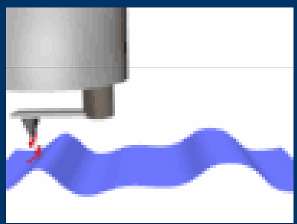
ULTRASONIC FORCE MICROSCOPY ON A NEW SCAFFOLD FORMED OF POLYELECTROLYTE COMPLEXES

Teresa Cuberes



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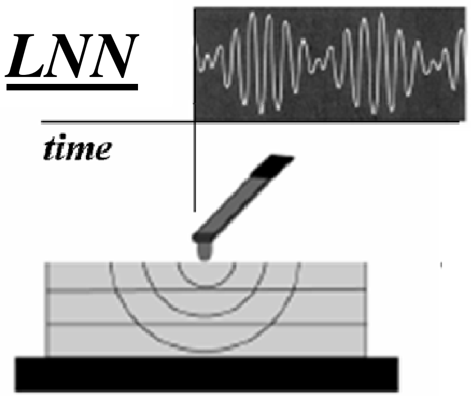
The Laboratory of Nanotechnology, Almaden, SPAIN

LNN



Outline

- ***Ultrasonic Force Microscopy***
  - *-The Mechanical-Diode (MD) effect*
  - *- Information from UFM*

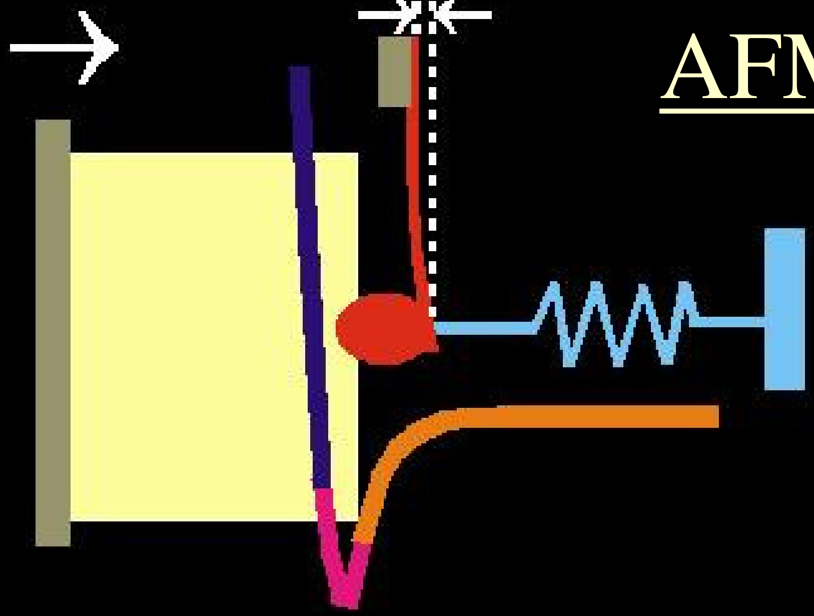
- ***Some examples of UFM applications***
  - *- UFM on Polymeric Hydrogels*
  - *- UFM on Phospolipide Bilayers*

- ***UFM on polyelectrolyte complexes***
  - *- Poly[Q-co-H] / AlgNa (Ca^{2+}) / PLL complexes*
  - *- UFM on AlgNa (Ca^{2+}) / PLL / mica*
  - *- UFM on Poly[Q-co-H] / AlgNa (Ca^{2+}) / PLL / mica*

- ***Summary***

ACOUSTIC MICROSCOPY IN THE NEAR-FIELD?

ULTRASONIC - AFM:



<u>AFM:</u>

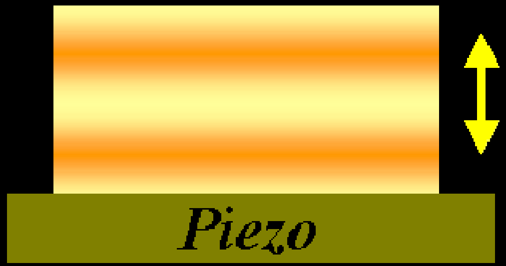
Longitudinal acoustic waves

$v \approx 10^3$ m/s

$\lambda \approx$ mm

Is it possible to detect ultrasonic vibration at a sample surface in the near-field regime, with a lateral resolution in the nanometer scale, using the tip of an AFM?

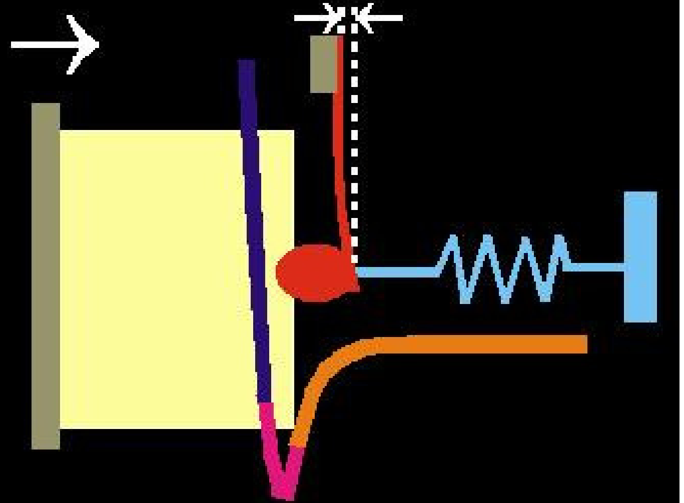
ULTRASONIC - AFM



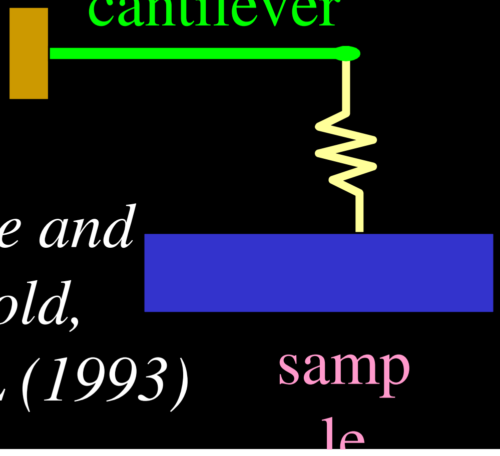
$v \approx 10^3$ m/s

$\lambda \approx$ mm

Longitudinal acoustic waves

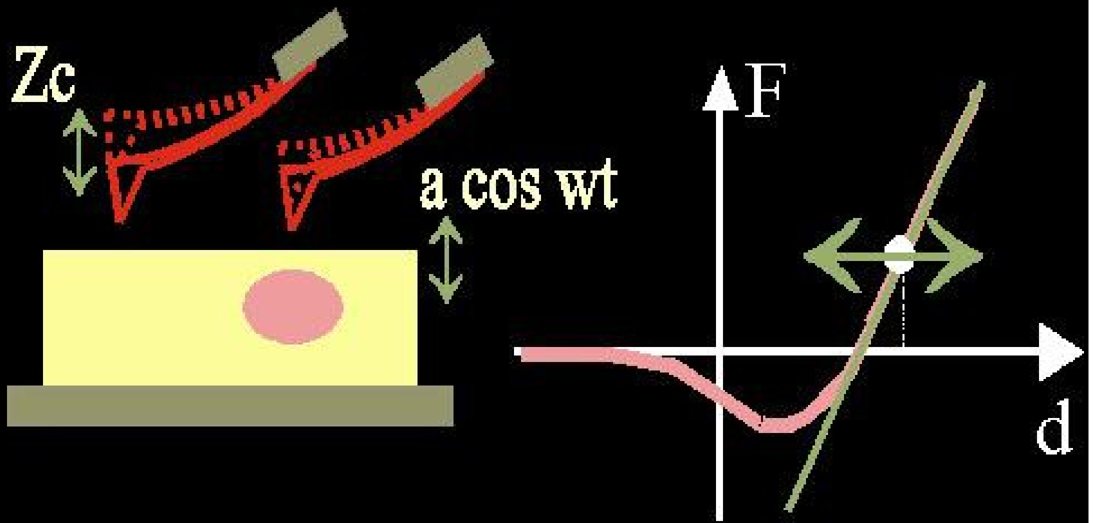


<u>CONTACT RESONANCES</u>

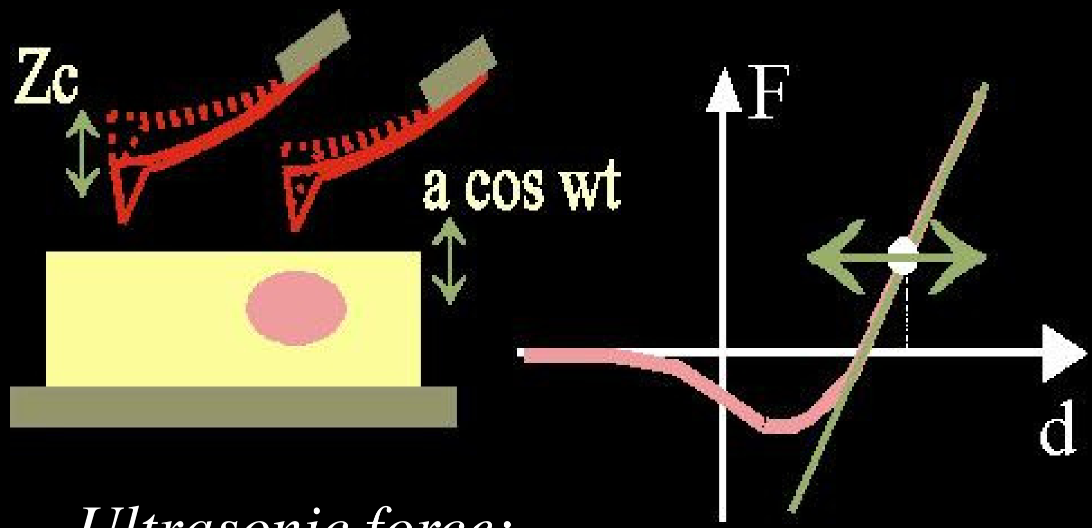


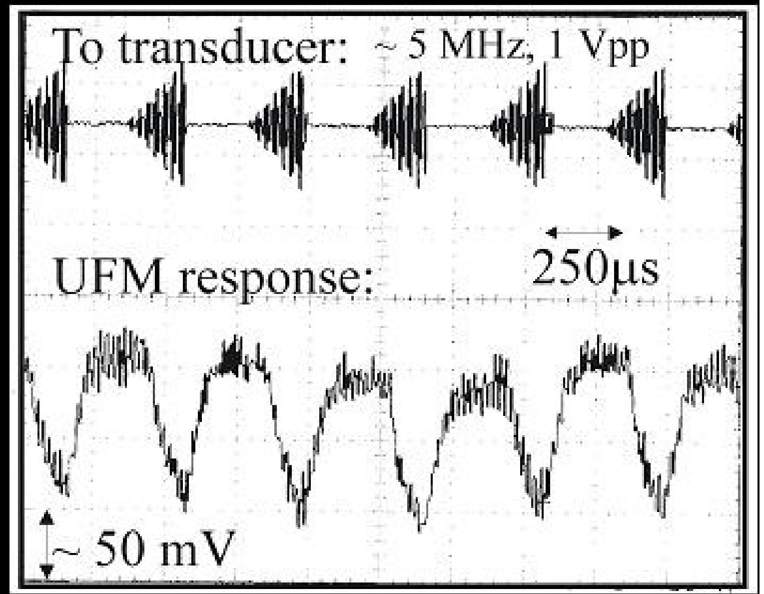
Rabe and Arnold, APL (1993)

<u>MECHANICAL DIODE</u>



ULTRASONIC FORCE MICROSCOPY





Ultrasonic force:

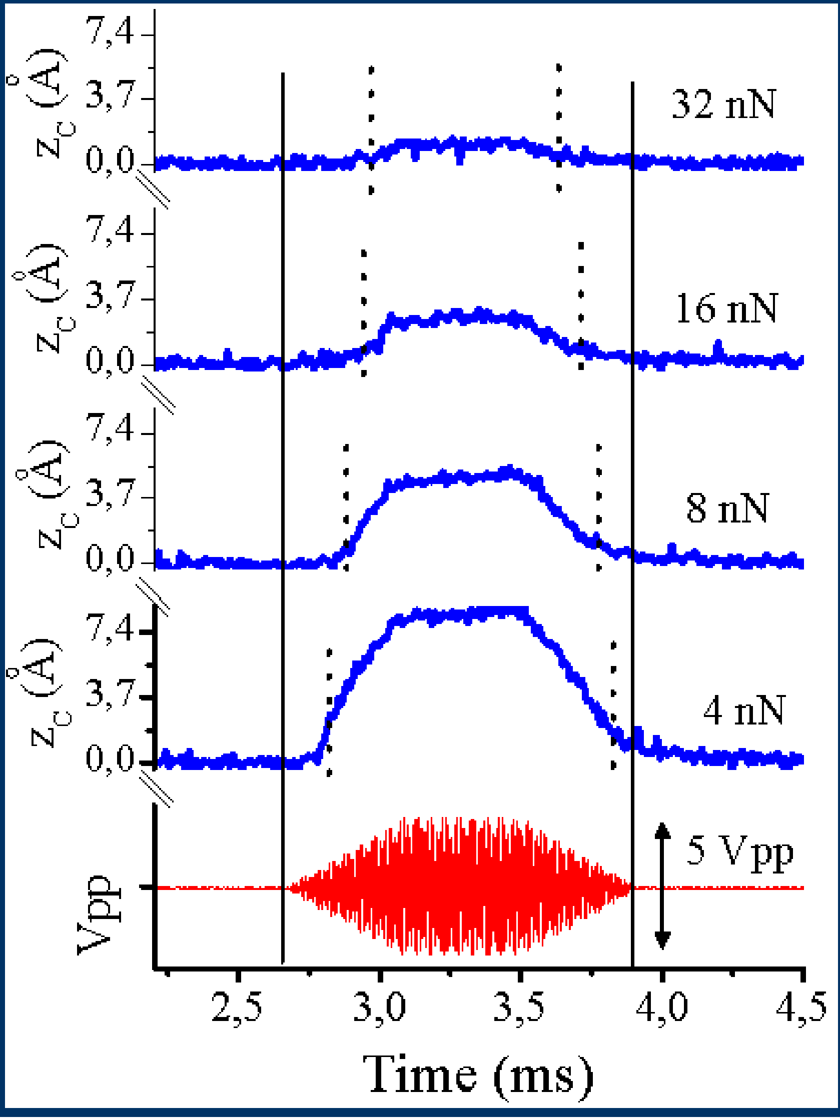
$$kz_c = \frac{1}{T}\int_0^T F(z_c - z_s - A\cos wt)\,dt$$

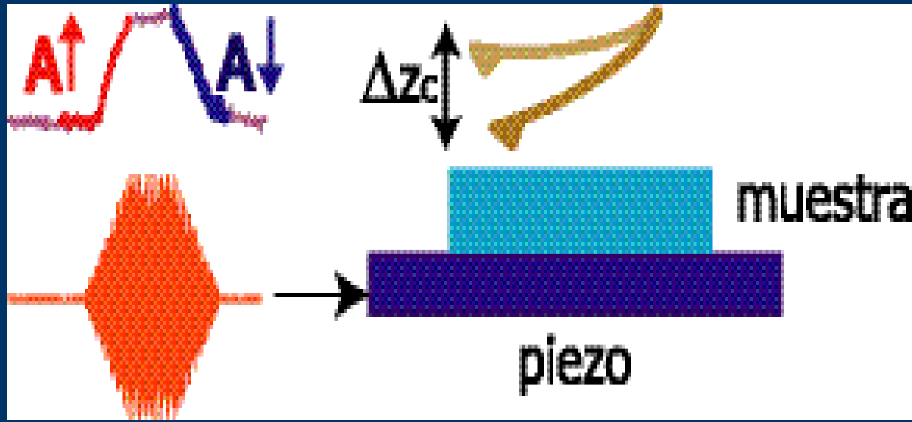
O. Kolosov and K. Yamanaka, Jpn. J. Appl. Phys. 32, L1095 (1993)

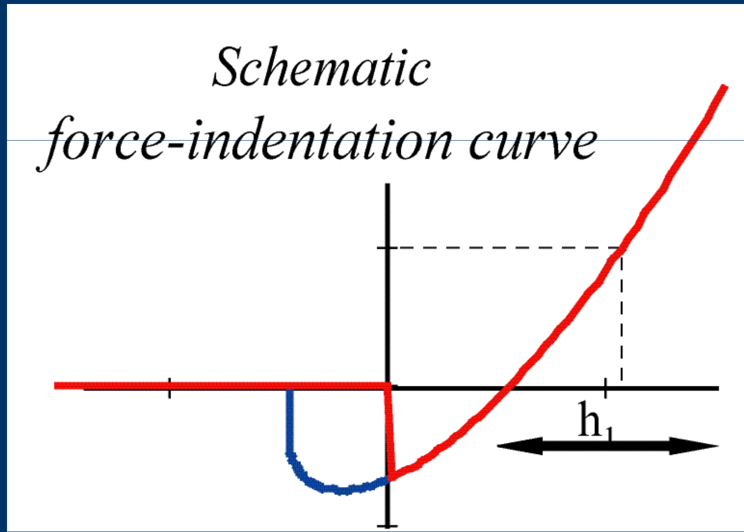
UFM *provides information about* sample elasticity and adhesion with nanoscale lateral resolution. Measured magnitude: static cantilever displacement induced by the *ultrasonic force*.

QUANTITATIVE ULTRASONIC FORCE MICROSCOPY

Cantilever response to ultrasonic vibration for different set-point forces (initial indentations):

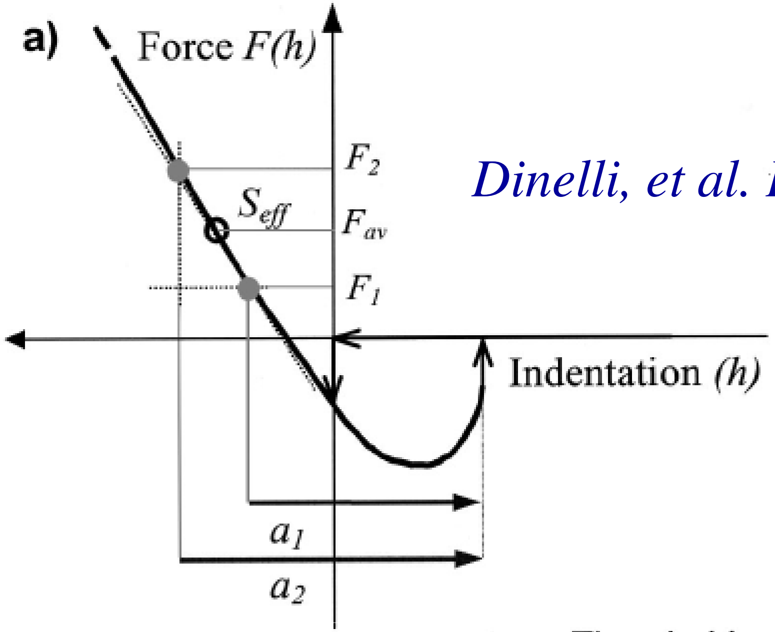




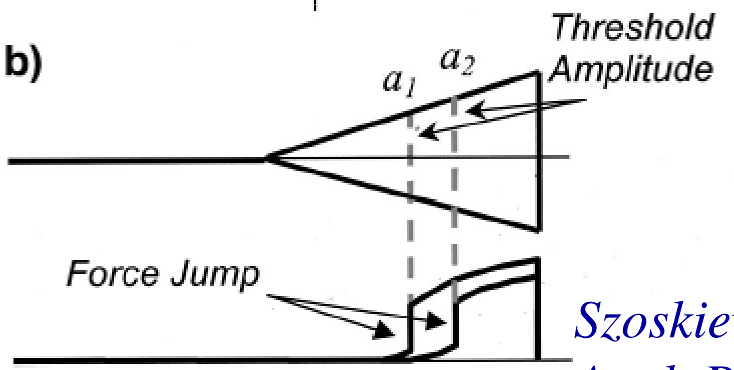


UFM signal vs us amplitude spectra *should* allow us to *quantify* the Young Modulus and Adhesion.

ELASTIC MODULUS AND ADHESION

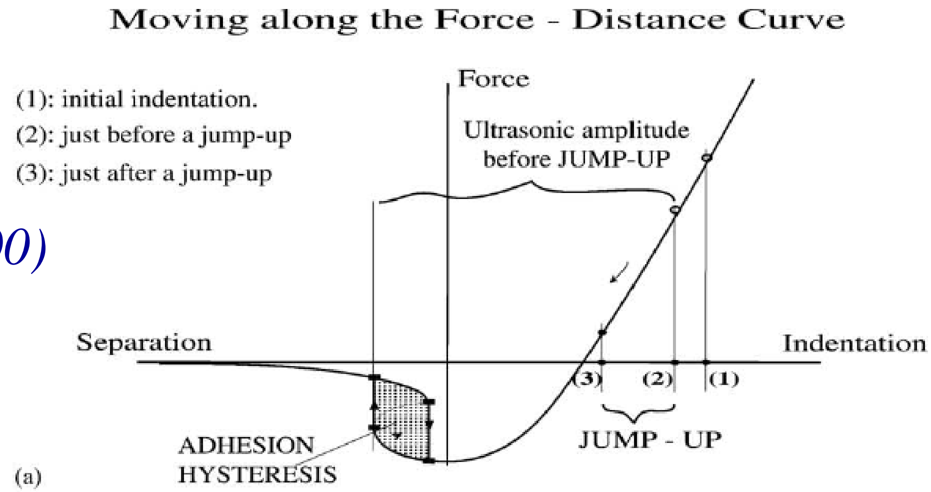


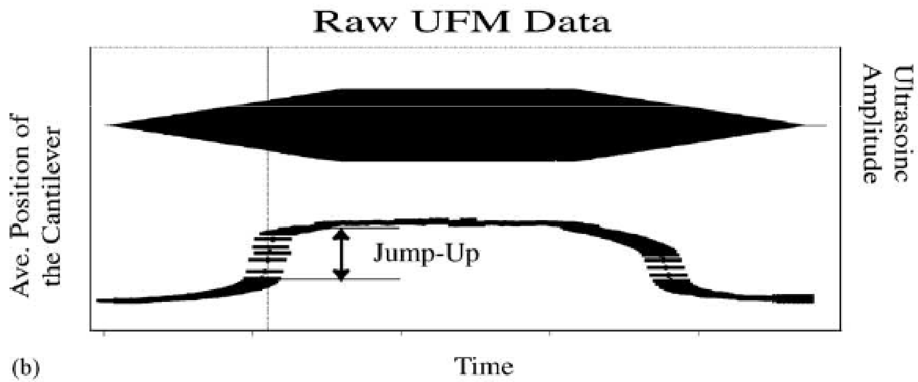
Dinelli, et al. PRB (2000)

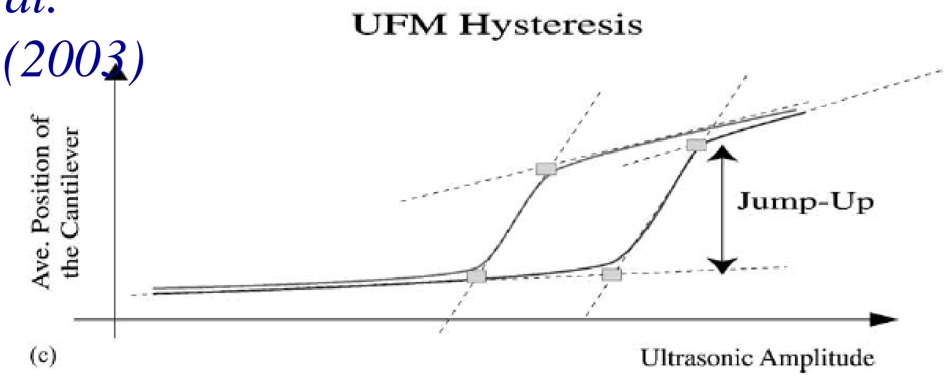


Szoskiewicz03 et al. Appl. Phys. Lett. (2003)

$$S_{eff}(F_{av}) = \frac{F_2 - F_1}{a_2 - a_1}$$







Outline

- ***Ultrasonic Force Microscopy***

  -The Mechanical-Diode (MD) effect

  - Information from UFM

- ***Some examples of UFM applications***

  - UFM on Polymeric Hydrogels

  - UFM on Phospolipide Bilayers

- ***UFM on polyelectrolyte complexes***

  - Poly[Q-co-H] / AlgNa (Ca^{2+}) / PLL complexes

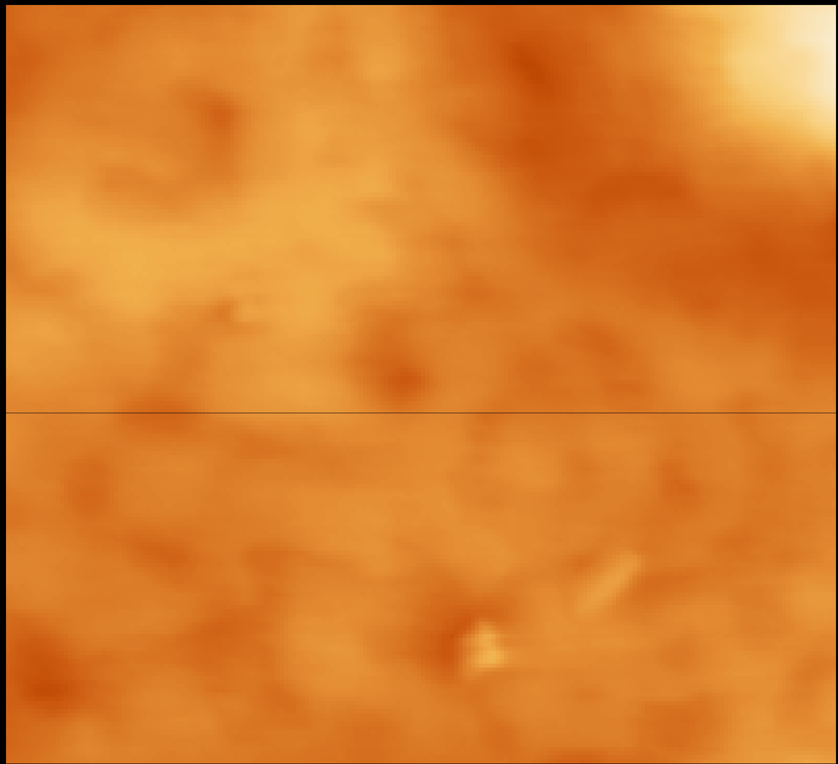
  - UFM on AlgNa (Ca^{2+}) / PLL / mica

  - UFM on Poly[Q-co-H] / AlgNa (Ca^{2+}) / PLL / mica

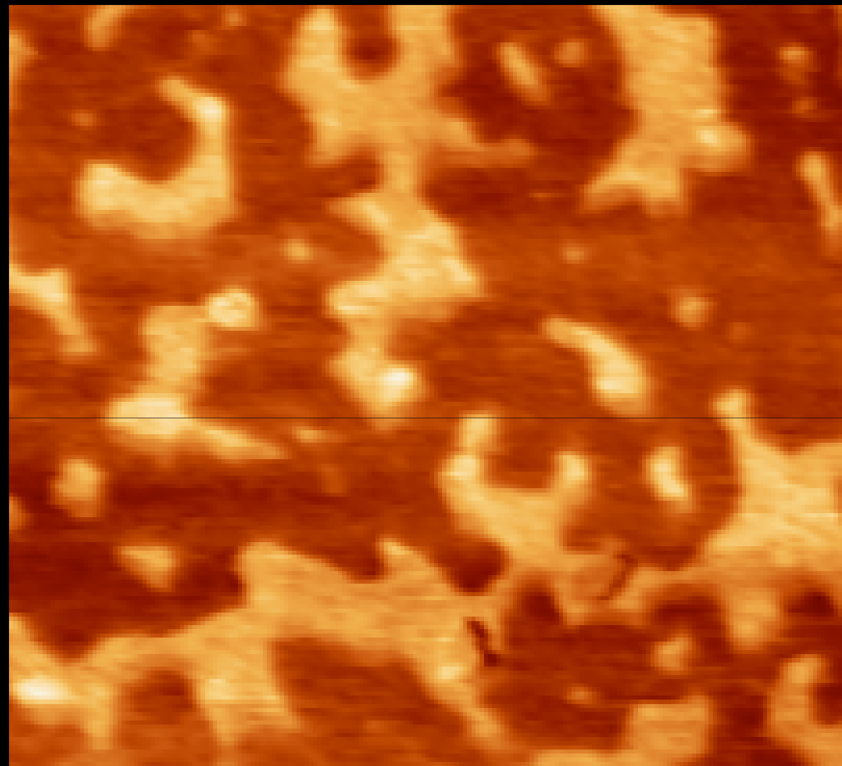
- ***Summary***

UFM on poly(acrylic acid) hydrogels

TOPOGRAPHY



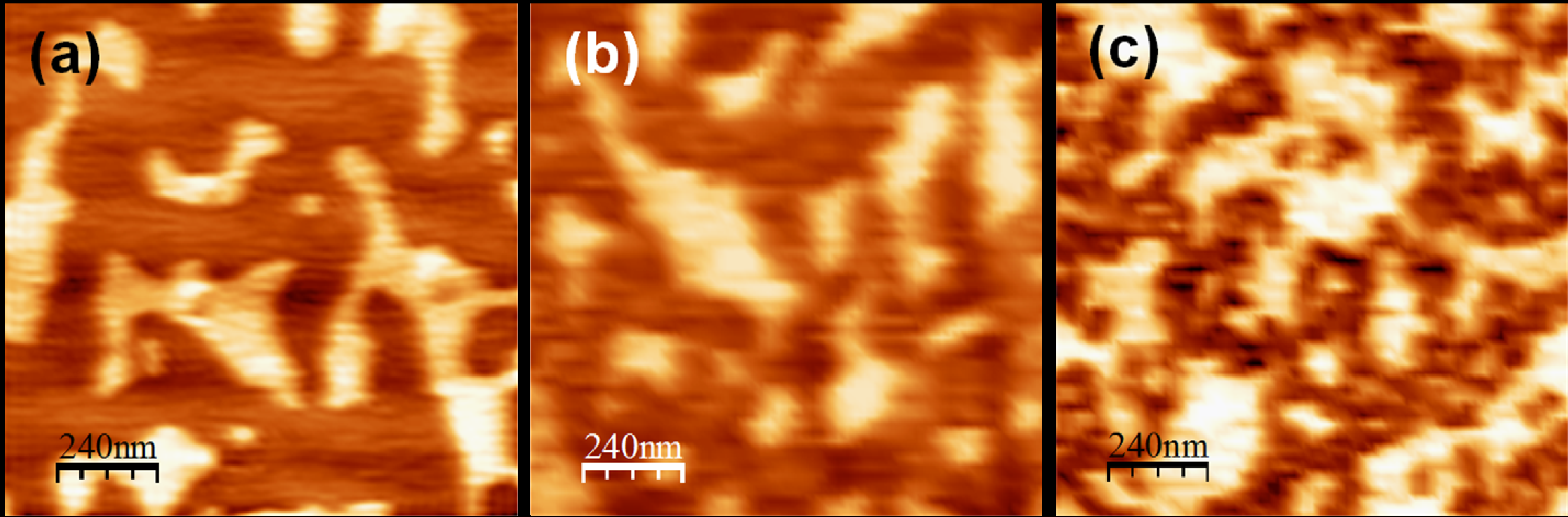
UFM



Surface area: (1.2 x 1.2)μm

B. Talavera , J. J. Martínez, F. Santiago, and M. T. Cuberes, Mater. Res. Soc. Symp. Proc. Spring Meeting (2008)

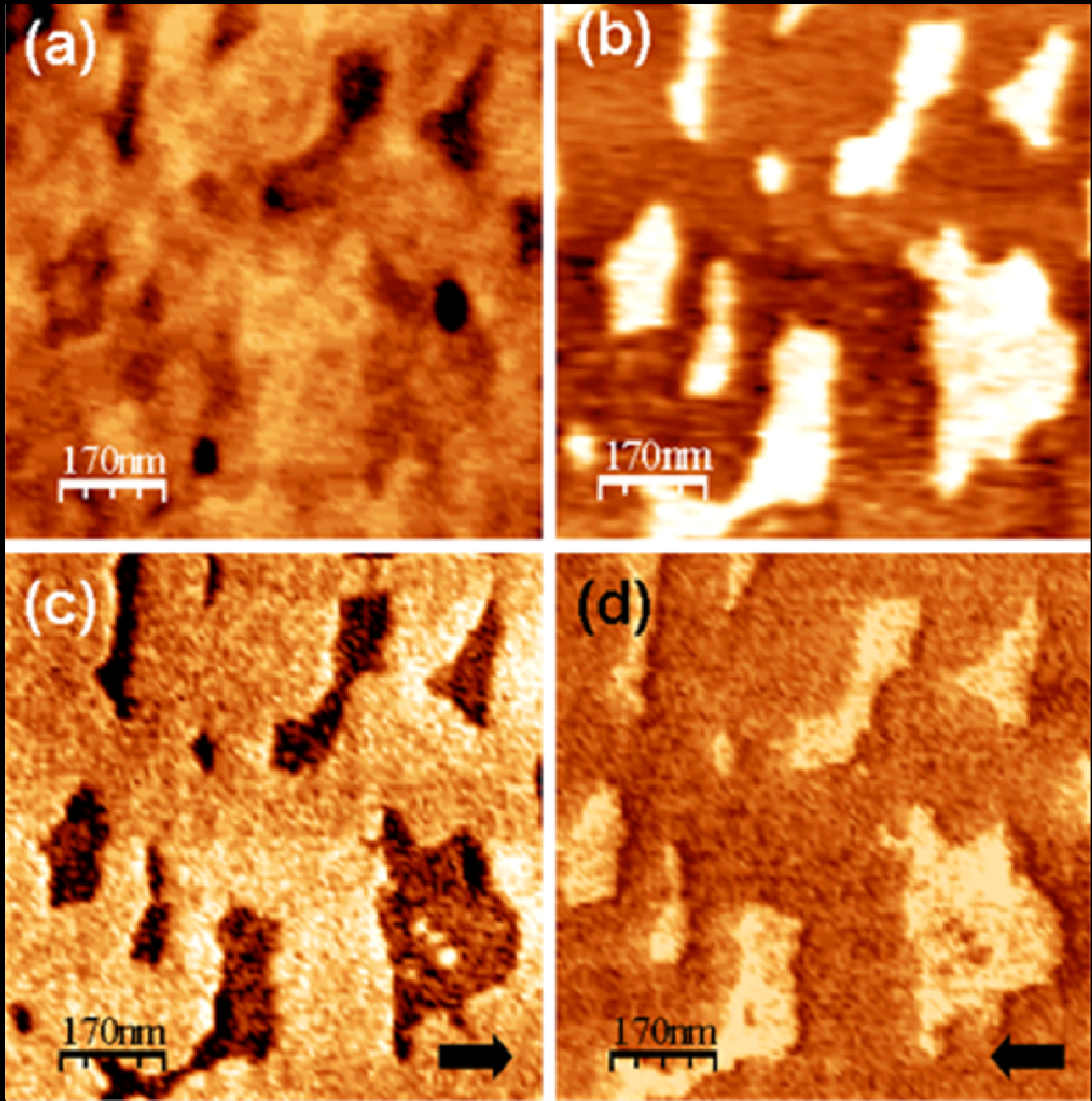
UFM on poly(acrylic acid) hydrogels



Increasing the amount of crosslinker, the size of the phase-separated domains decreases, and their packing density increases; *their distribution* on the gel surface becomes *more homogeneous*.

B. Talavera , J. J. Martínez, F. Santiago, and M. T. Cuberes
Mater. Res. Soc. Symp. Proc. Spring Meeting (2008)

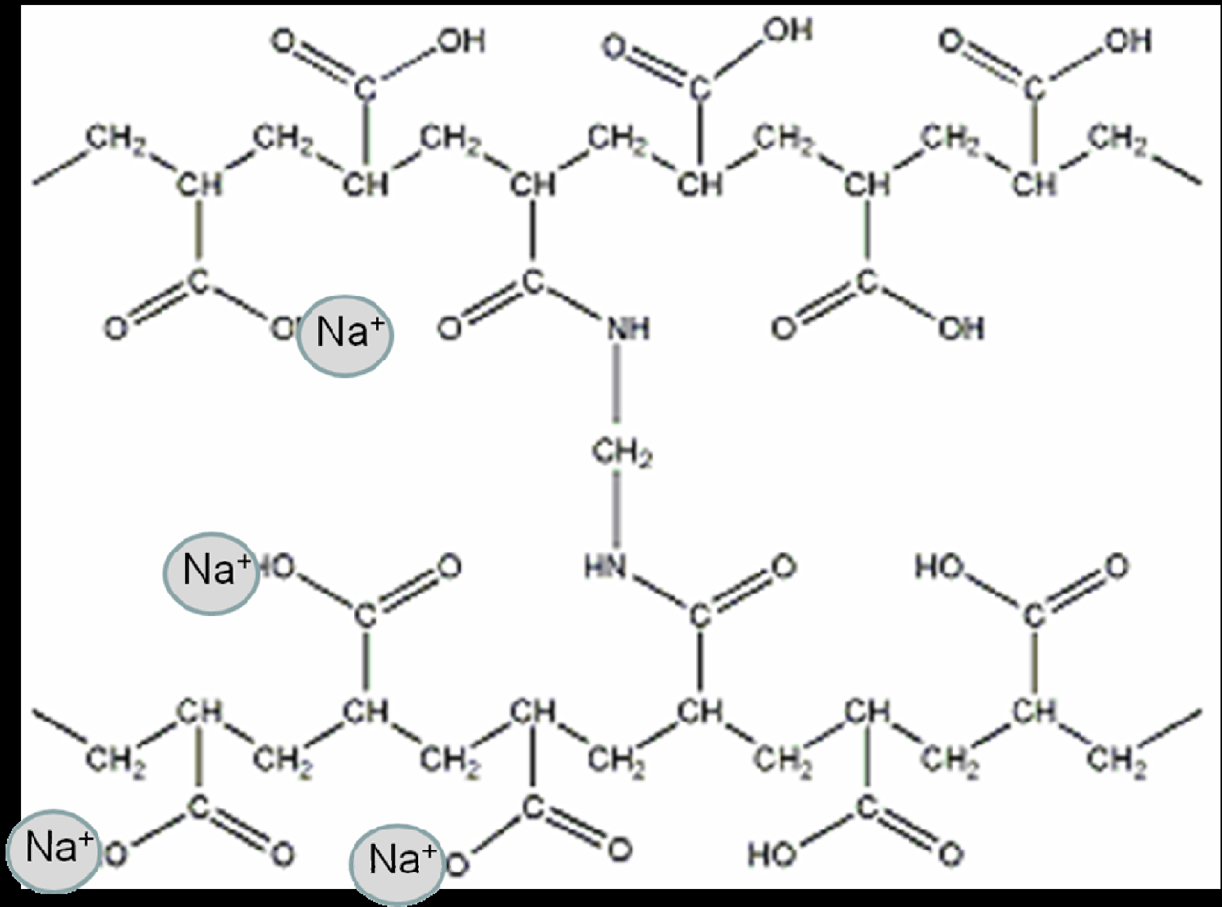
TOPOGRAPHY, ELASTICITY AND FRICTION



Domains with a higher topography are softer and present lower friction; those are attributed to a sodium acrylate rich phase. *High friction stiff domains* correspond to *acrylic acid rich phases.*

Talavera , Martínez, Santiago, and Cuberes Mater. Res. Soc. Symp. Proc. Spring Meeting (2008)

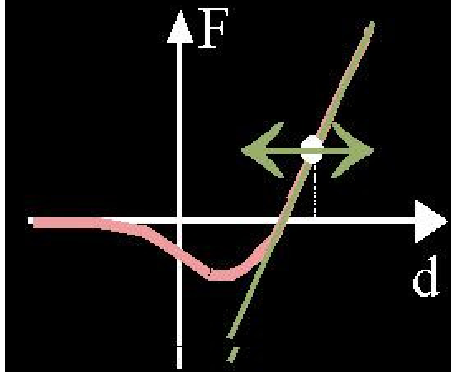
UFM on poly(acrylic acid) hydrogels

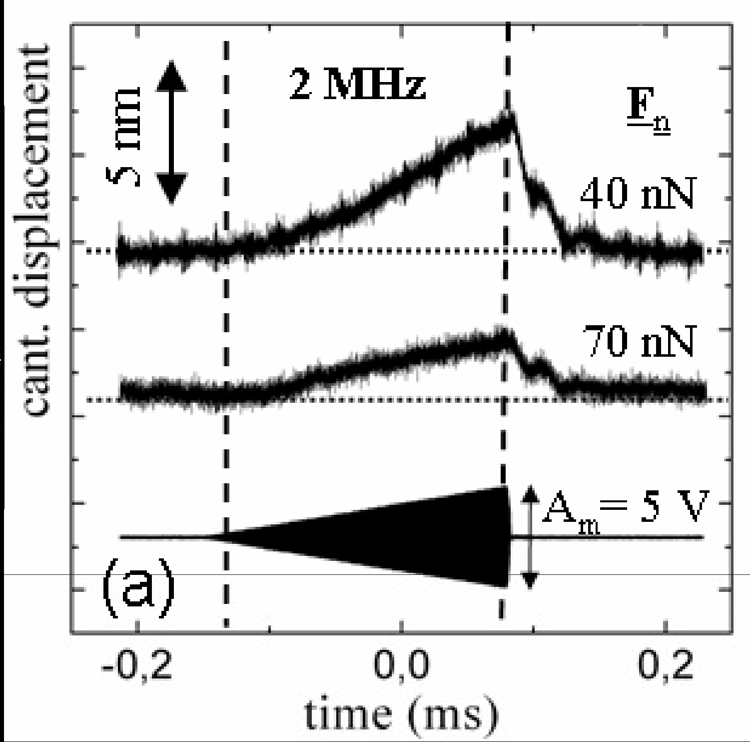


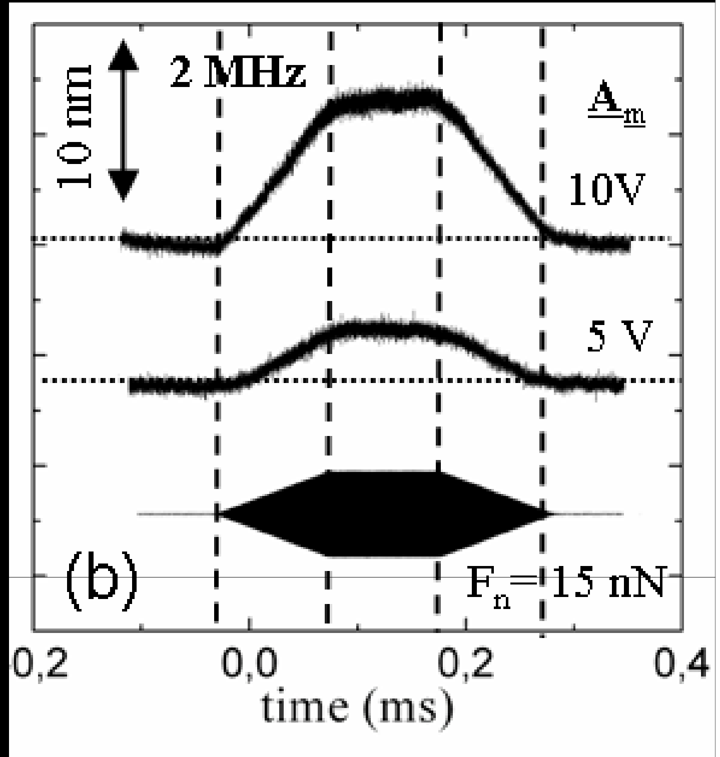
*Talavera , Martínez,
Santiago, and Cuberes
Mater. Res. Soc. Symp.
Proc. Spring Meeting*

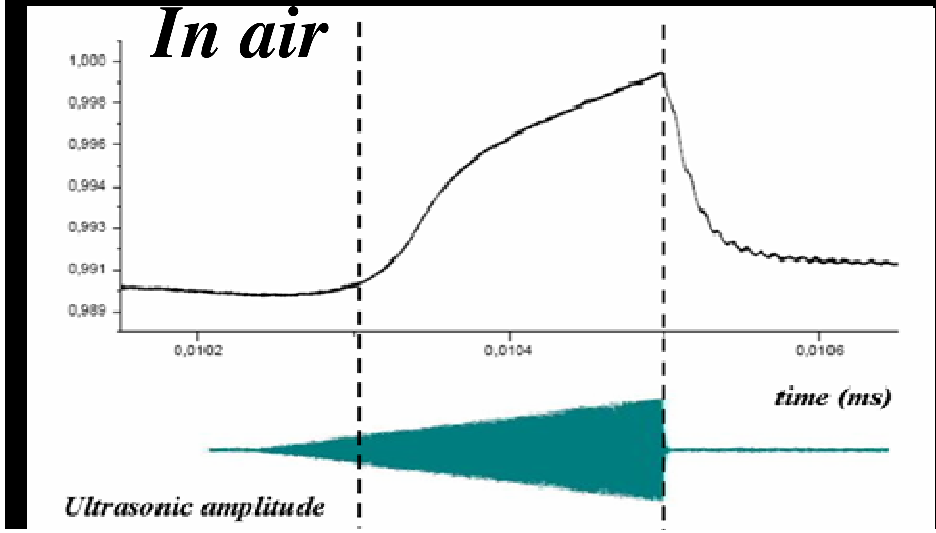
Poli (acrylic acid - co - sodium acrylate) *(PAAcNaAc)* gels were prepared *by free radical polymerization* of acrylic acid monomers partially *neutralized by sodium hydroxide* using N, N'-methylen-bis-acrylamide as a crosslinker and potasium persufate as an initiator.

UFM cantilever response on Si(111) in milliQ water





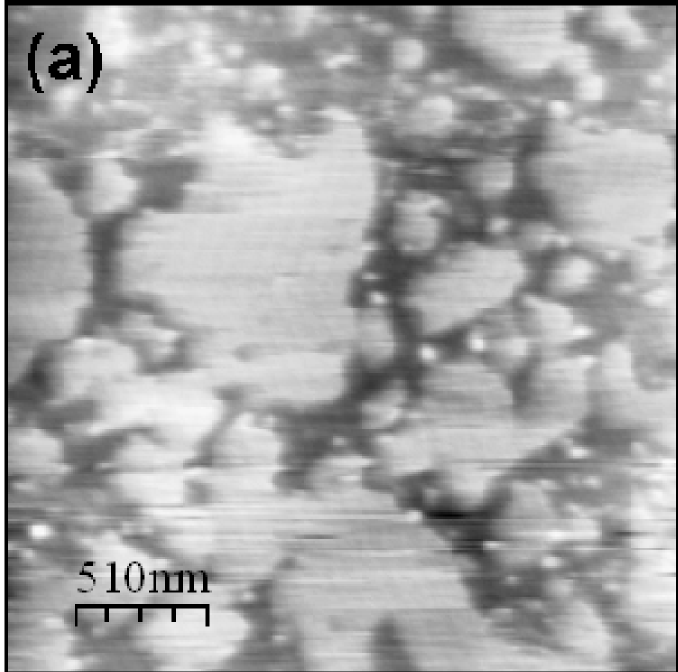




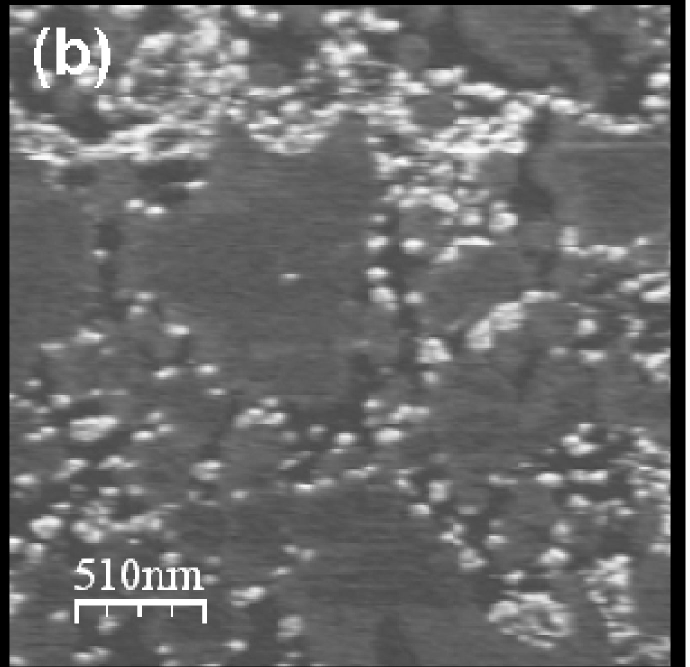
The **qualitative dependence** of the **UFM signal** on ***load*** and ***ultrasonic amplitude*** **in liquid is similar as in air**

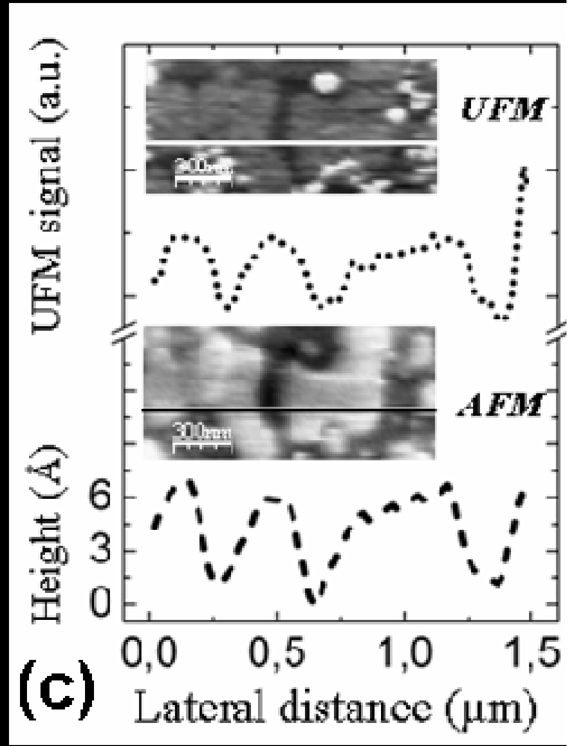
UFM on Phosholipid bilayers*

TOPOGRAPHY



UFM





UFM on **surface planar bilayers of phospholipids** yields **reasonable elastic contrast** on the gel and fluid phases and reveals a third more rigid phase within the fluid domains.

M. T. Cuberes, J. of Physics: Conf. Ser. 100 (2008) 052013

**Samples prepared in collaboration with M. Vélez*

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- **Summary**

Poly[Q-co-H] / AlgNa (Ca^{2+}) / PLL complexes

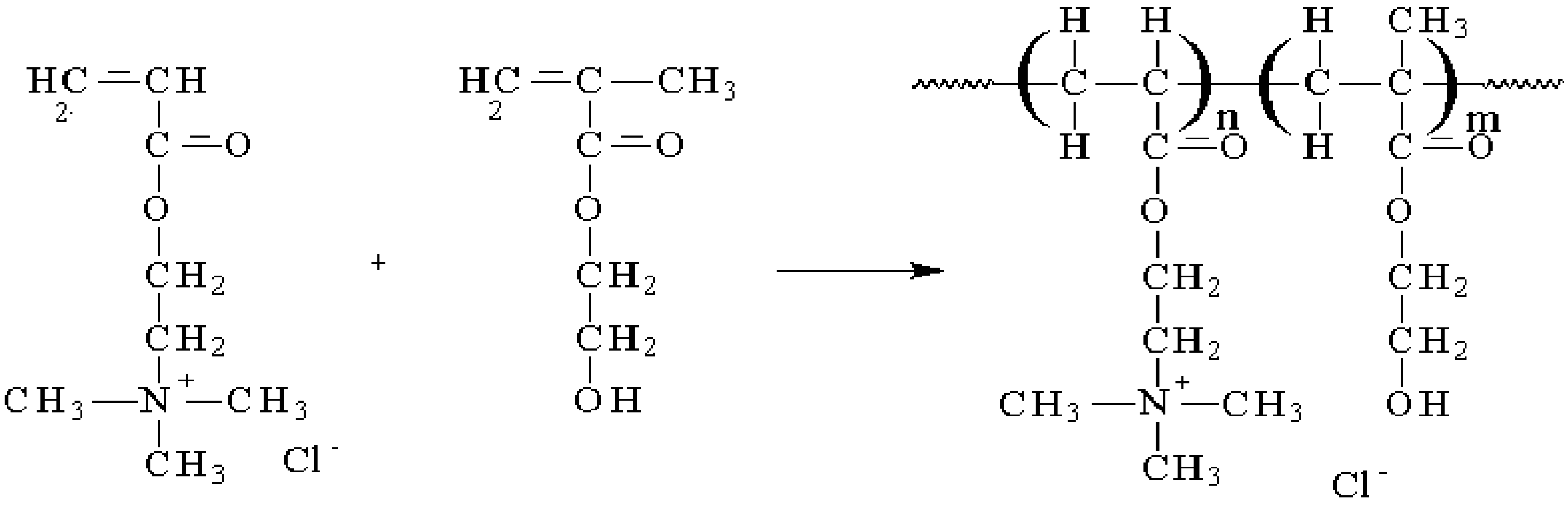
Motivation: learn about the **elastic nanostructure** ***of Poly[Q-co-H]-AlgnNa(Ca^{2+}) complexes supported on mica susbtrates*** using **AFM / UFM**

Previous work in the literature on these complexes:

- ***Synthesis and Characterization of Poly(Q-co-H): A study of its interaction with Sodium Alginate***, **O. Valdés**, D.Monnet, L. Agüero, D. Zaldívar, L. Alexandrova, and I. Katime, J. of Appl. Polym. Sci. 108 (2008), 1680-1688

- ***Adhesion and growth of goat mammary epithelial cell on novel polyelectrolyte complex***, **O. Valdés**, L. Agüero, M. P. Rodríguez, D. Zaldívar, and I. Katime, Colloid Polym. Sci. 286 (2008), 464-467

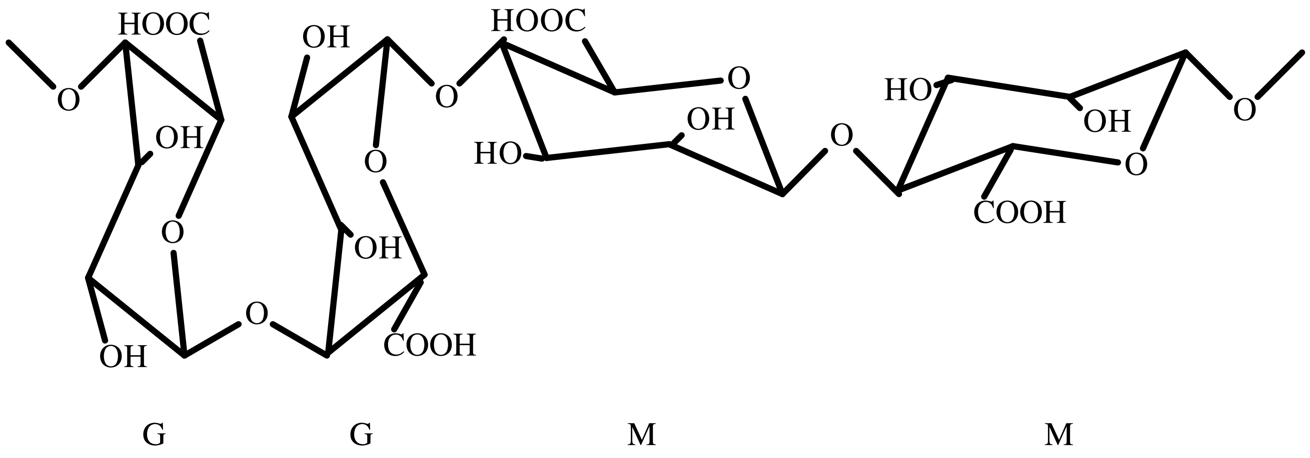
Poly(acryloxyethyltrimethylammonium chloride-co-2-dyhydroxyethyl-methacrylate):



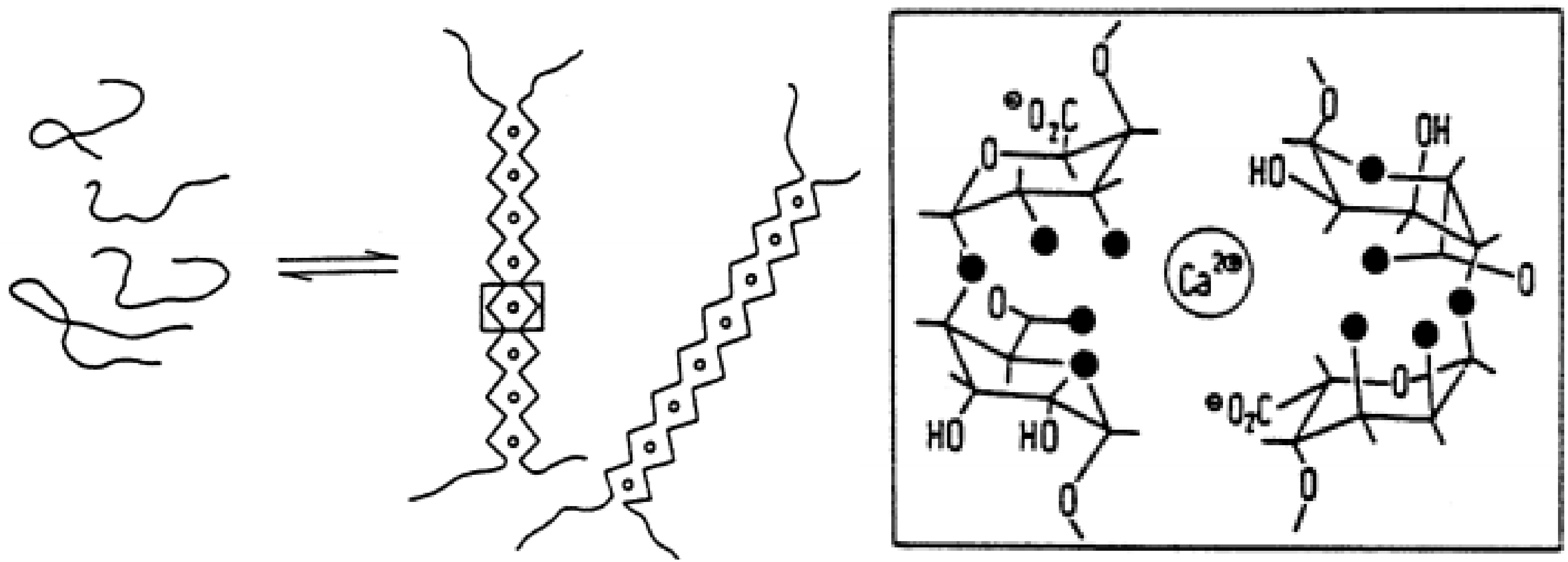
Q9 **HEMA** **poli(Q9/HEMA)**

J. of Appl. Polym. Sci. , O. Valdés et al. 108 (2008), 1680-1688

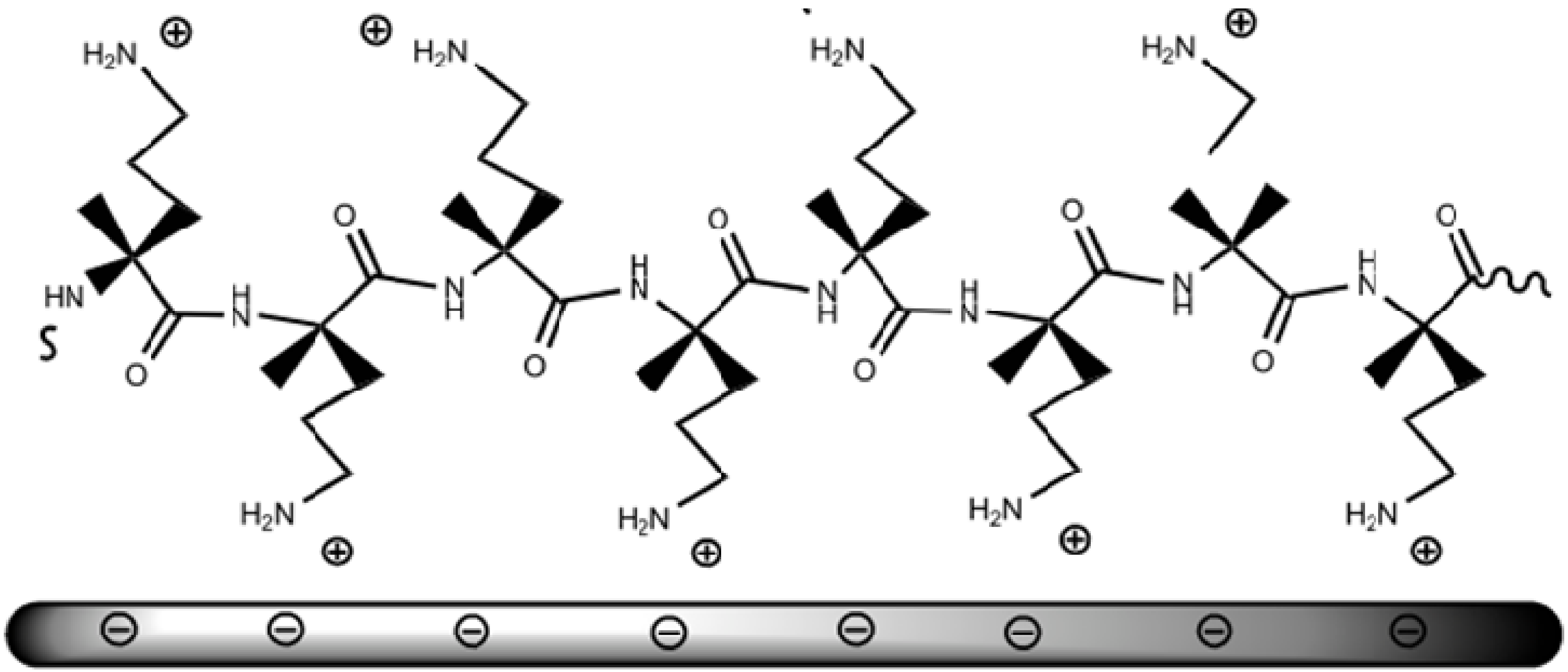
Sodium Alginate:

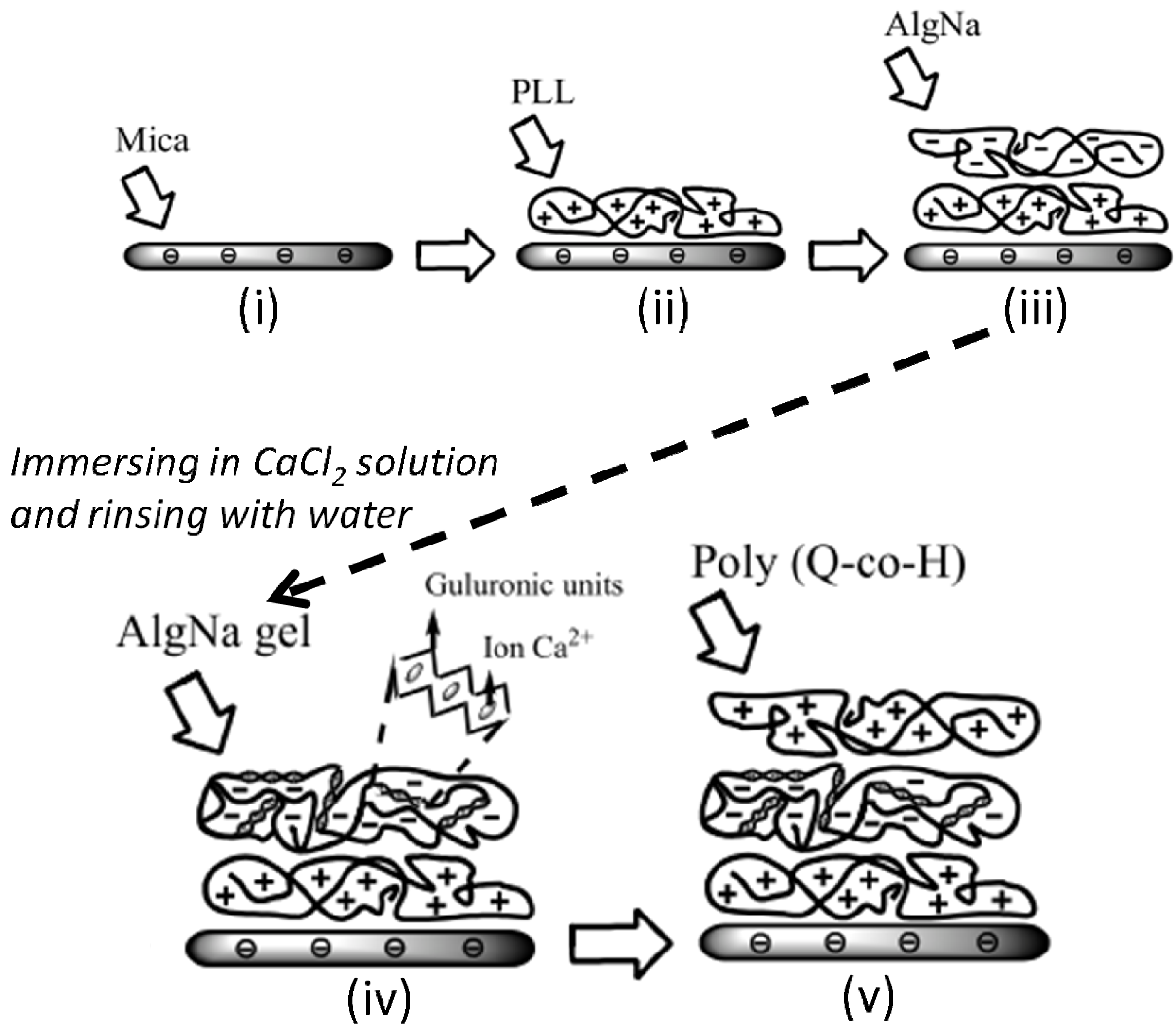


Ionic gellation (Ca^{2+}) of Sodium Alginate:



Poly-l-lysine:



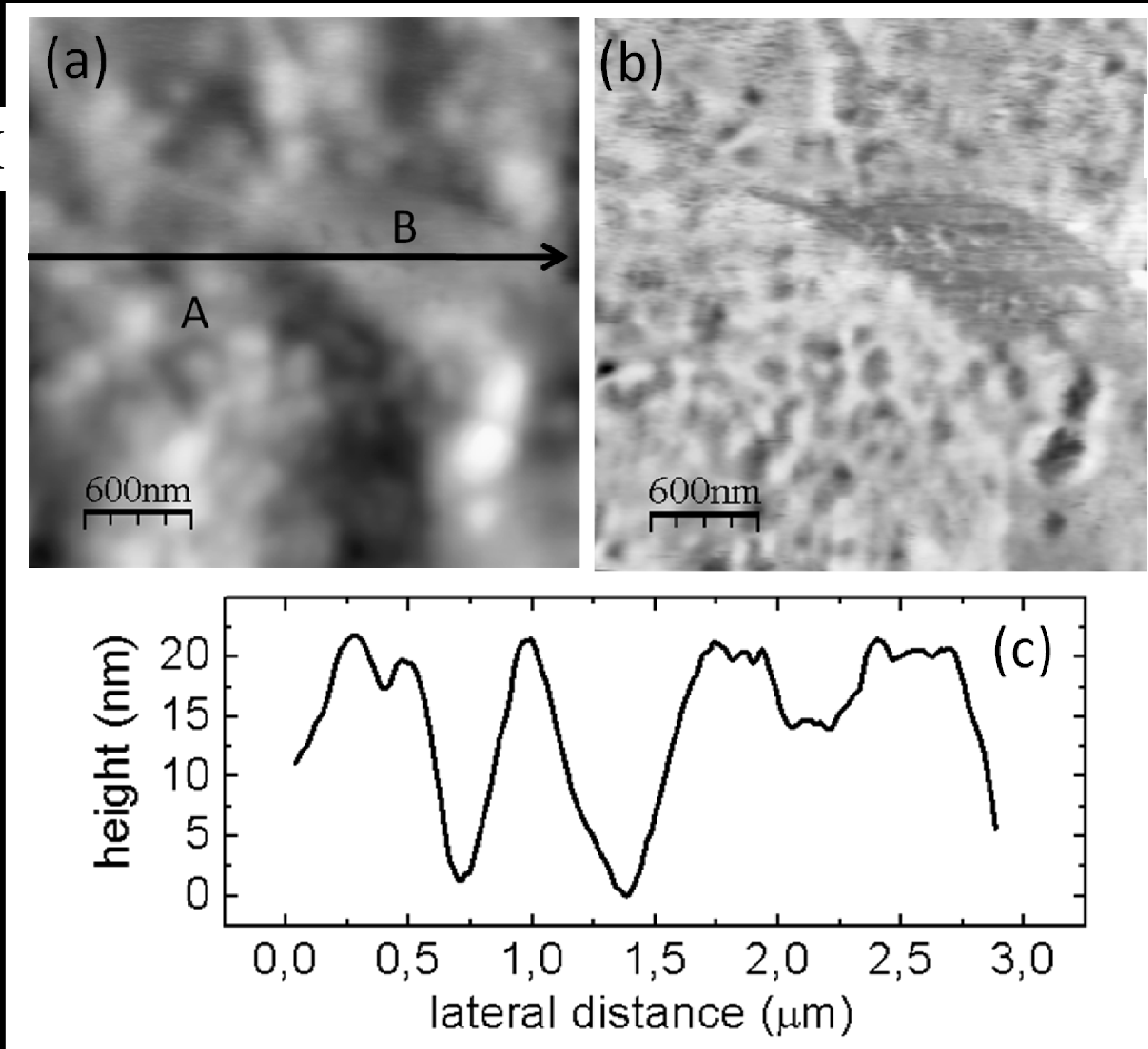


Mica
PLL
AlgNa
(i)
(ii)
(iii)
Immersing in CaCl2 solution
and rinsing with water
AlgNa gel
Guluronic units
Ion Ca2+
Poly (Q-co-H)
(iv)
(v)

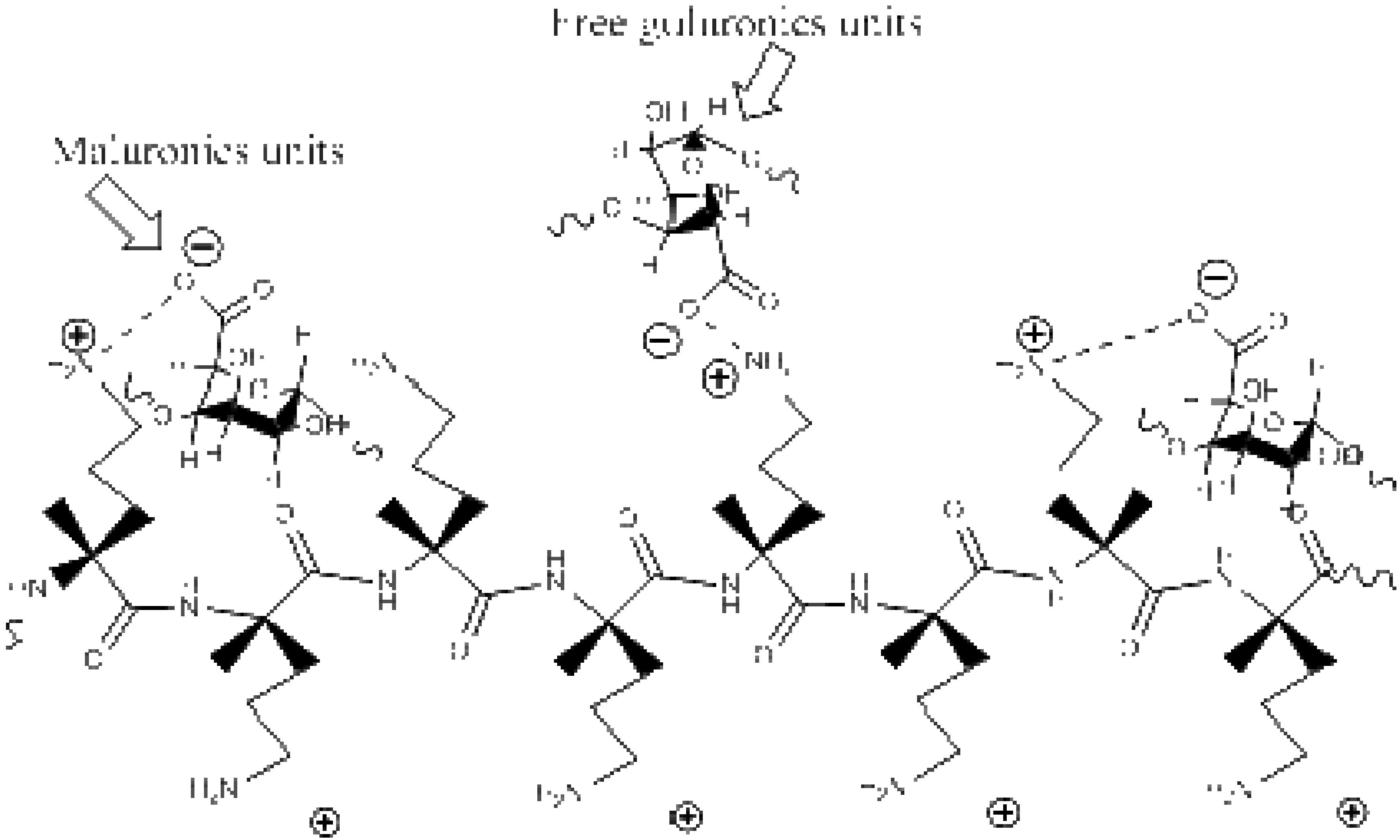
UFM on AlgNa (Ca^{2+}) / PLL / mica

AFM

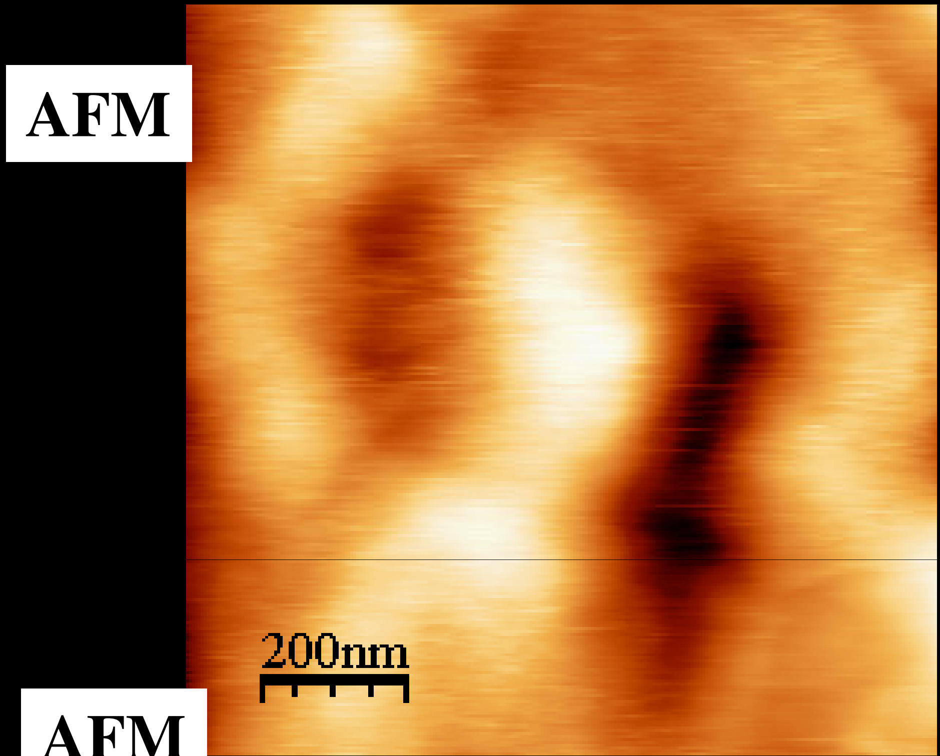
UFM

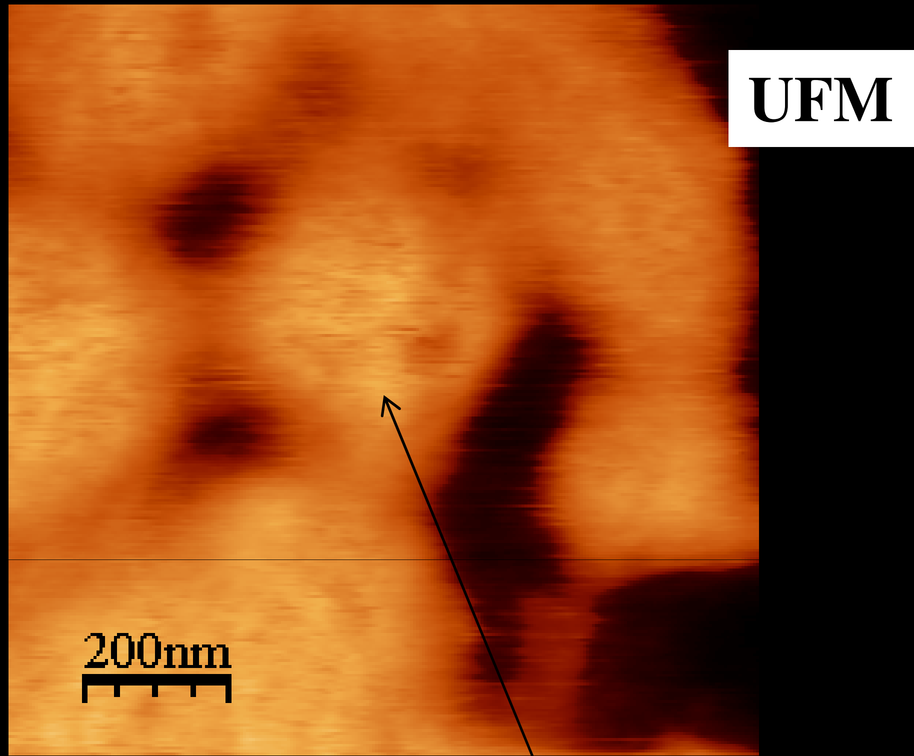


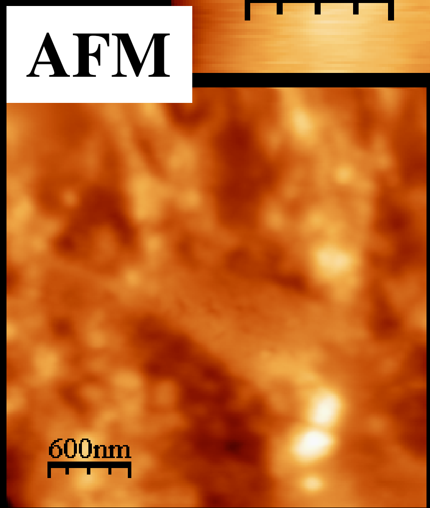
Electrostatic interactions between PLL and AlgNa:



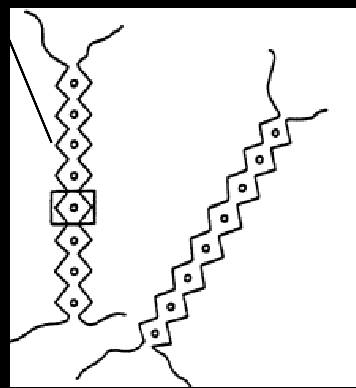
UFM on AlgNa (Ca^{2+}) / PLL / mica



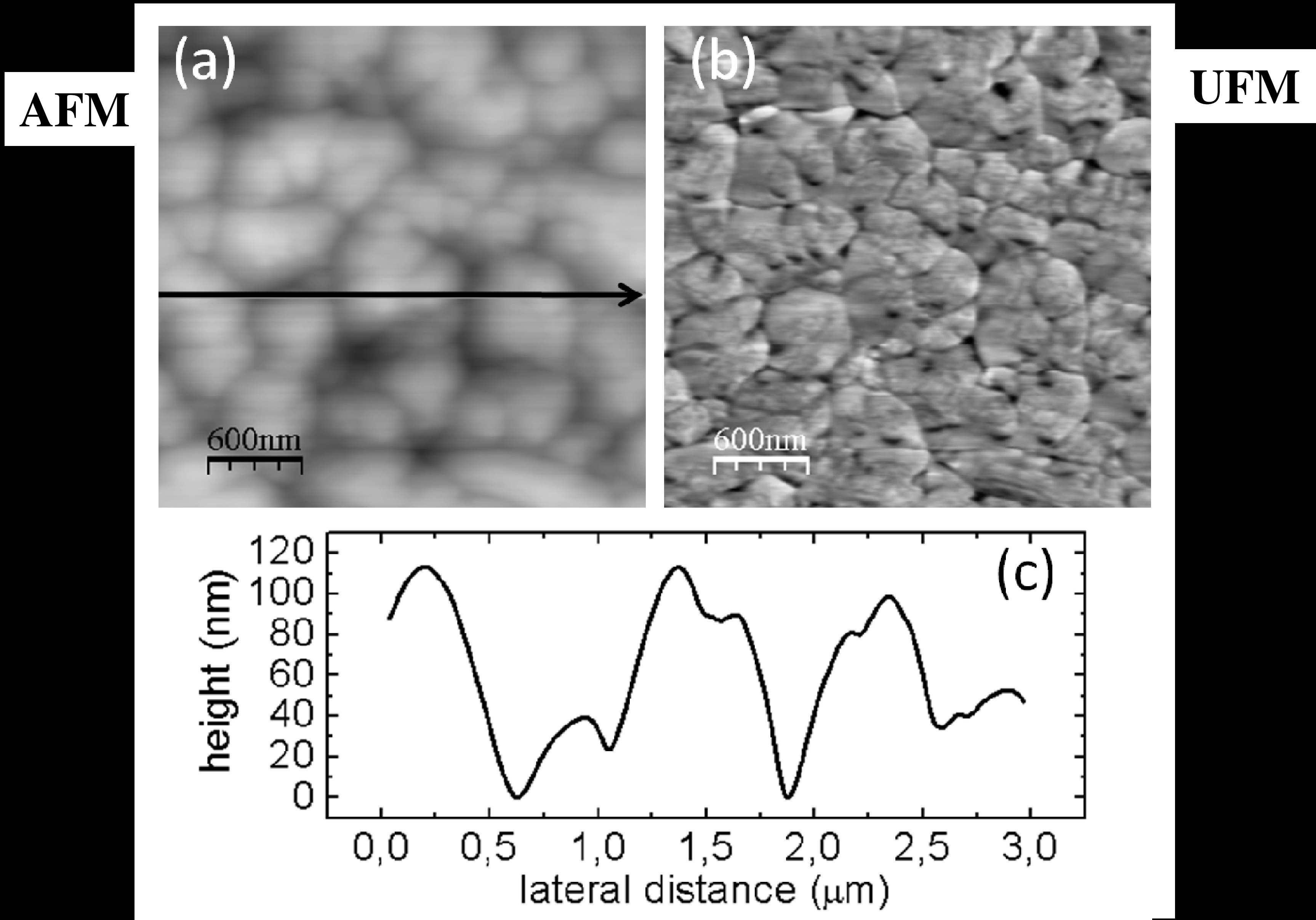


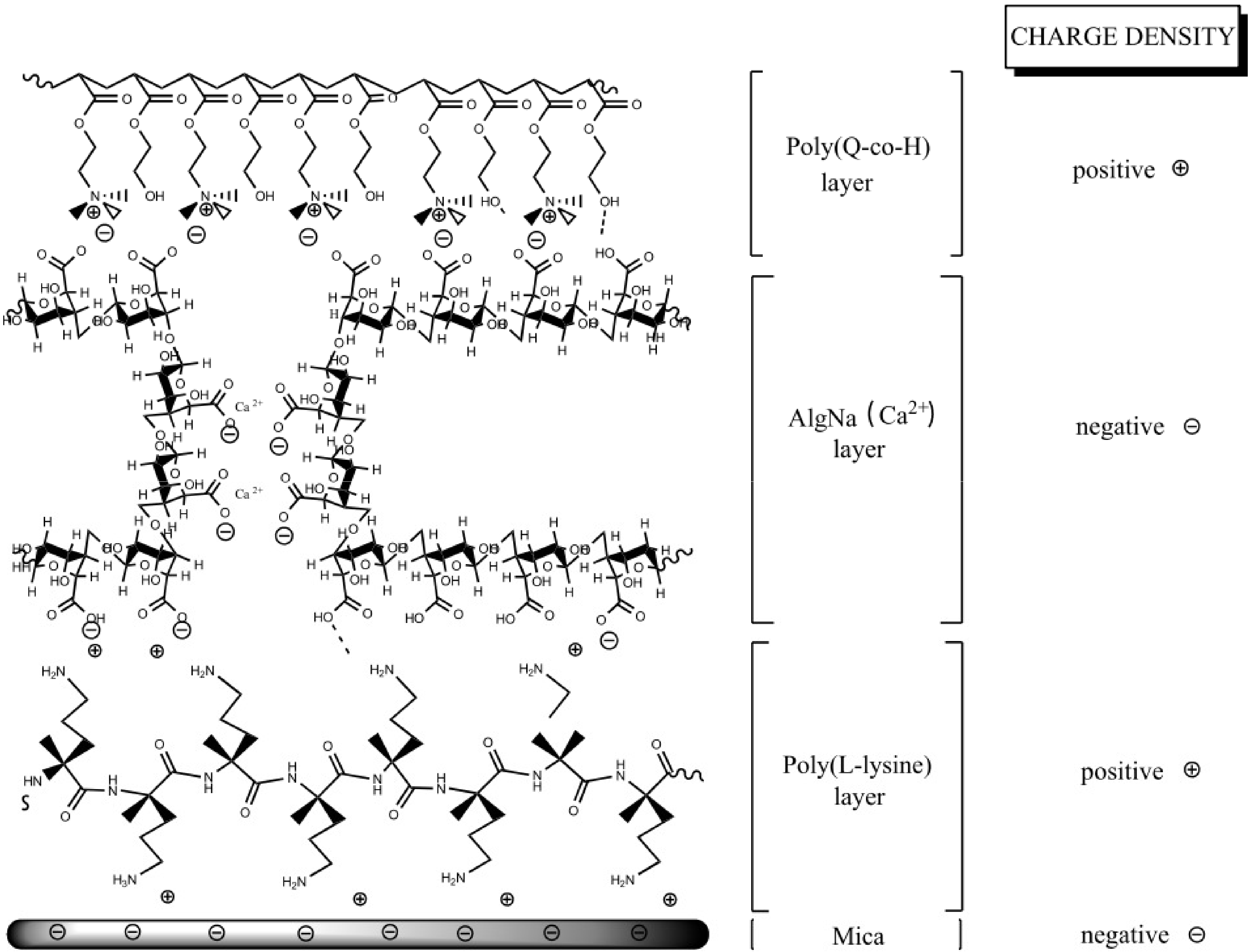


O. Valdés and M. T. Cuberes, J. Biomed. Nanotechnol. 5 (2009) 716-721

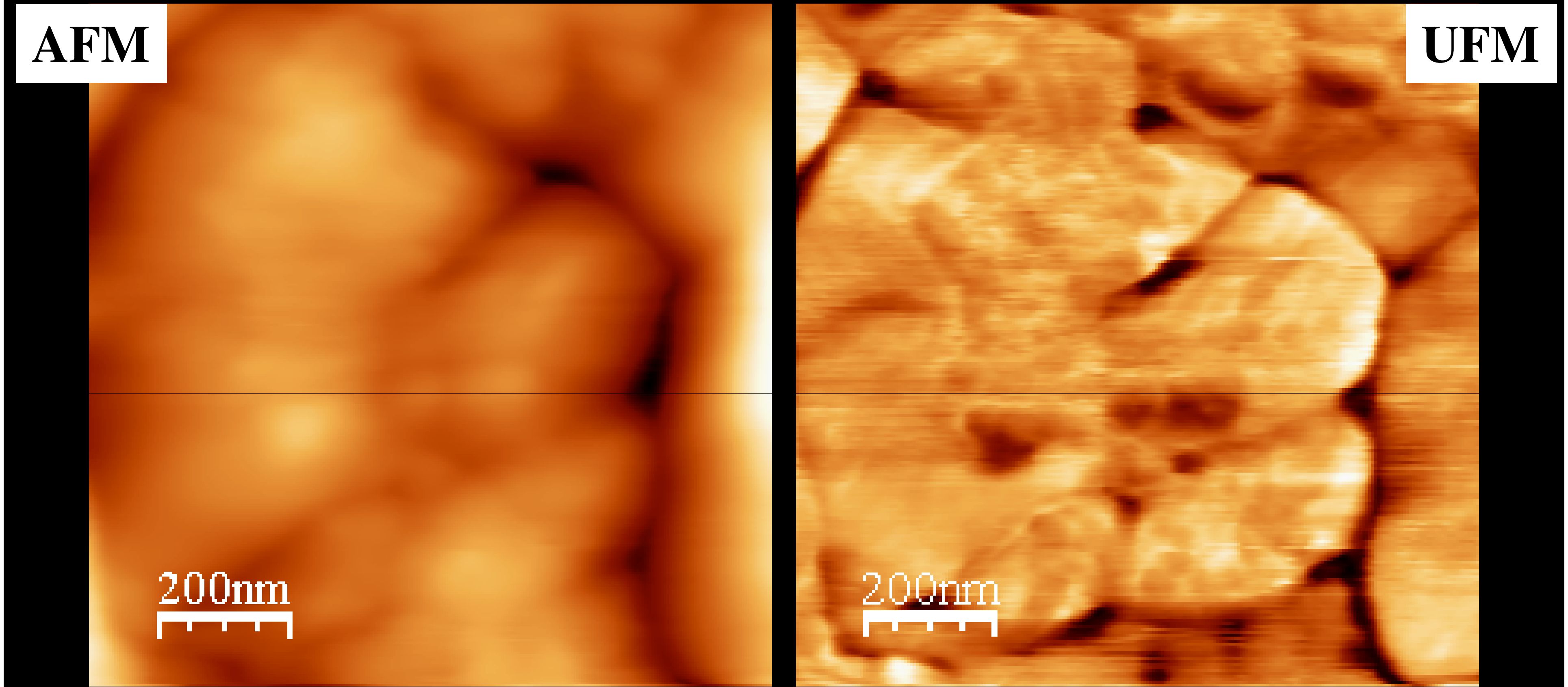


UFM on Poly[Q-co-H] / AlgNa (Ca^{2+}) / PLL / mica




CHARGE DENSITY
Poly(Q-co-H) layer
positive ⊕
AlgNa (Ca2+) layer
negative ⊖
Poly(L-lysine) layer
positive ⊕
Mica
negative ⊖

UFM on Poly[Q-co-H] / AlgNa (Ca^{2+}) / PLL / mica



O. Valdés and M. T. Cuberes, J. Biomed. Nanotechnol . (2009) 716-721

Summary

- ***Ultrasonic Force Microscopy***

  -UFM provides a valuable technique for the study of polymer gels, lipid bilayers and polyelectrolyte complexes

- ***Some examples of UFM applications***

  - UFM on Polymeric Hydrogels

  - UFM on Phospolipide Bilayers

- ***UFM on polyelectrolyte complexes***

  - UFM on Poly[Q-co-H] / AlgNa (Ca^{2+}) / PLL / mica: the subsurface sensitivity provided by UFM allows us to resolve the elastic bonding distribution in the buried biopolymer network by imaging from the poly(Q-co-H) overlayer.

ACKNOWLEDGEMENTS

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UCLM Group: ***Nanotechnology and Materials***

Salvatore Marino
Juanjo Martínez,
Carmen Iniesta
Alejandro Rodríguez

http://www.uclm.es/organos/vic_investigacion/gruposweb/nanotecnologia/

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