

Particles 2009, Berlin

Mechanical characterization of microcapsules using AFM force spectroscopy

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Department Physical Chemistry II

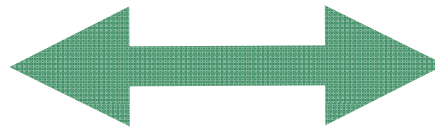


Bayreuth Center for Colloids and Interfaces

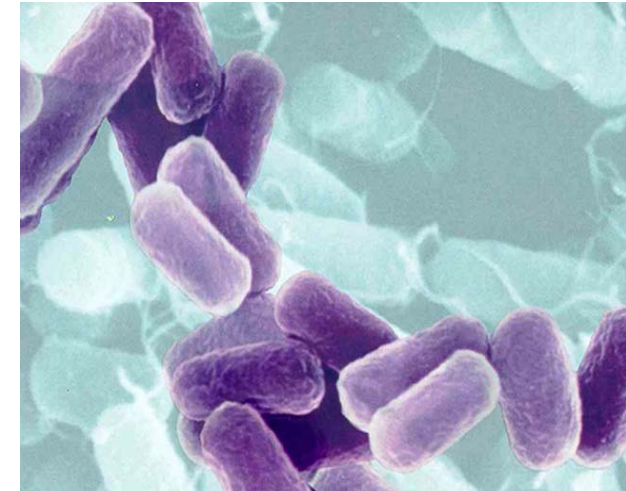
Microcapsules



Encapsulation :
pharmaceutics, cosmetics,
food design,....



Biosystems :
abundance of capsules
(bacterial and viral
capsids,...)

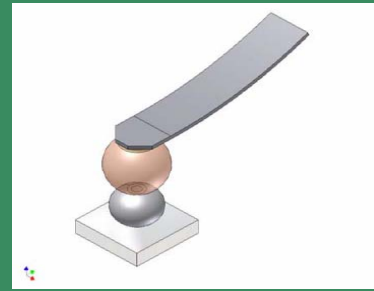


Mechanical properties

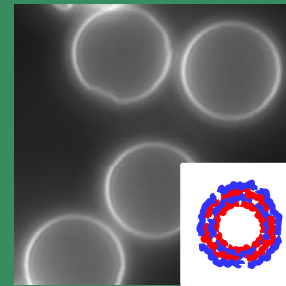
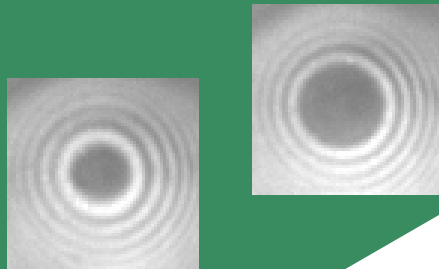
- Stability
- Insight in physical state of the wall material
- Stimulus sensitivity
- Transport properties in flow, Rheology
- Adhesion (interplay mechanics-surface forces)



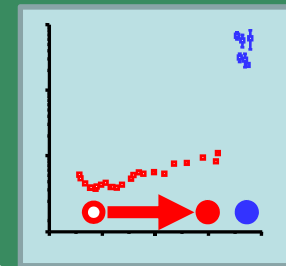
New tools for
Investigations on
Single microcapsule
level needed



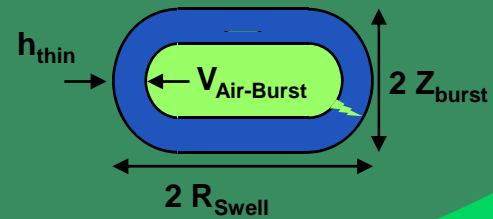
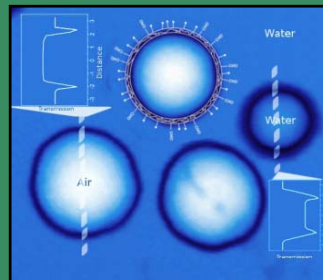
Combination of AFM
with optical microscopy



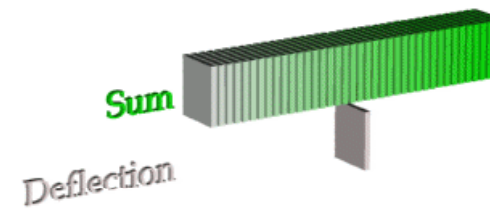
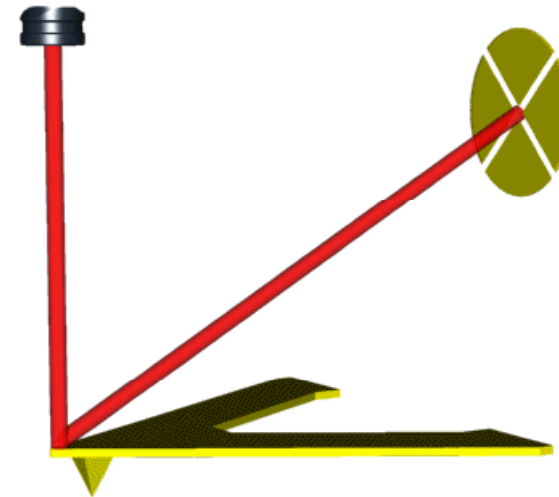
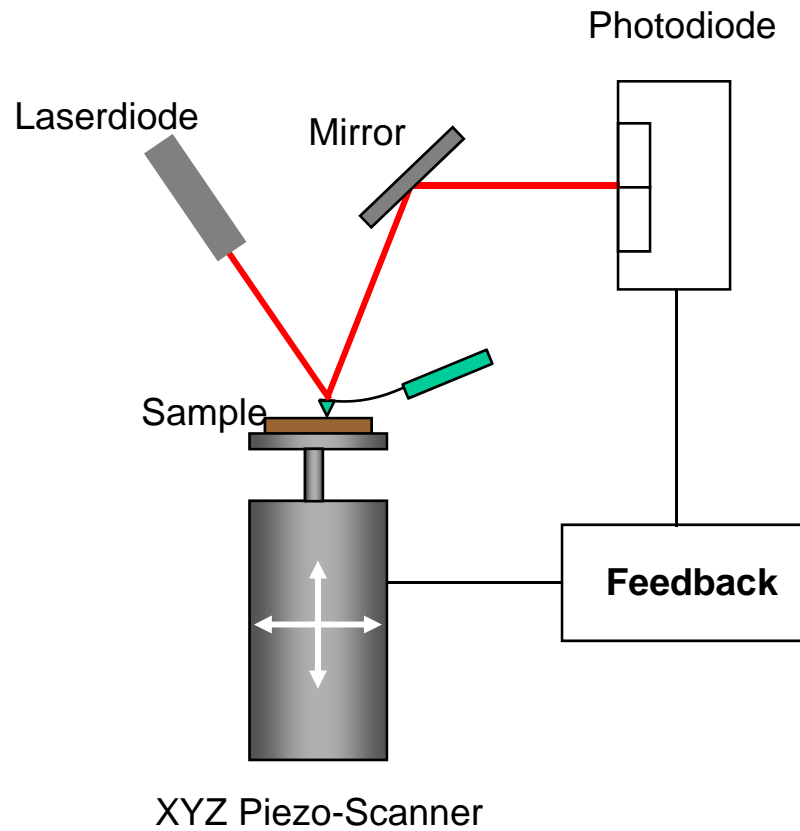
Layer-by-layer
capsules



Microballoons

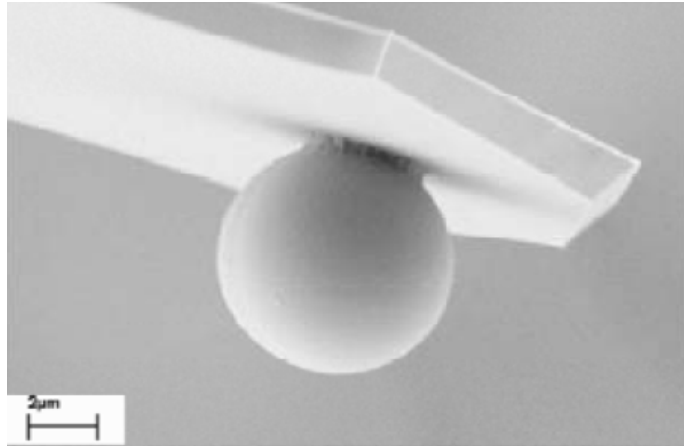


AFM schematically



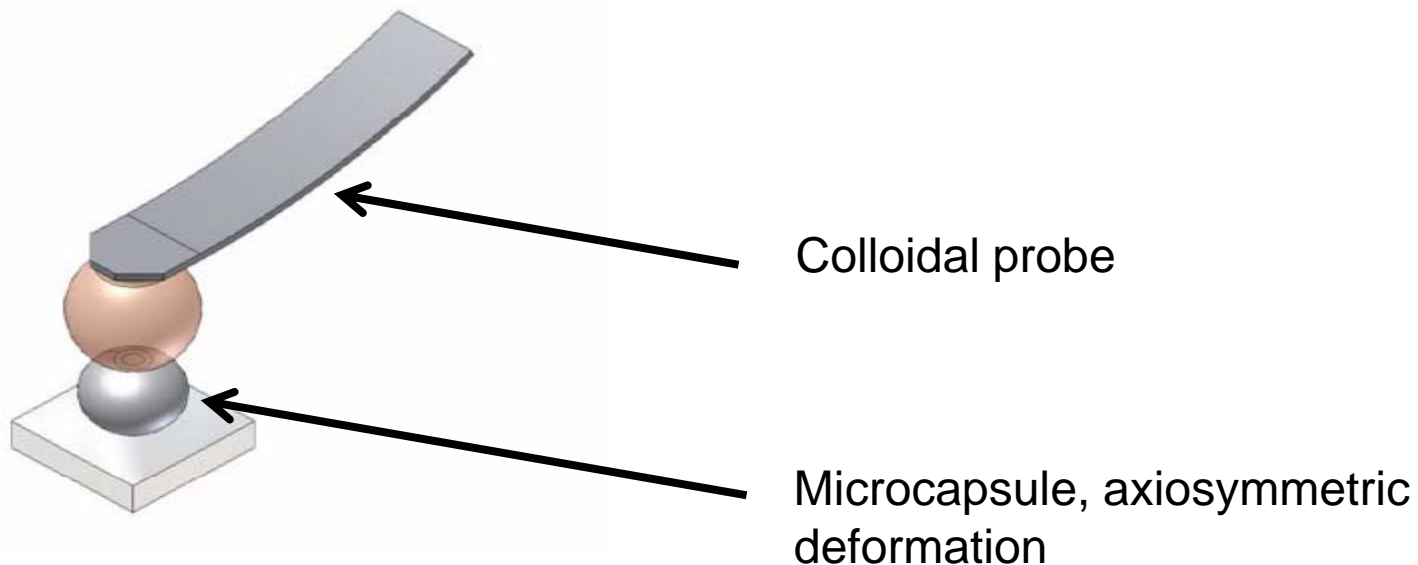
Force detection or imaging possible

AFM: Force information

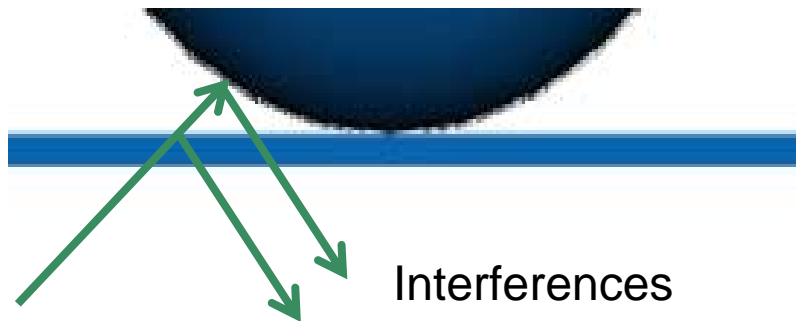


Usage of colloidal probe-cantilever¹ ensures well defined deformation-geometry

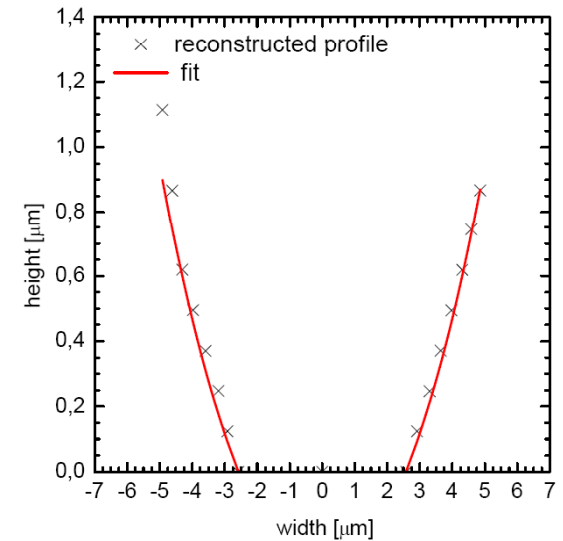
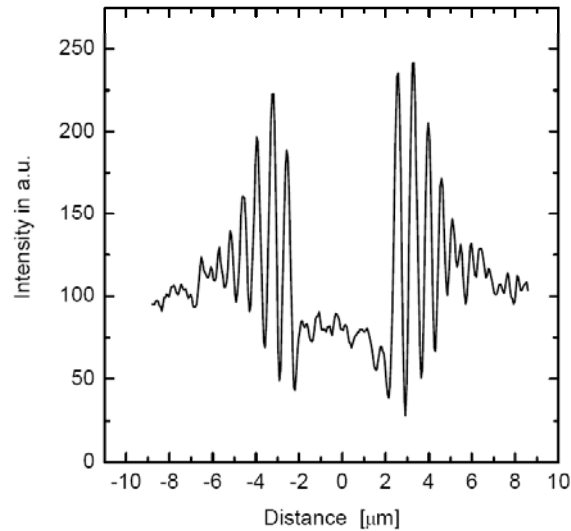
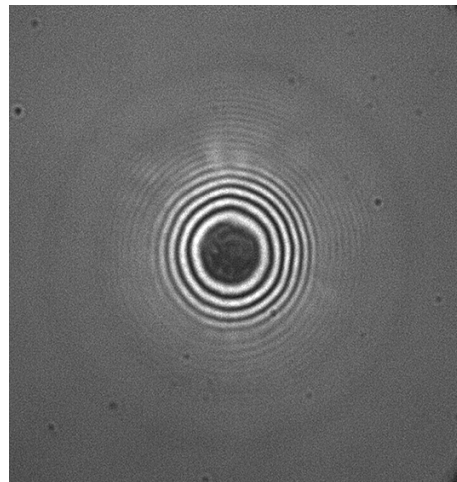
¹Butt HJ. Biophysical Journal 1991; 60 (6): 1438-1444.



RICM: Shape Reconstruction

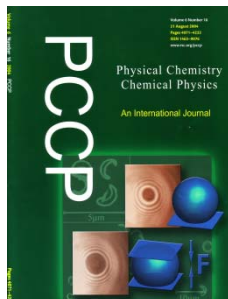
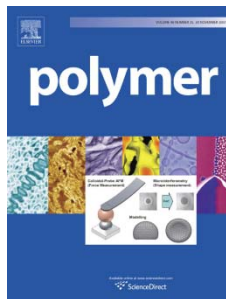
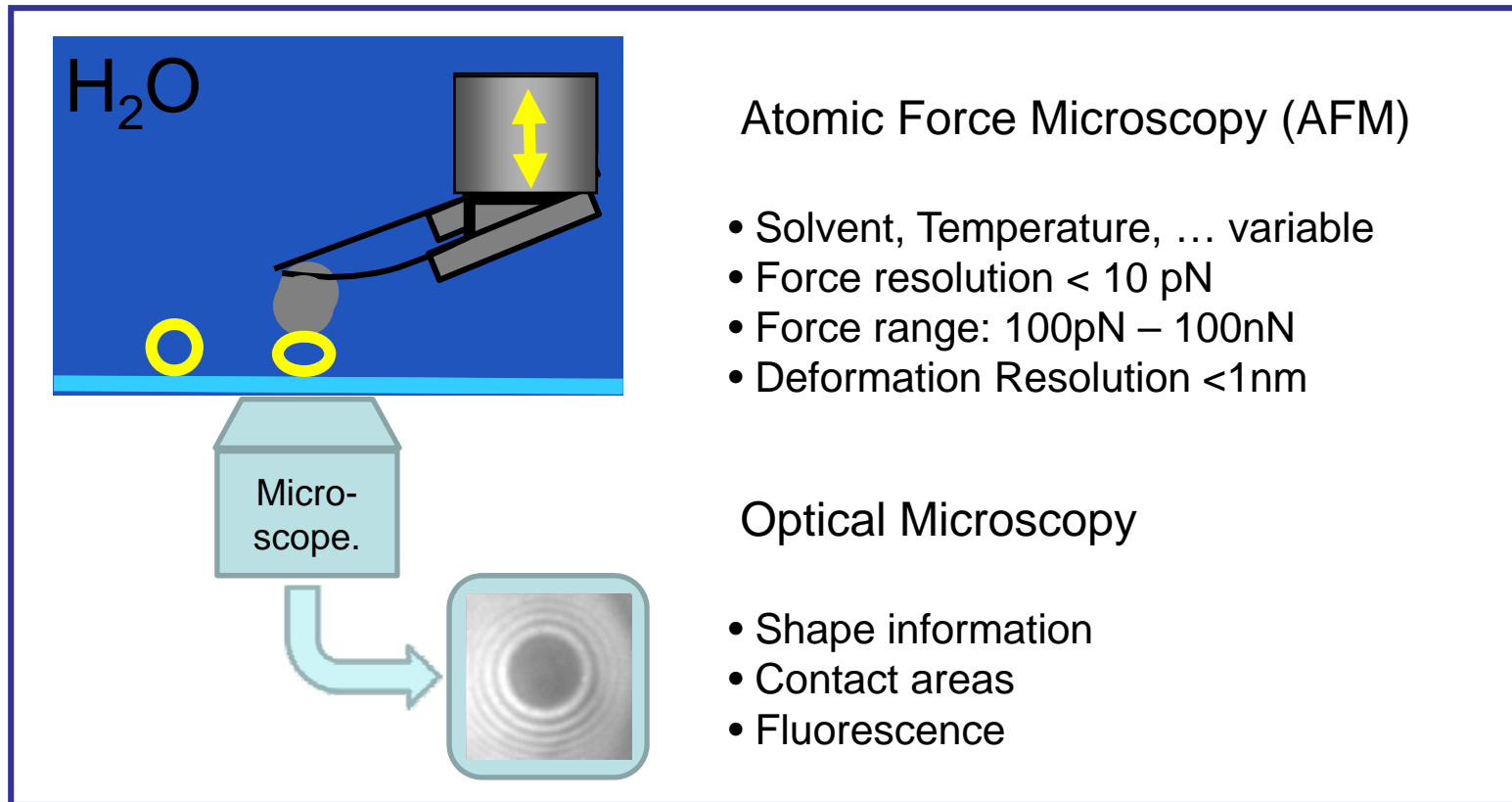


Reflection Interference Contrast Microscopy (RICM) allows reconstruction of shape



J. Rädler, E. Sackmann; *J. Phys France II* **3**: 727 (1993)
Dubreuil, F., N. Elsner, A. Fery *Europhys. J. E* **12(2)** 215 (2003)

Single Microcapsule Deformation : Method

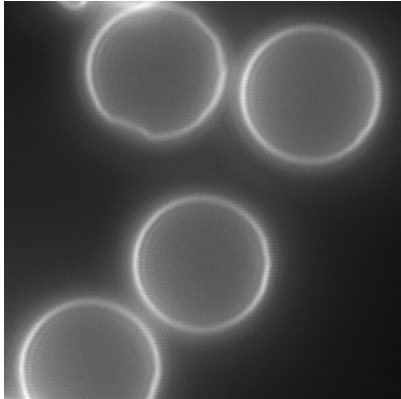


Europhys. J. E, **12 (2)**, 215-221 (2003)

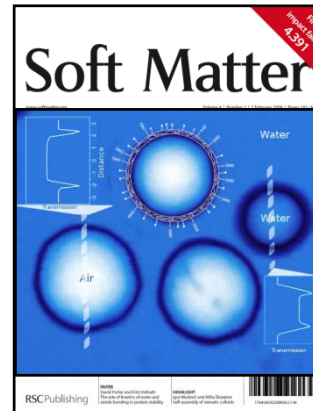
review article :

Polymer, **48** 7221-7235 (2007)

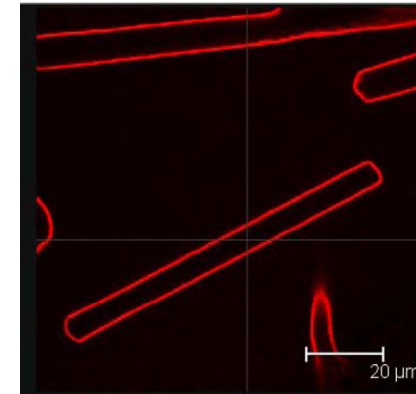
Microcapsule Systems



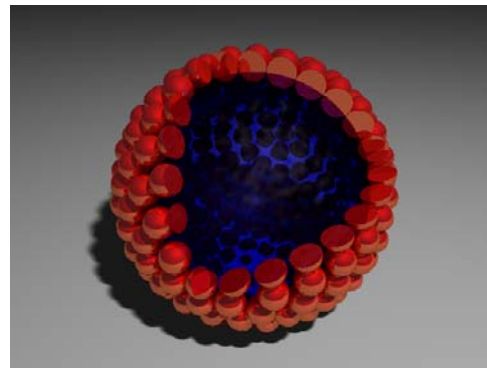
Polyelectrolyte Multilayer Capsules



Micro -Bubbles



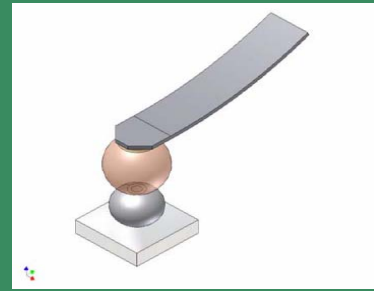
Polyelectrolyte Multilayer Tubes¹



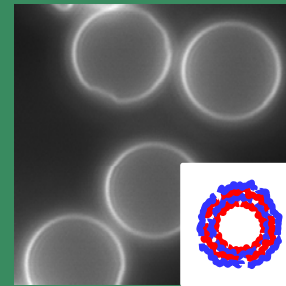
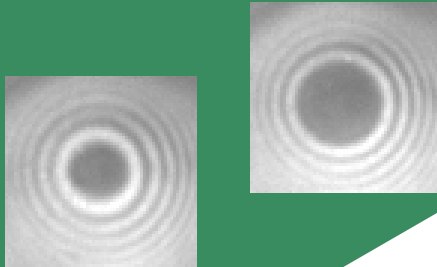
Pickering Emulsions²

¹ : R. Müller & al. *Polymer* **48** 2520 (2007); R. Müller et al. *J. Phys. Chem. B* **111** 8547 (2007)

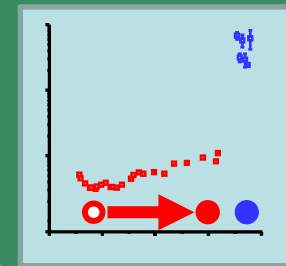
² : Russell et. al. *Angew. Chem. Int. Ed.* **44** 2420 (2005); Ferri et al. *Soft Matter* **11** 2259 (2008)



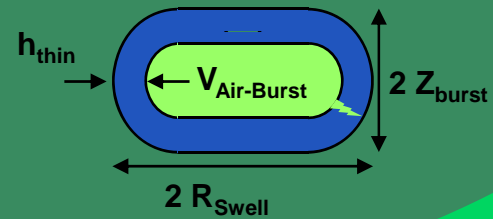
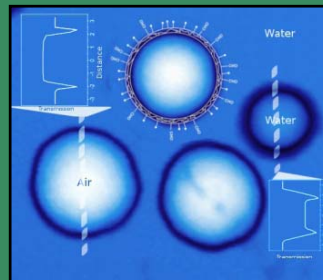
Combination of AFM
with optical microscopy



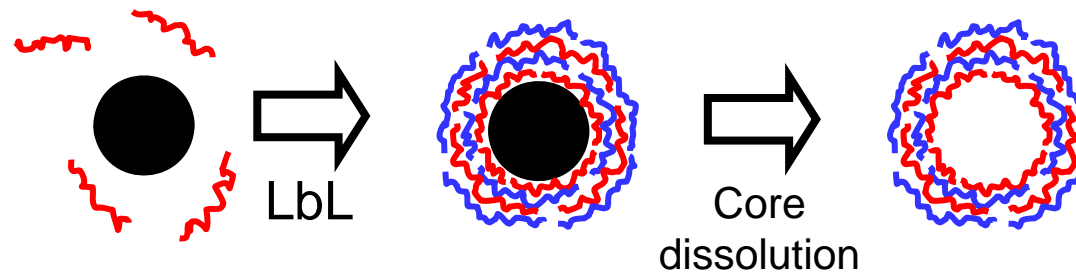
Layer-by-layer
capsules



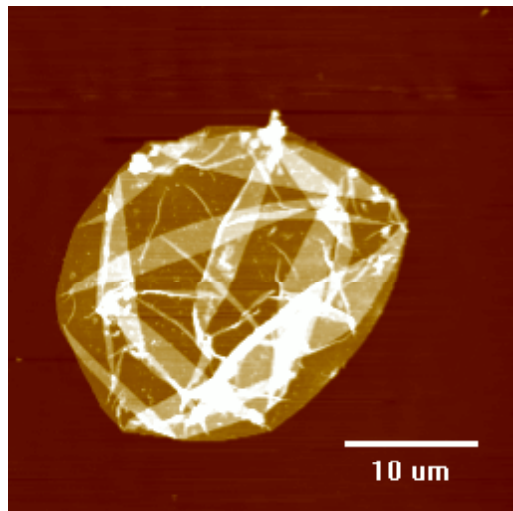
Microballoons



PE-Multilayer capsules

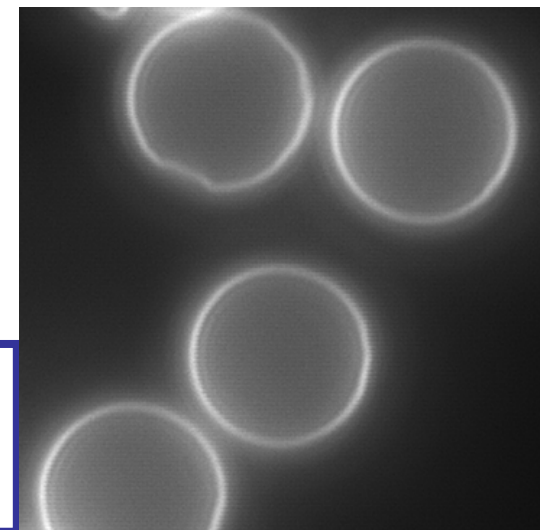


E. Donath, G. B. Sukhorukov, F. Caruso, S. A. Davis and H. Möhwald, *Angewandte Chemie, International Ed. in English.* **37**, 2202-2205, (1998)

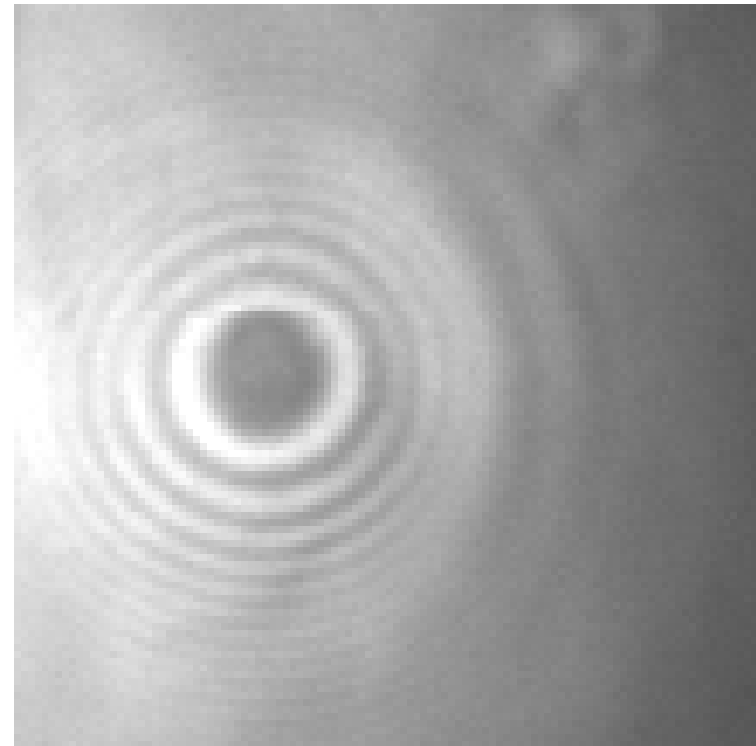
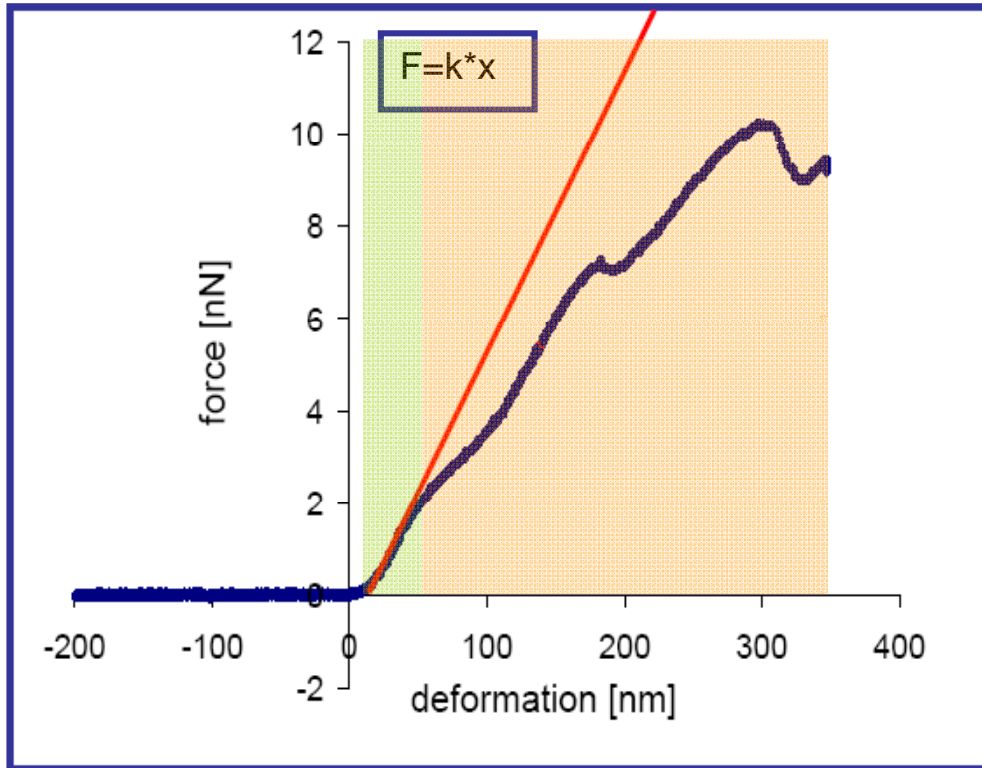


wall properties
(thickness, composition)
defined by multilayer

shape
(size, monodispersity)
defined by template particle



Qualitative look at PEM capsule deformation



Buckling transition from spherical shape to indented sphere

Eur. Phys. J. E **12**(2): 215 (2003)
Prog. Coll. Pol. Sci. **132**: 117 (2006)

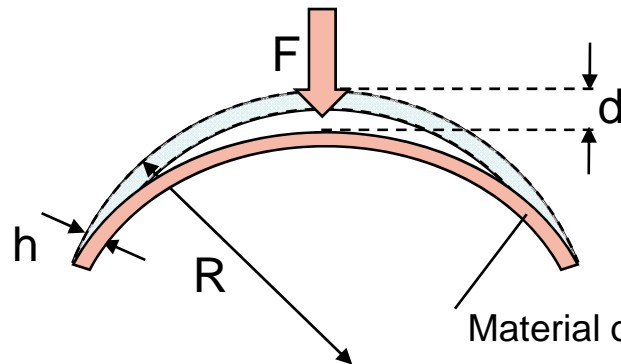
Small Deformation Approach



Ping Pong Ball : plastic deformation and no volume conservation



Playing Ping-Pong :
Deformations on the
order of the
membrane thickness ^{1,2} :



$$F \propto \frac{d}{R} E h^2$$

E : Young's modulus
R : radius of curvature
h : membrane thickness

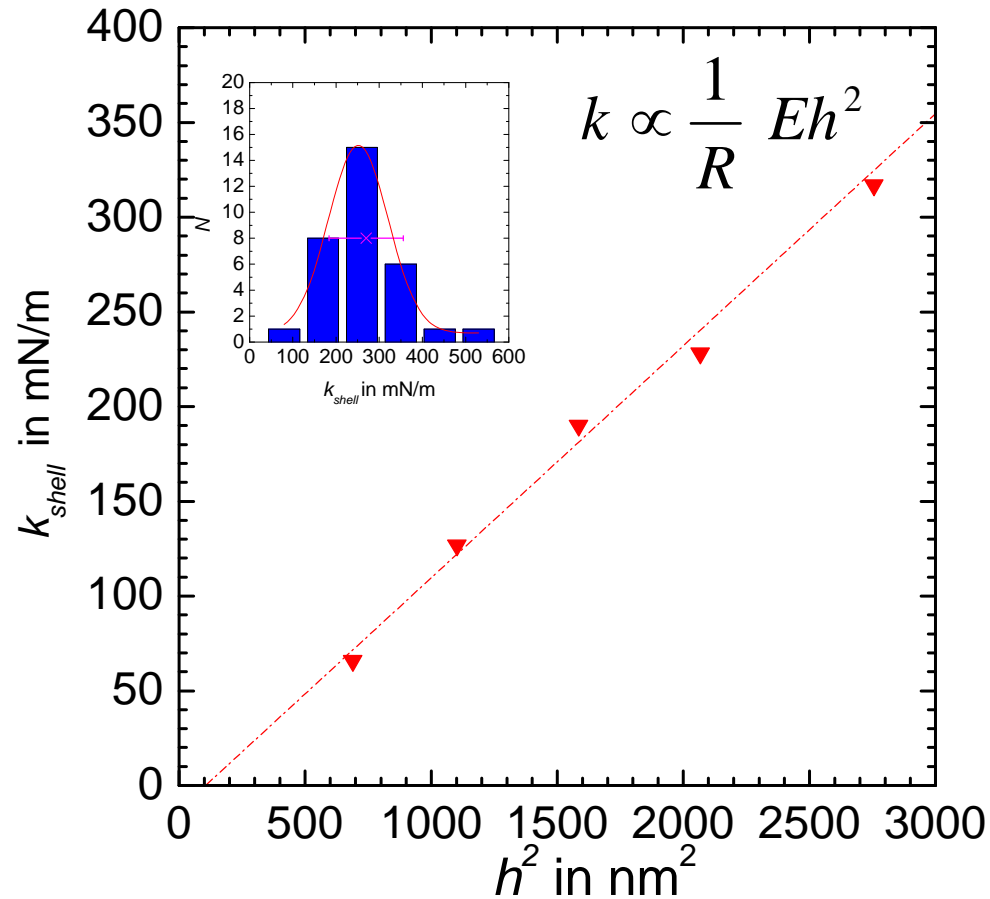
¹: L. Pauchard and S. Rica *Philosophical Magazine B* **78** 225-233 (1998)

²: E. Reissner *J. Mat. Phys.* **25** 80 (1946)

Wall-thickness effect and Young's modulus



System : Polystyrenesulfonate (PSS) / Polyallylamine (PAH) in water



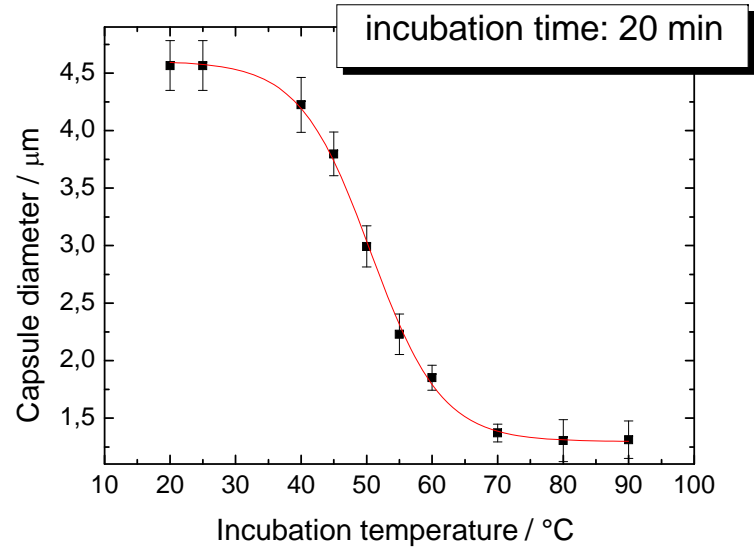
Capsule stiffness can be controlled by wall thickness

Young's modulus
 $E = 294 \pm 94 * 10^6$ Pa

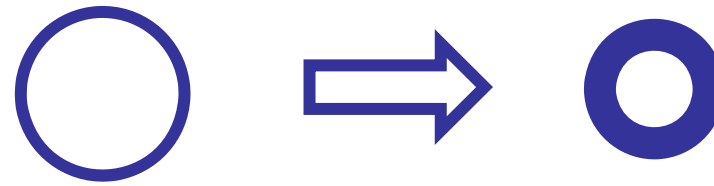
Diffusion-coefficient
 $D < 10^{-15}$ cm²/sec

immobile chains,
glasslike material

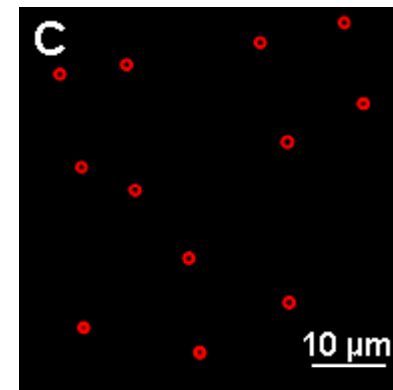
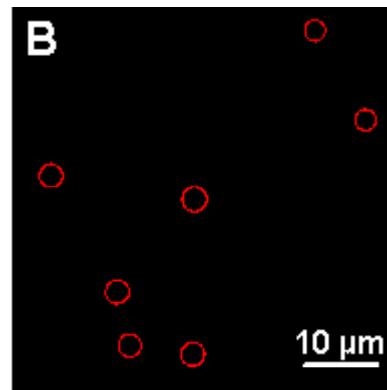
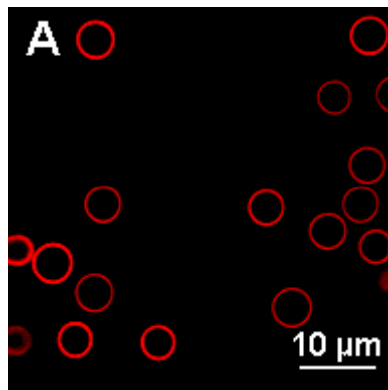
Stimulus sensitivity : Temperature



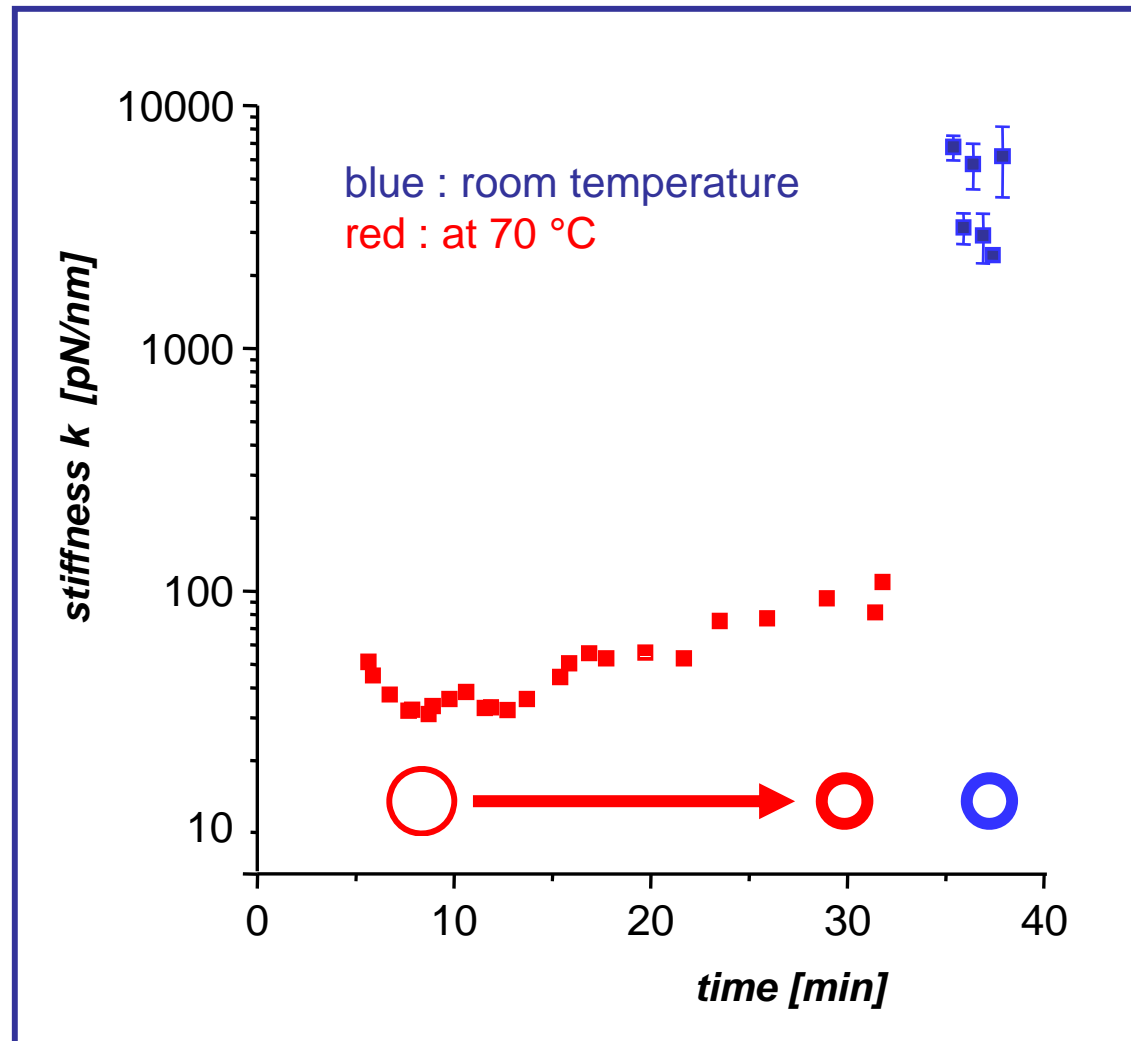
Effect of temperature ($T > 35^{\circ}\text{C}$) :
System Poly-diallyl-dimethyl-ammonium /PSS



Shrinking and thickness increase
(irreversible)



Change of Young's Modulus with temperature



Upon, cooling, shape is frozen

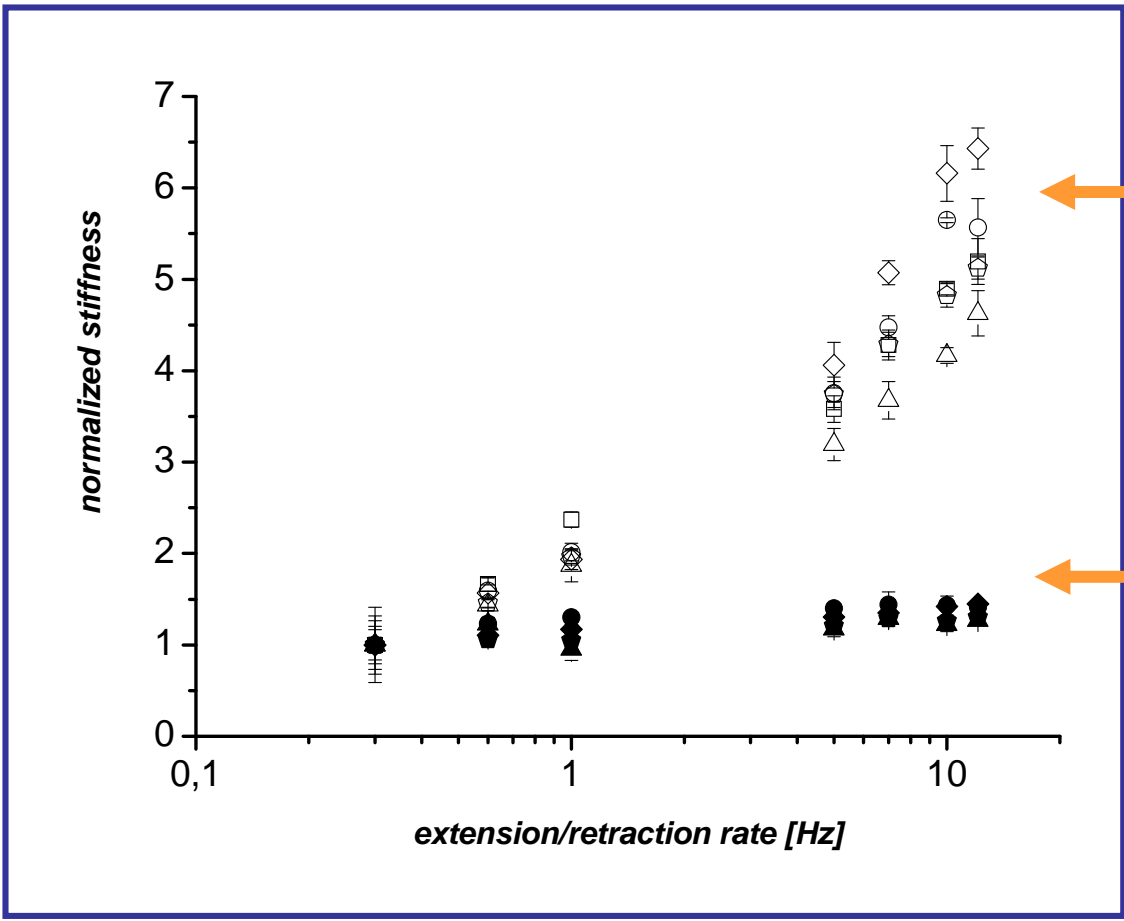


Change in $k \sim$ Change in E

E changes by two orders of magnitude upon cooling,

E is in MPa range at high temperature

Rate dependency of elastic constants



open symbols :
high temperature,
pronounced rate
dependency

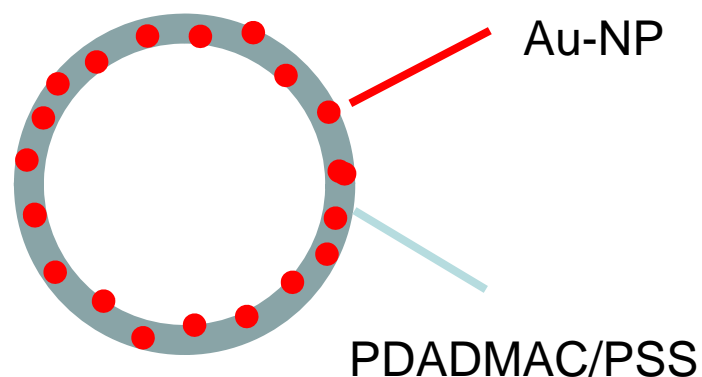
filled symbols:
low temperature,
little variation
over 2 decades
of deformation rate

Transition from frozen to viscoelastic state

Gold-NP containing capsules

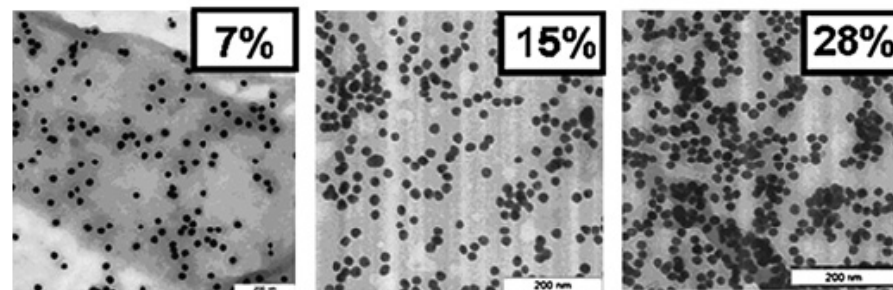
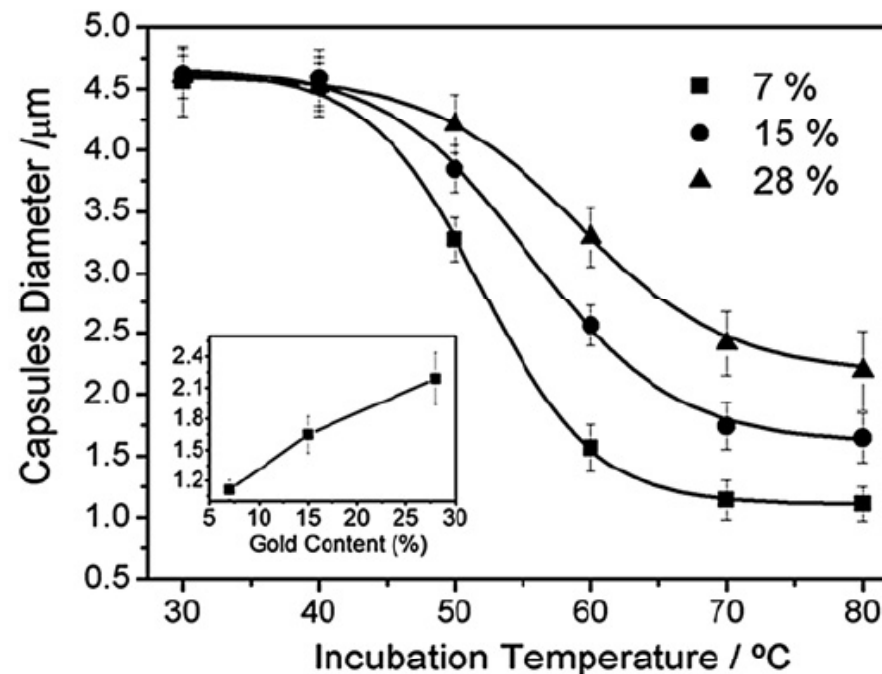


System: Sukhorukov, Skirtach



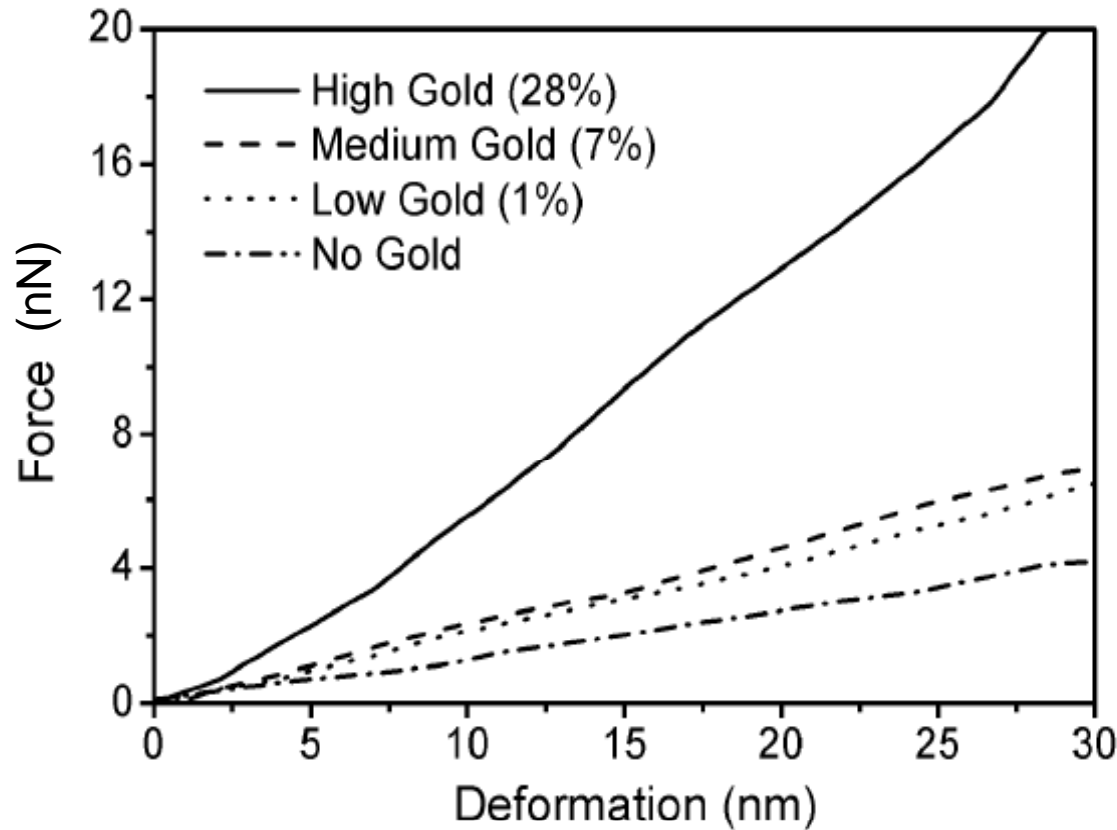
Talk M. Bedard Tue, 15:30
for details

Here : Shrinking process
stops at well defined radius,
depending on Au-NP content



1. Bedard MF, Munoz-Javier A, Muller R, del Pino P, Fery A, Parak WJ, Skirtach AG and Sukhorukov GB. *Soft Matter* 2009; 5 (1): 148-155.

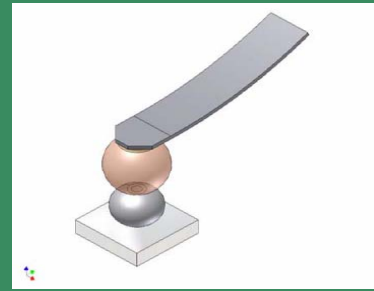
Mechanical characterization



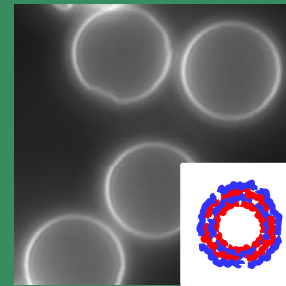
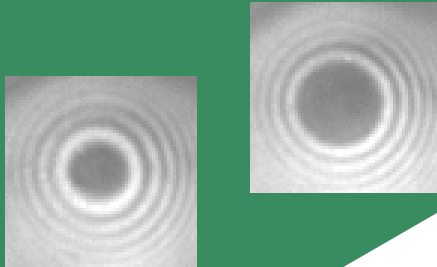
Nonlinear dependency
Of mechanical properties
on Au-NP content



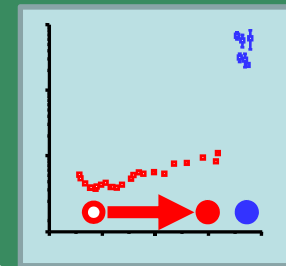
- Regime 1: gold embedded in PDADMAC/PSS matrix, surface tension dominates
- Regime 2: gold NPs percolate, shrinking stops



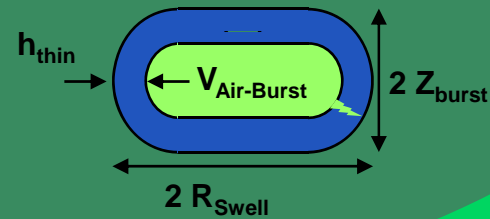
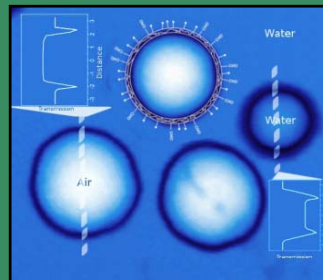
Combination of AFM
with optical microscopy



Layer-by-layer
capsules



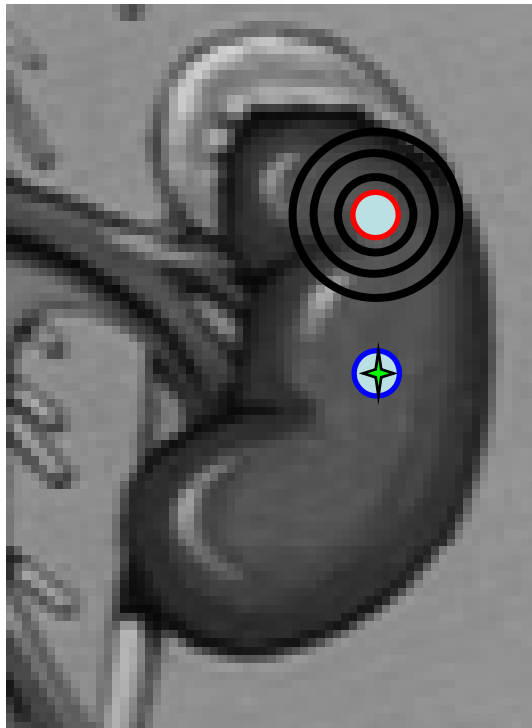
Microballoons



Microballoons in Theragnostics



Micro-balloons = gas filled microcapsules



Micro-balloons act as strong scatterers for ultrasound in the body (large density difference)



- contrast enhancement
- therapy by encapsulation and release of therapeutic gases



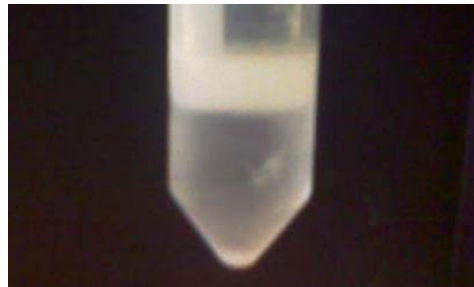
Systems for in-situ theragnostics using micro-particles triggered by ultra-sound

PVA Microballoons

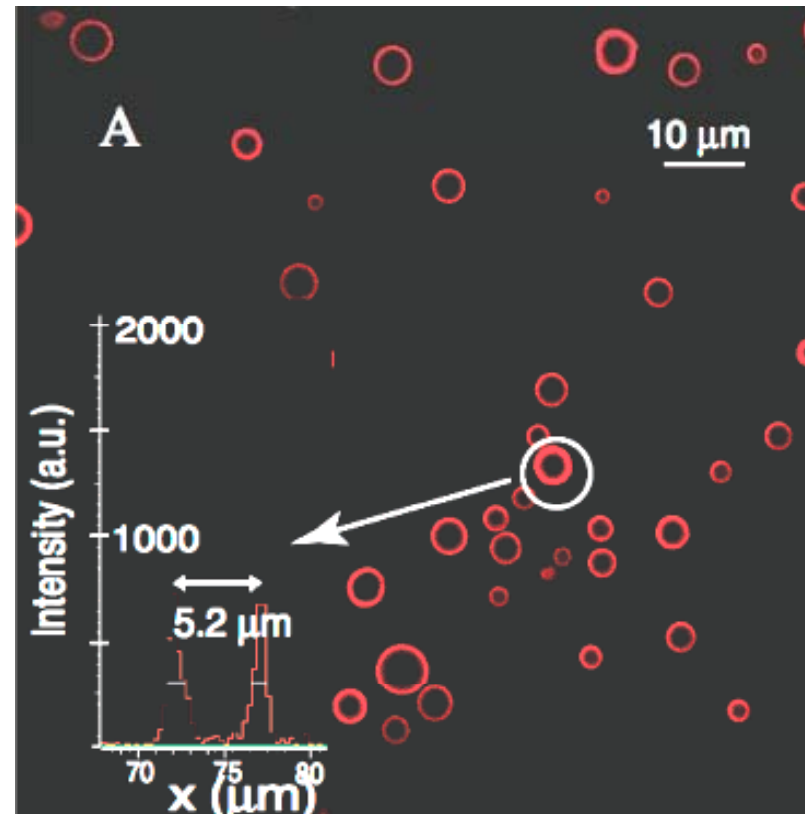
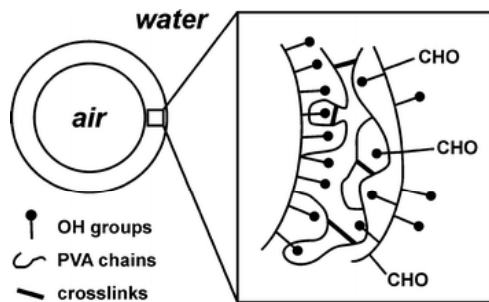


Microballoon Synthesis (G. Paradossi / F. Cavallieri)

Polymerization of poly(vinyl alcohol) under agitation

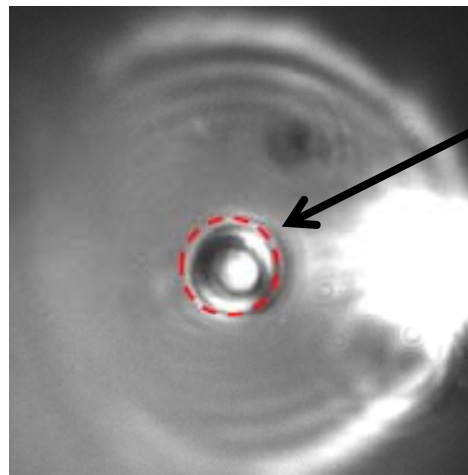


Macroscopic creaming
Shelf lifetime months



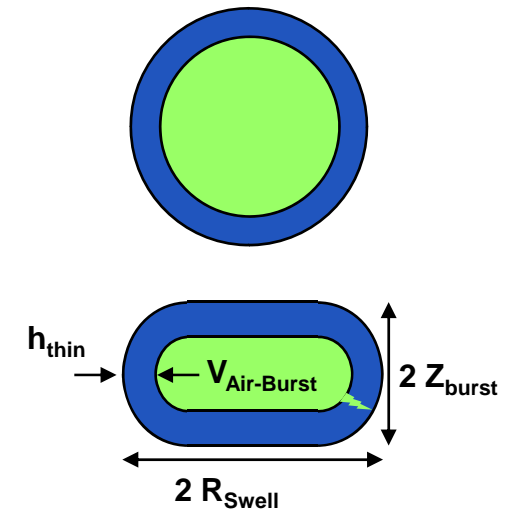
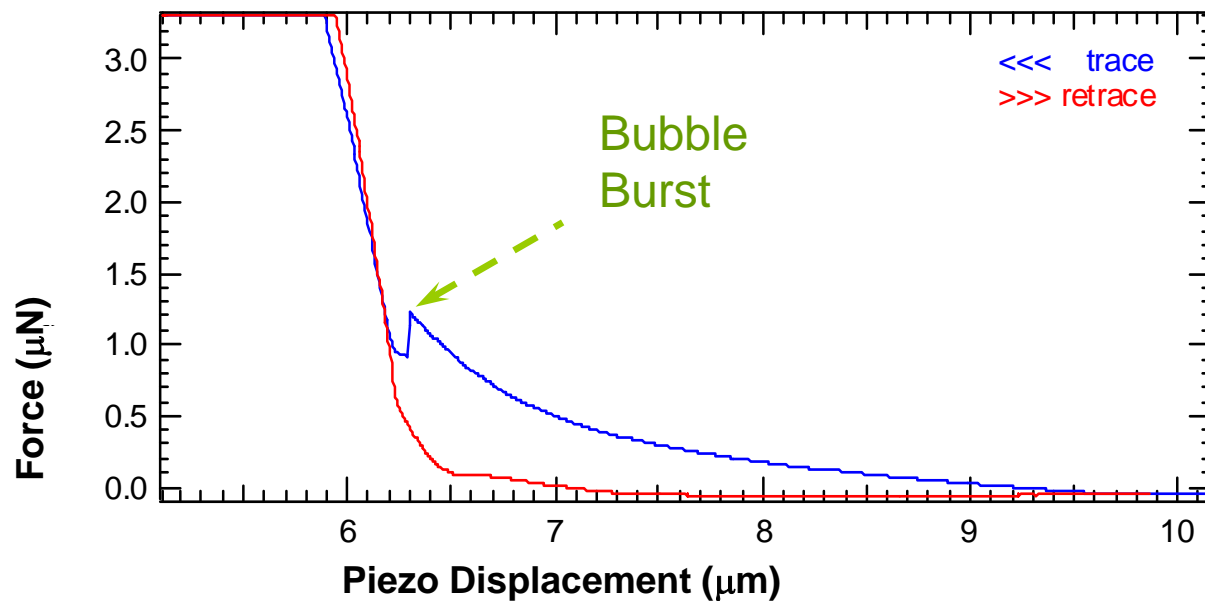
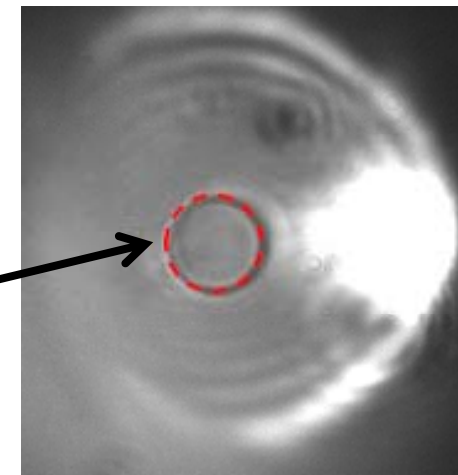
Cavallieri, Hamassi, Chiessi and Paradossi, *Langmuir* **2005**, 21, 8758
Soft X-ray Microscopy: *Langmuir* **2008**, 24, 13677; *Soft Matter* **2008**, 4, 510

Micro-Balloon Deformation - Bursting

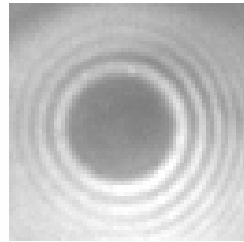
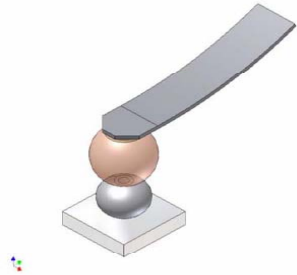


Gas filled MB
(strong scattering)

Same MB after
Bursting
(weak scattering)

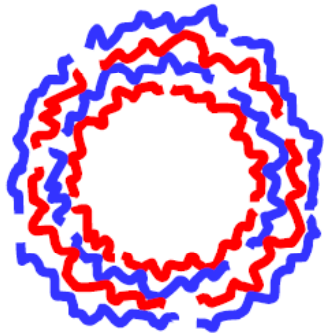


Conclusions



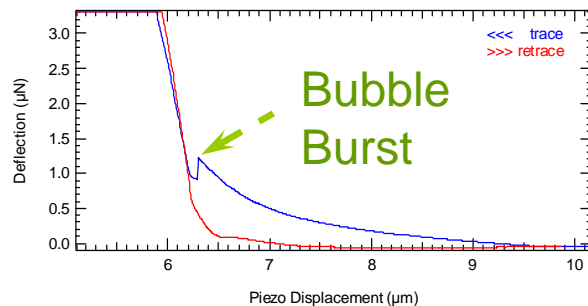
Combination RICM-AFM:

- Shape information can be obtained in situ
 - Fewer assumptions on deformation
- Mechanism necessary



PE-Multilayer capsules:

- deformation described by shell theory
- shrinking effects upon „melting“
- composite shells show two distinct regimes



Microballoons:

- gas release can be monitored in situ
- Compressible interior, volume forces dominant

Coworkers :

F. Dubreuil (microcapsule mechanics)
R. Müller (microcapsule T-effects)
N. Elsner (microcapsule pH-effects)
P. Fernandes, M. Pretzl, C. Hanske
(Micro-balloons)



Cooperations :

PE Capsules:

G.B. Sukhorukov (Queen Mary Coll.)
H. Möhwald, A. Skirtach (MPI Golm)

Micro-balloons:

G. Paradossi, F. Cavallieri (University of Rome
,Tor Vergata'): MB preparation



Financial support : DFG, European Framework Program 6



Thank you for your attention !