LECTURE 23: NANOINDENTATION 2 :OLIVER-PHARR METHOD AND ONE LITERATURE EXAMPLE : NACRE

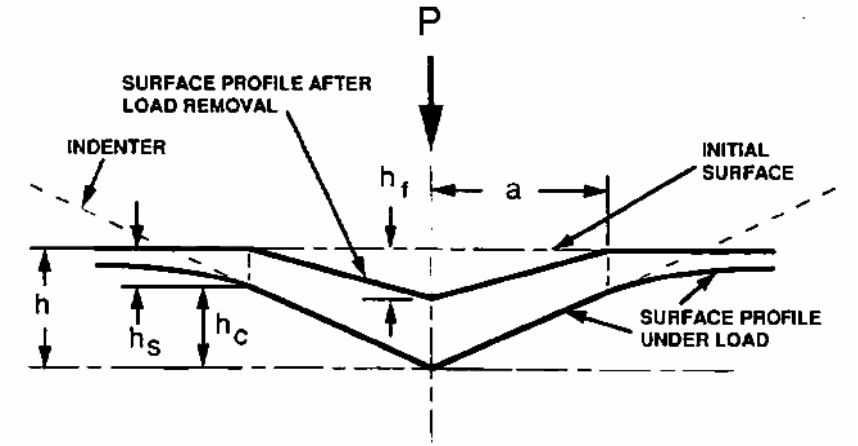
Outline :

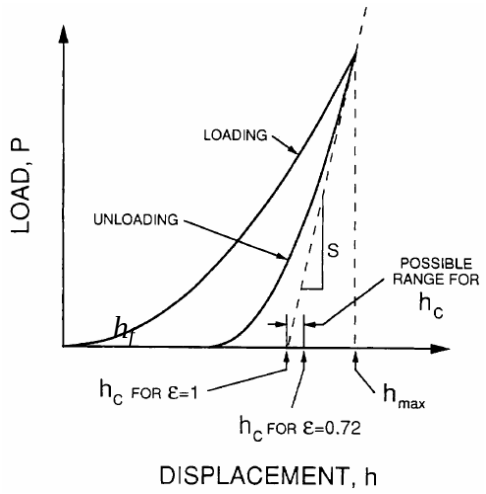
Objectives: To understand how nanoindentation experiments can be applied to different biological systems

Readings: Course Reader Documents 45 (one of the most cited papers in Materials Science)-46, Bruet, et al. "Nanoscale morphology and indentation of individual nacre tablets from the gastropod mollusc Trochus niloticus," *JMR* 20(9), **2005**.

REVIEW LECTURE 22 : THEORETICAL ASPECTS OF NANOINDENTATION

-Definition (why called nano?), comparison of AFM based-indentation to instrumented indentation, indenter geometries,
-Types of deformation; forms of P-h curves for elastic, plastic, elastoplastic : $h_r = h_f$ = residual / final depth, U_e = elastic energy, U_r = energy dissipated (elastoplastic / inelastic), U_{total} = total work of deformation= $U_e + U_r$
Oliver-Pharr analysis- linear Elastic, Isotropic, Continuum Contact Mechanics Theory (*Oliver and Pharr, 1992 JMR, 7(6) 1564*) : Geometry set-up and definitions of geometric parameters : assumes "sink-in"





Courtesy of George M. Pharr and Journal of Materials Research. Used with permission.

P = applied load, P_{max} = peak applied load
h = indentation depth (at P_{max}; $h = h_{max}$ maximum depth)
a = radius of contact circle
h_c = contact depth, vertical distance along which contact is made between sample and tip
h_s = displacement of the surface at the perimeter of contact
From geometry : $h = h_c + h_s$
$A(h_c)$ = contact (projected) area at h_c

$$E_r^{-1} = \text{reduced modulus} = \left(\frac{1-\nu^2}{E}\right)_{\text{sample}} + \left(\frac{1-\nu_i^2}{E_i}\right)_{\text{indenter}}$$

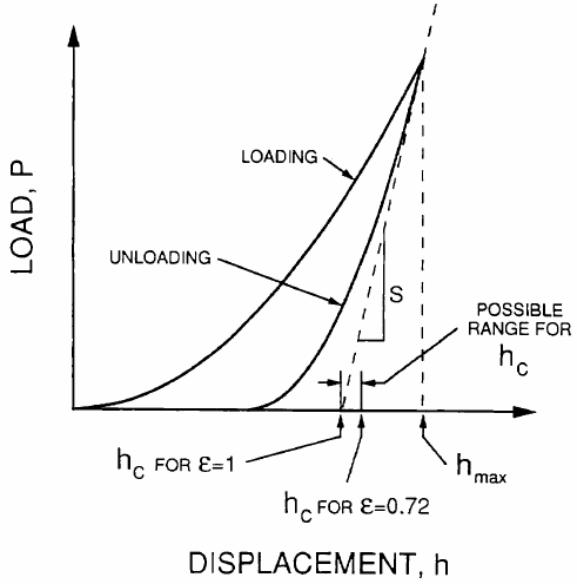
(i.e. two springs in series)
E = modulus
ν = Poisson's ratio
h_f = residual final depth (indicates inelasticity; e.g. viscoelasticity, plasticity)

$$S = \text{contact (initial unloading) stiffness} = \left(\frac{dP}{dh}\right)_{P_{max}}$$

(typically evalulated between 95% and 20% of P_{max})

OLIVER-PHARR ANALYSIS : MATHEMATICAL FORMULATION

(*Oliver and Pharr, 1992 JMR, 7(6) 1564*)



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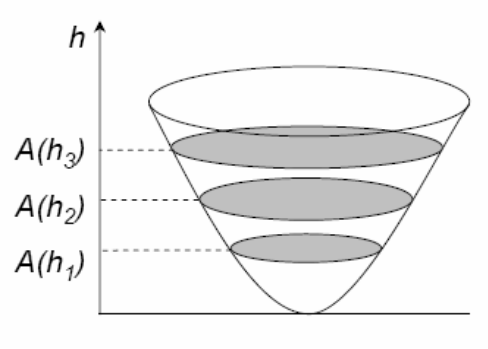


Schematic courtesy of B. Bruet

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A(h_c)}} S \rightarrow \textit{holds for any indenter geometry (1)}$$

S is measured directly from the data (typically evalulated between 95% and 20% of P_{max})

$$h_c = h_{max} - \frac{\varepsilon P_{max}}{S} (2) \rightarrow \textit{takes into account sink - in}$$

Tip Geometry	ε
flat-ended cylindrical punch	1
paraboloid of revolution	0.75
Cone	$2(\pi-2)/\pi$

Indenter (Probe Tip) Area Function Calibration :

$A(h_c)$ = tip area function; representative of tip geometry, can be calibrated on sample of known modulus (e.g. fused quartz) by inverting equation *(1)*;

$$A(h_c) = \frac{\pi}{4}\left(\frac{S}{E_r}\right)^2 (3)$$

Carry out indentations at successively higher loads; at each P_{max} calculate $h_{c(max)}$ and $A(h_c)$ from (3), these data are fit to a polynomial :

$$A(h_c) = C_o h_c^2 + C_1 h_c + C_2 h_c^{0.5} + C_3 h_c^{0.25} + C_4 h_c^{1/8} + C_5 h_c^{1/16}$$

Gives $A(h_c)$ *for every indentation depth,* h_c

$C_o = 24.5; A(h_c) = 24.5 h_c^2$ (Ideal Berkovich Geometry) *(4)*

(see Appendix Lecture 22 for Derivation), coefficients reflect indenter geometry

Note : Danielle will be reviewing finite element analysis (numerical/computational approach to reducing material properties from nanoindentation data) in recitation friday

HARDNESS, PILEUP, and SINK-IN

General Definition :

$$H(Pa) = \frac{P(N)}{A(m^2)}$$

Traditional Definition (microhardness): resistance to plastic or permanent deformation where penetrated by an indenter

$$H(Pa) = \frac{P(N)}{A_{residual}(m^2)}$$

$A_{residual}$ = projected area of residual impression after unloading

for nanoindentation can measure by AFM imaging

Nanoindentation Definition : total resistance to penetration (elastic and plastic) $H(Pa) = \frac{P_{max}(N)}{A(h_{c(max)})(m^2)}$

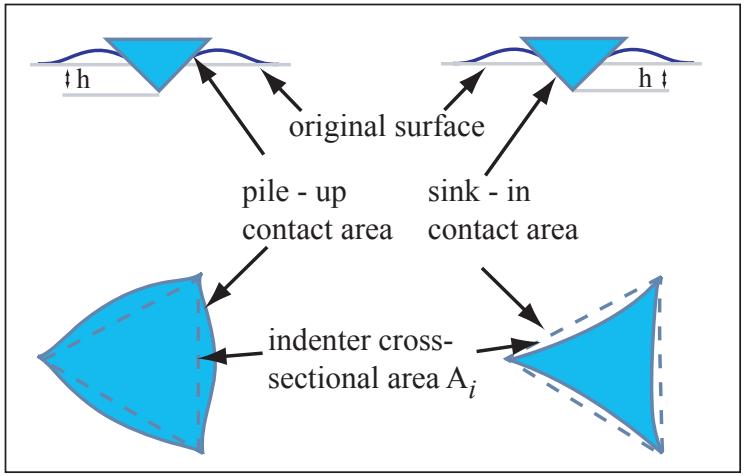
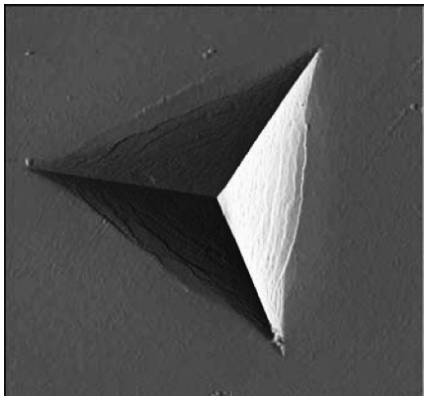
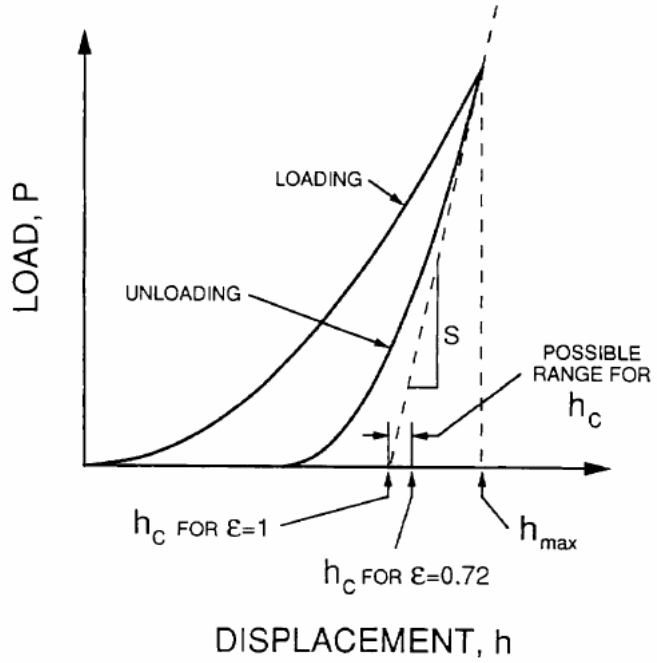


Figure by MIT OCW.

Pileup : A underestimated → E, H overestimated
Sinkin : A overestimated → E, H underestimated

Berkovich residual indent





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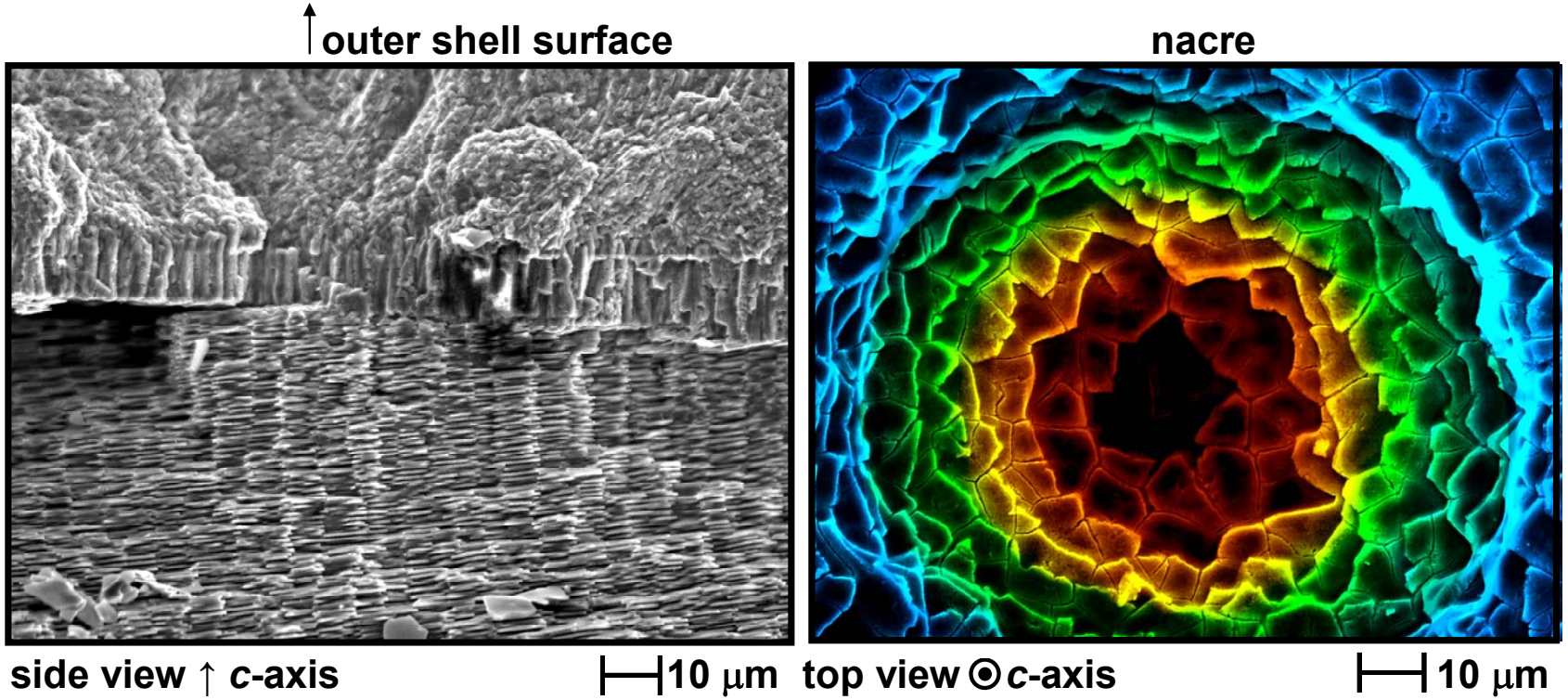
STRUCTURE OF SEASHELL NACRE (Courtesy of B. Bruet – Ortiz lab)



- **multilayered structure, inner nacreous layer has microscale "brick and mortar" structure ~95 wt.% of it is calcium carbonate ~5 wt.% biomacromolecules**

- **individual nacre tablets are complex organic-inorganic biocomposites in and of themselves (aragonite-based) composed of nanograins (~ 30 nm) with embedded biomacromolecules**

MECHANICAL PROPERTY AMPLIFICATION

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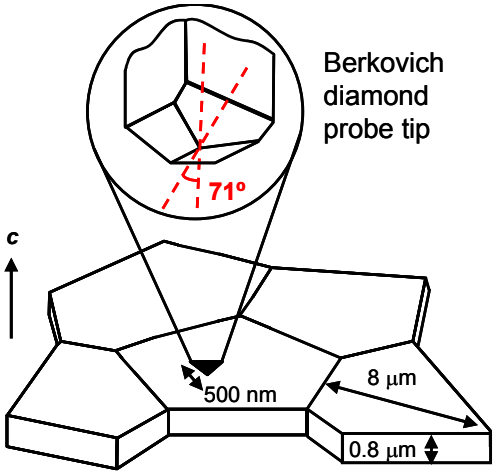
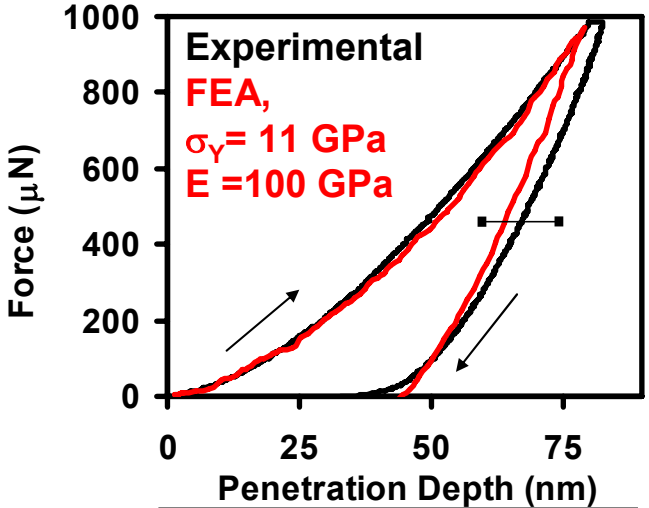
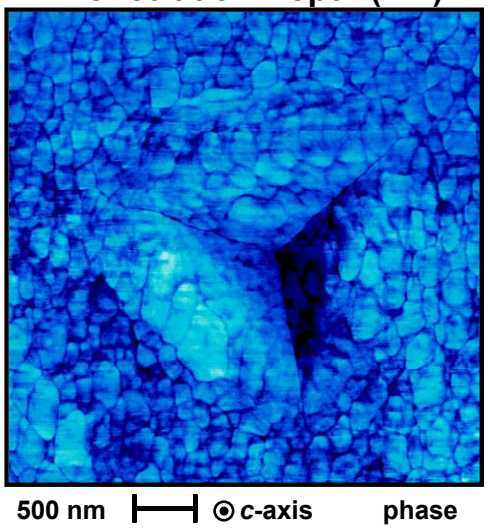
Ashby diagram of Fracture Toughness vs. Strength.

NANOINDENTATION OF SEASHELL NACRE (see Bruet, et al. JMR 20(9), 2005)







- At this small length scale the individual nacre tablets exhibit both a high yield stress and stiffness
- High yield stress of nacre can be largely attributed to the anisotropic dislocation nucleation / slip mechanisms of single crystal aragonite
- Nanograin structure further increases yield stress possibly due to lateral constraints of nanograin boundaries preventing dislocation nucleation / glide.
- Intra-nanograin adhesion is enormous (macromolecules)
- Small length scale of fundamental nanograins averts brittle fracture (Griffith flaw argument)→verified by comparison of nanoKnoop and microKnoop experiments

ROLE OF MACROMOLECULAR COMPONENT

- Lack of cleavage planes in aragonite (as opposed to calcite, for example) is also advantageous.
- Hardest crystallographic orientation (001) oriented appropriately with respect to the shell surface for impact loading in the environment
- This unique combination of both high local stiffness and strength for individual nacre tablets facilitates other experimentally observed energy dissipating mechanisms such as intertablet shear and pullout and rupture of sacrificial bond during extension of organic.