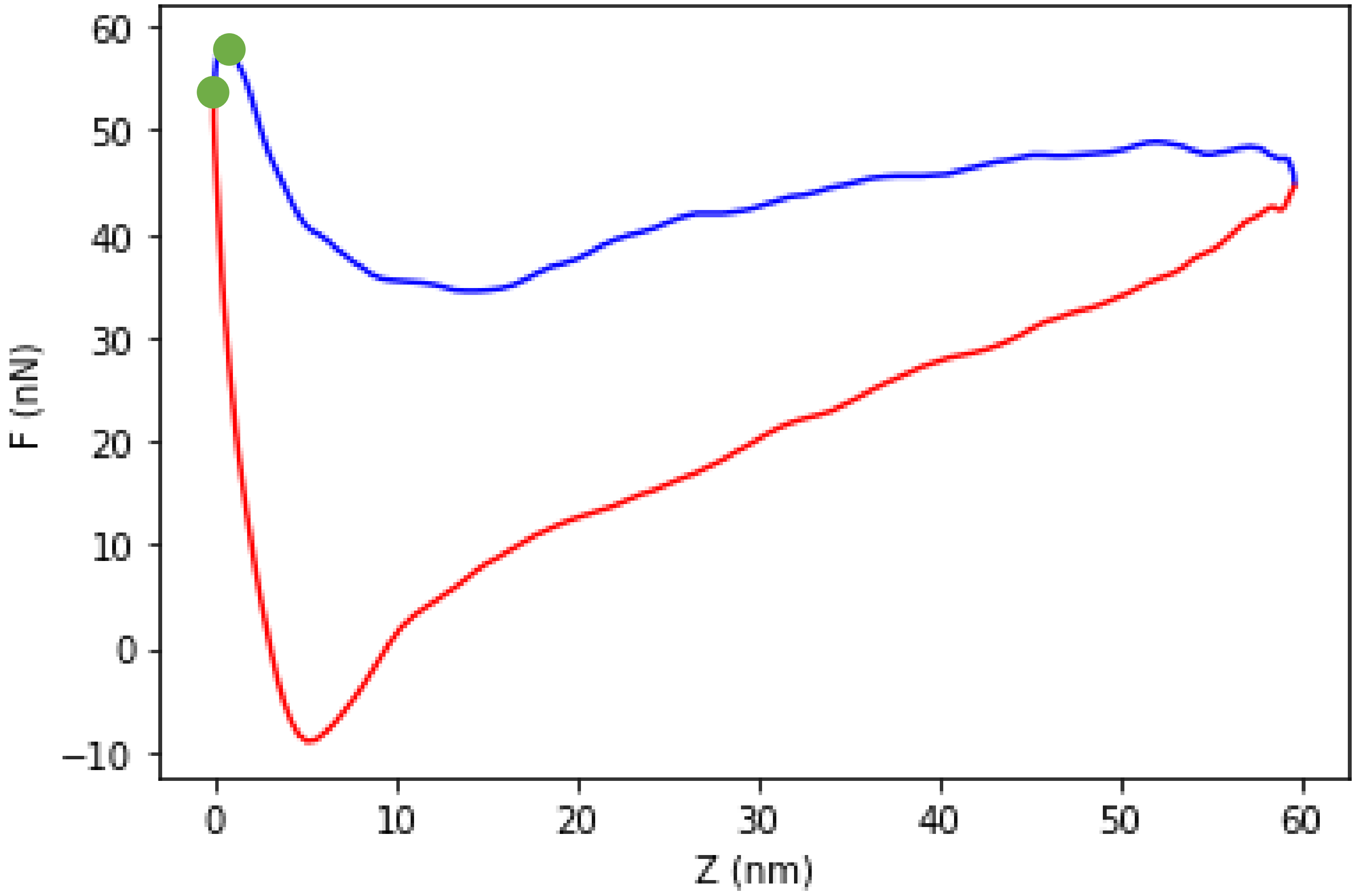
Machine Learning: Feature selection

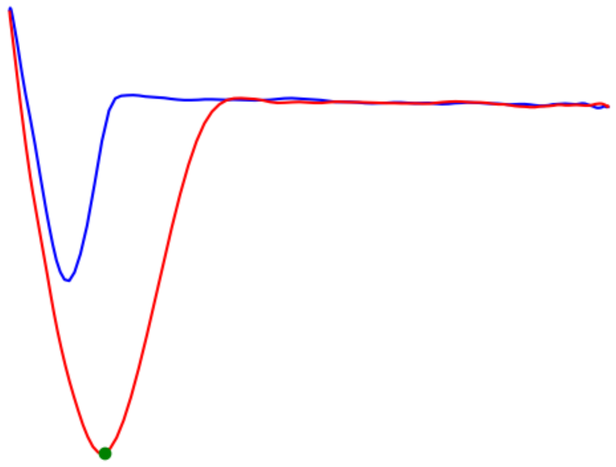




Difference of the max

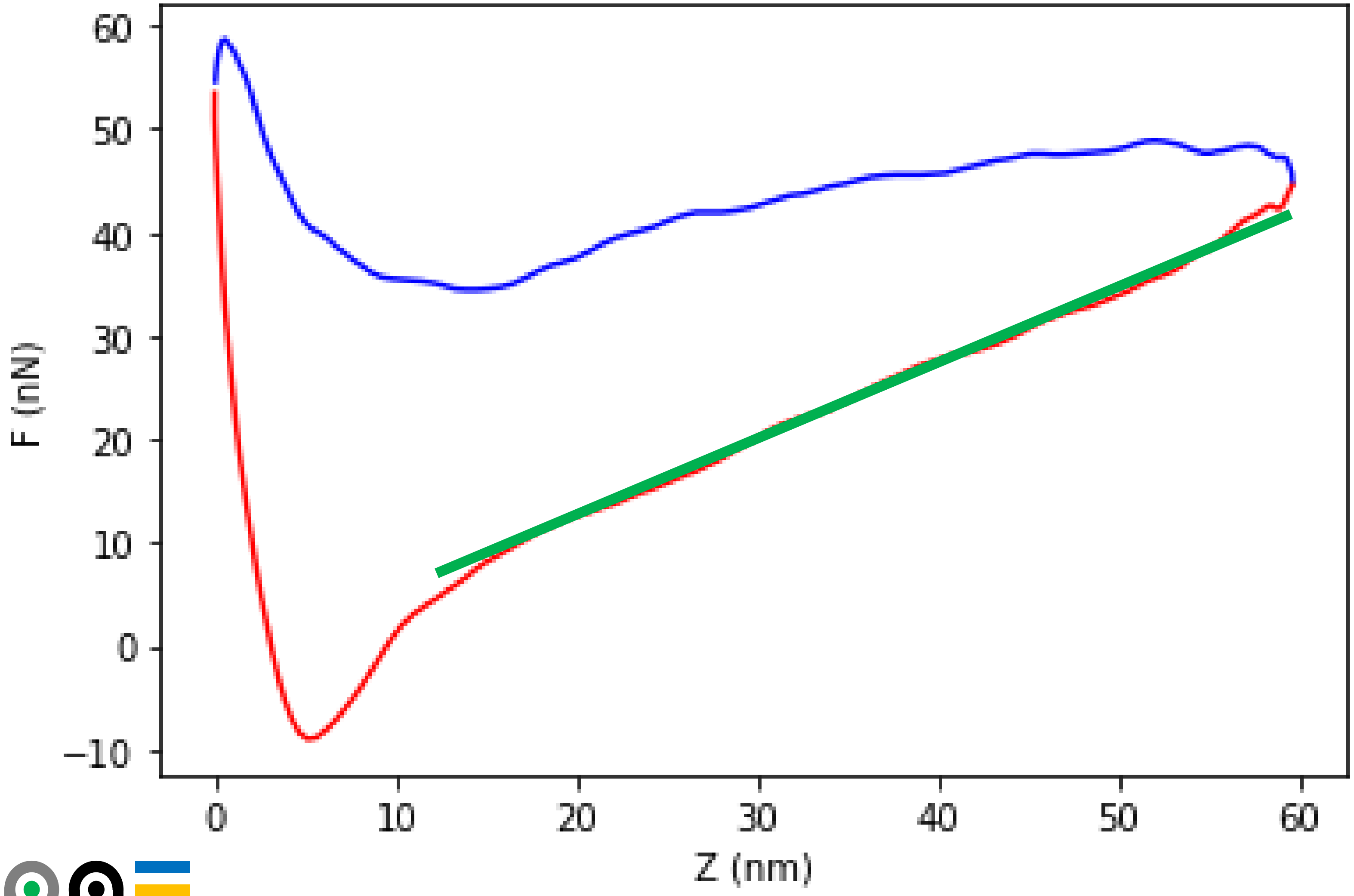
Machine Learning: Feature selection

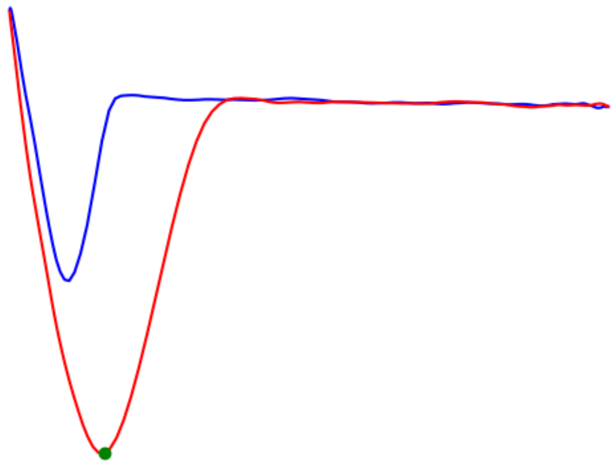




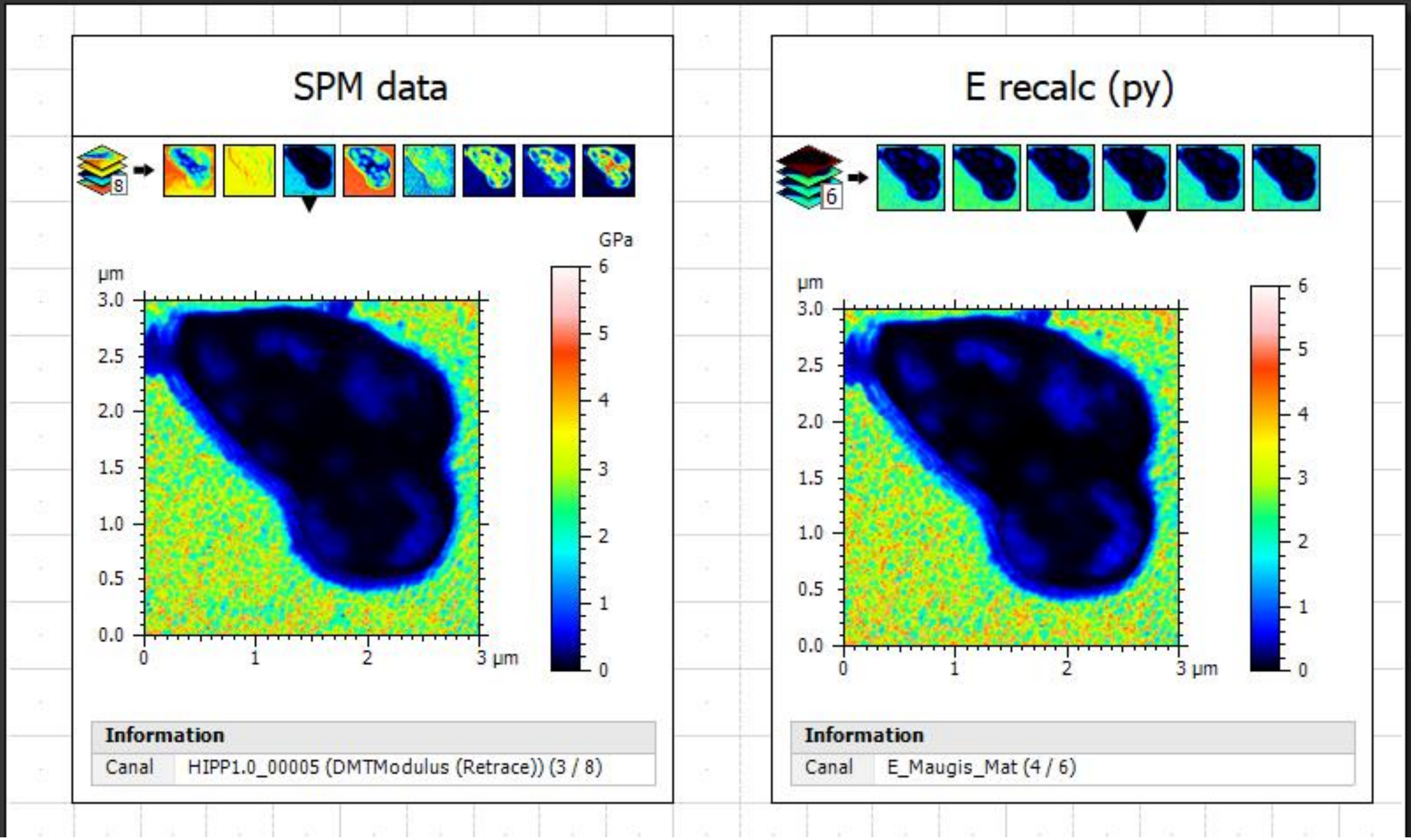
Ratio max final

perspectives



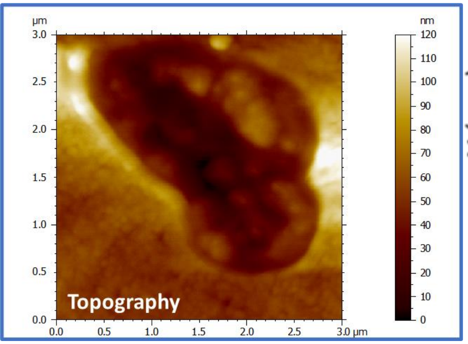


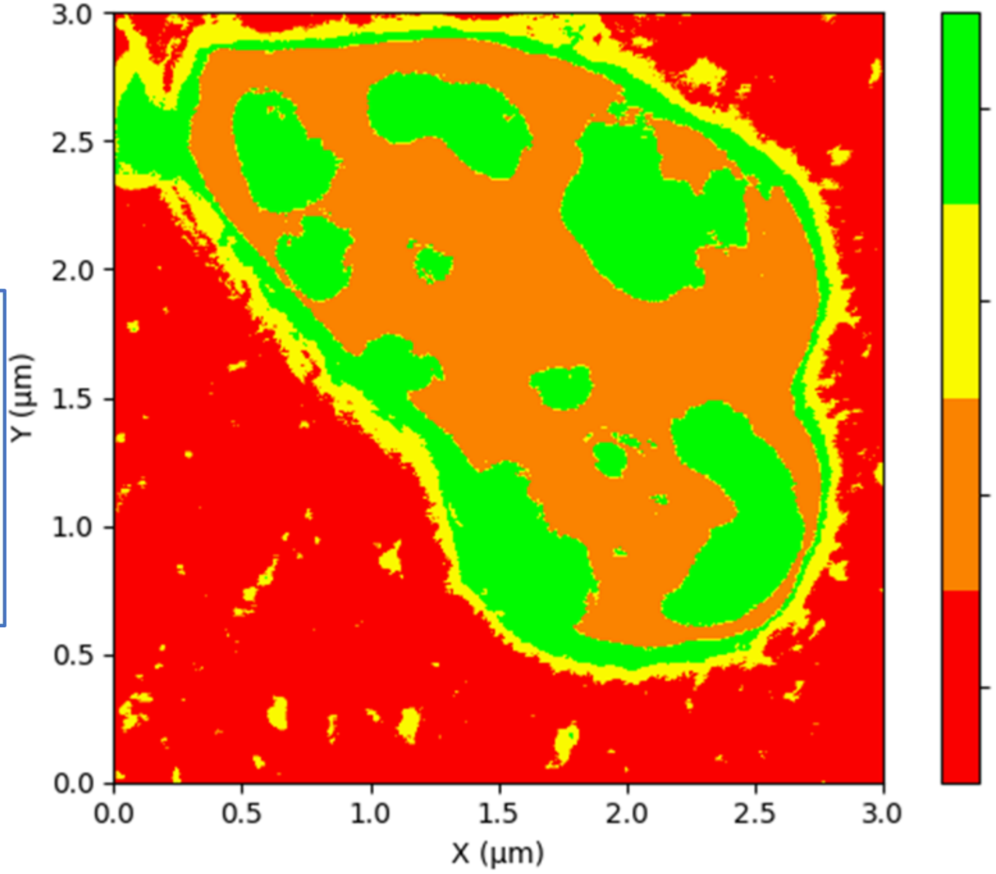
Baseline slope



SPM data
GPa
µm
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3 µm
6
5
4
3
2
1
0
Information
Canal
HIPP1.0_00005 (DMTModulus (Retrace)) (3 / 8)
E recalc (py)
µm
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3 µm
6
5
4
3
2
1
0
Information
Canal
E_Maugis_Mat (4 / 6)

Peak Force Tapping: the clustering



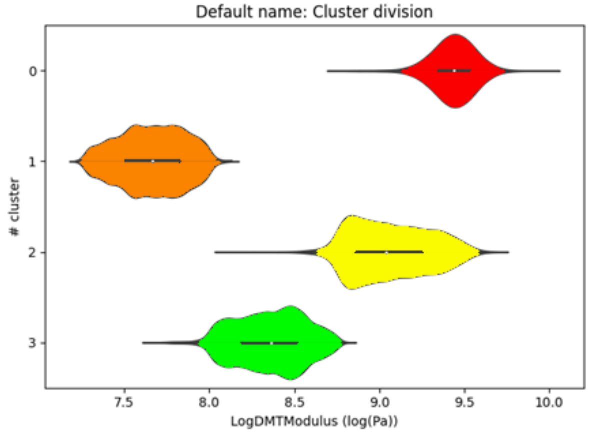


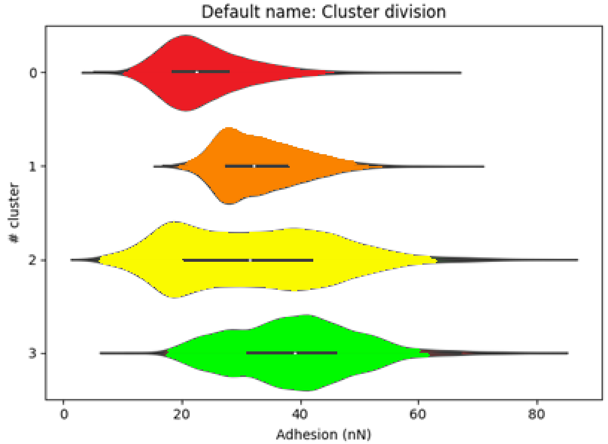
PE crystalline phase

Interphase

Rubber

PP matrix





- Raw Data
- Statistics on population
- Histogram
- Violin plot

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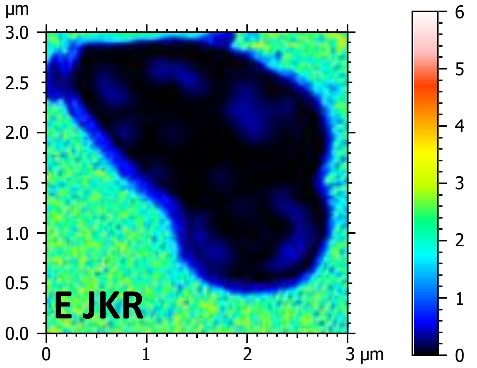
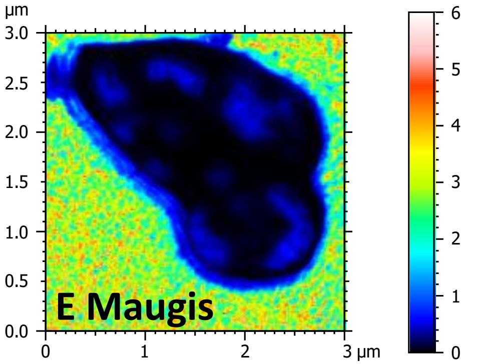
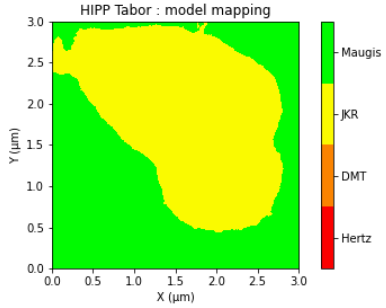
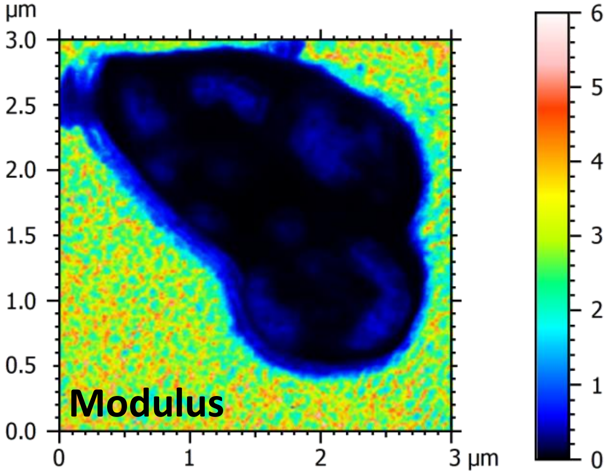
Modulus mapping



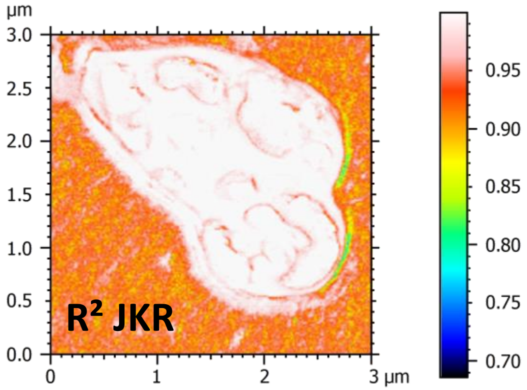


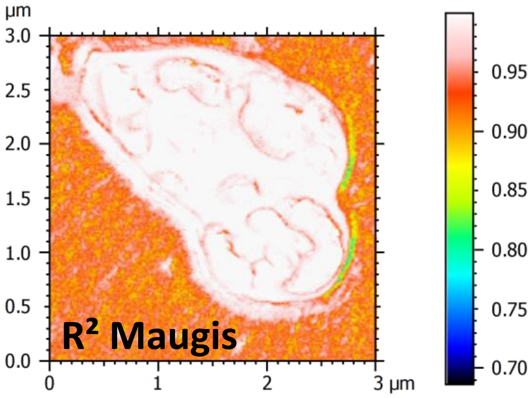
From tabor map





From R^2 map





DMT … or any available mechanical model