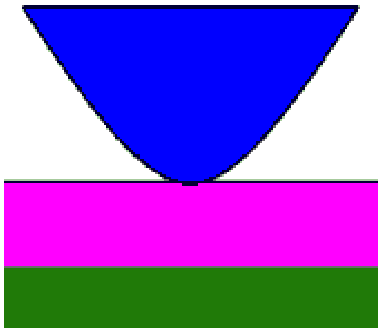
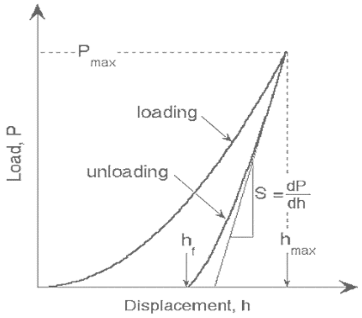
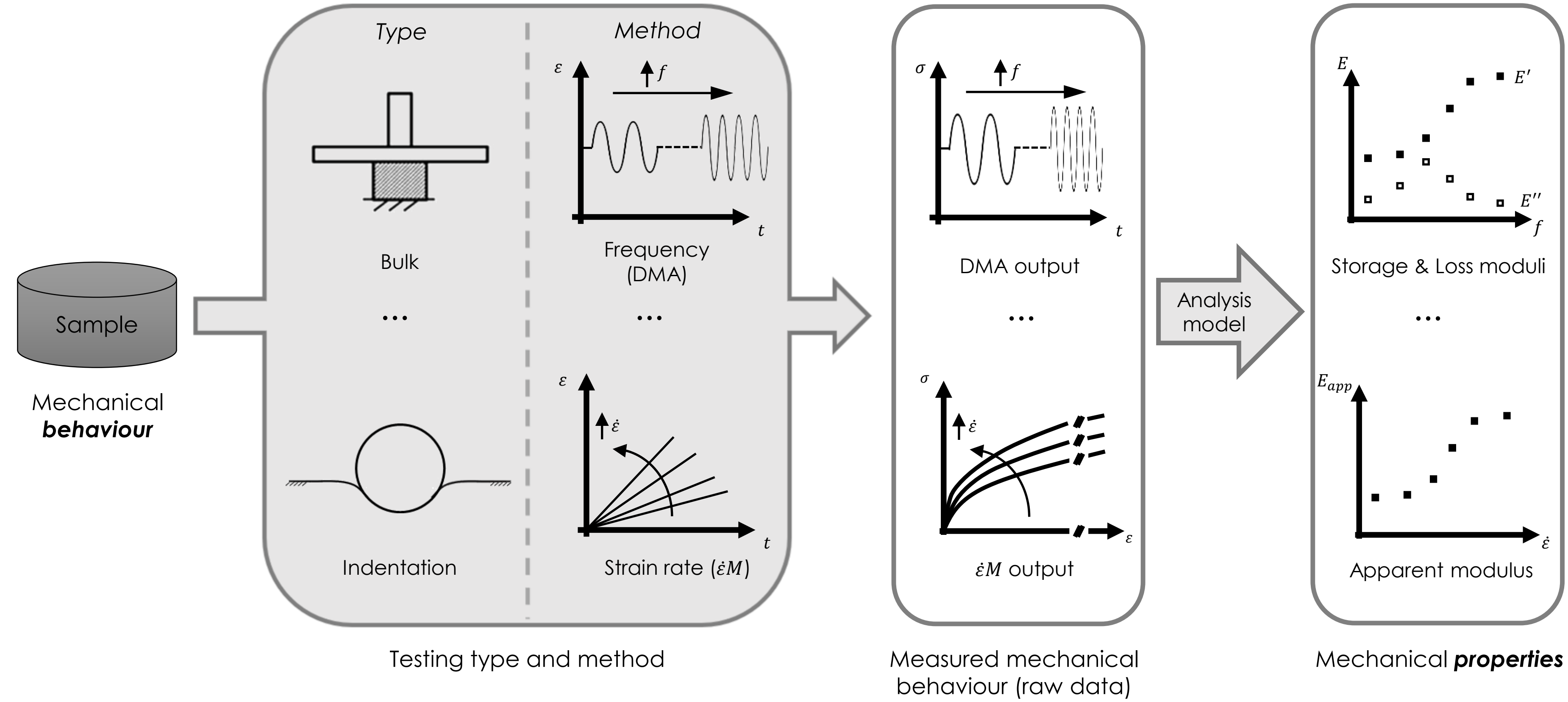




Nano-mechanics for Intelligent Materials (1/2)

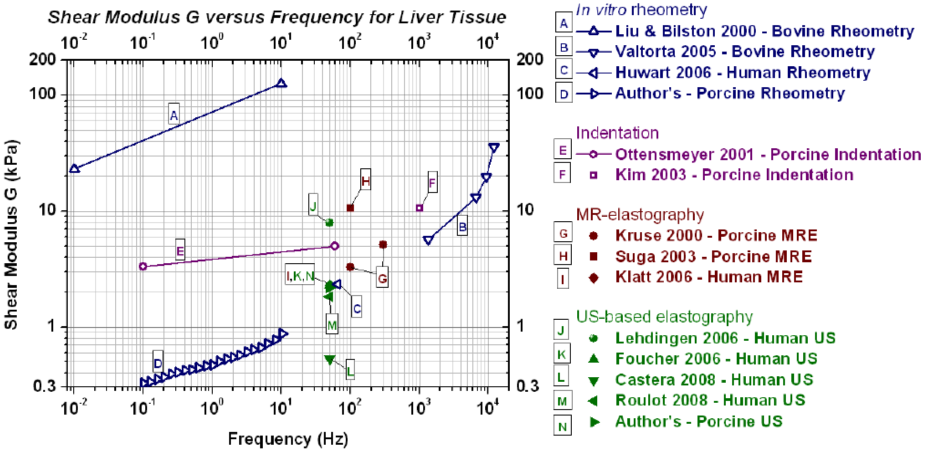
Giorgio MATTEI

From sample mechanical *behaviour* to *properties*

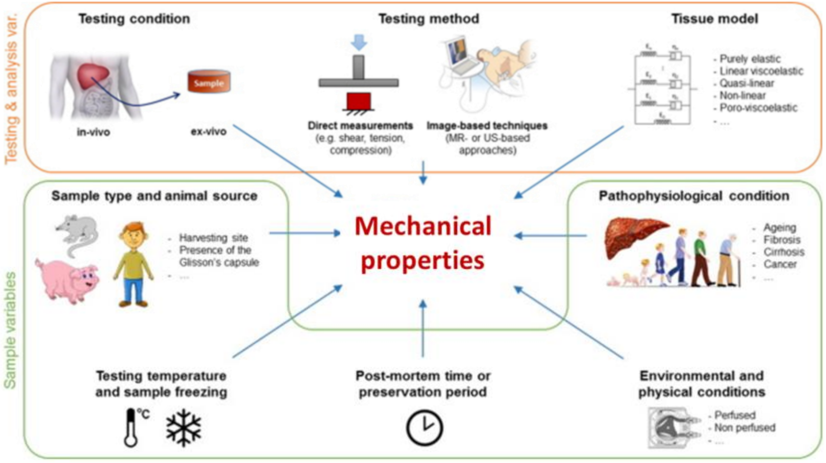


Material mechanical *properties*

- **Little consensus** in the literature

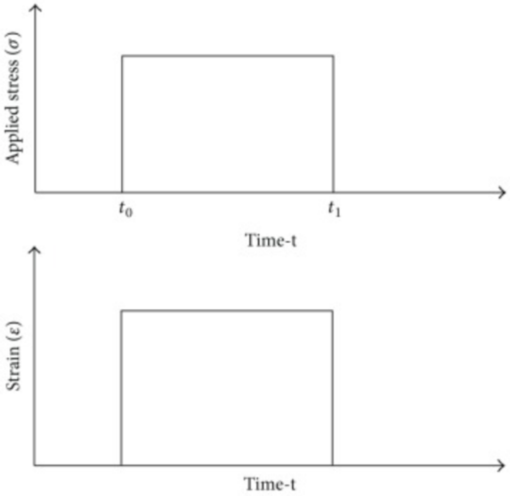


S Marchesseau et al, *Progr in Biophys and Mol Biol* 103:185-96 (2010)

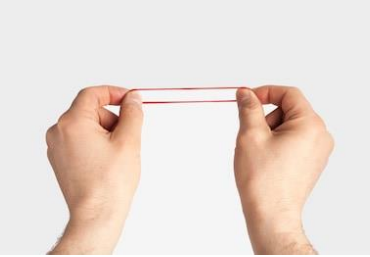


G Mattei and A Ahluwalia, *Acta Biom* 45:60-71 (2016)

Elastic, viscous and visco-elastic response

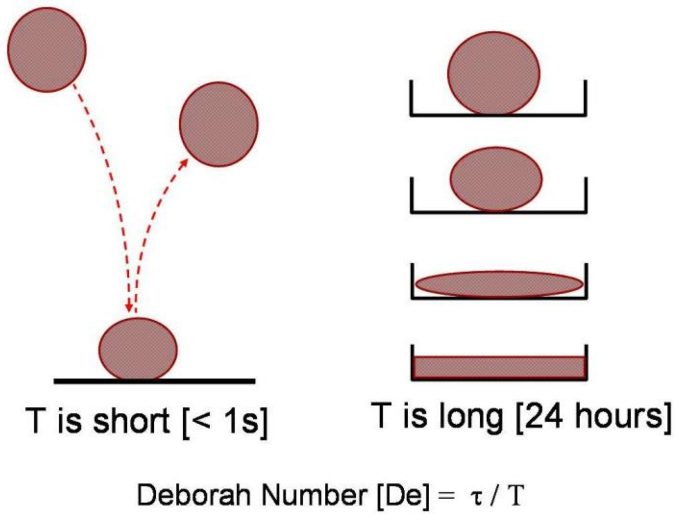


(a) Elastic response



Deborah Number

- Originally proposed by Markus Reiner, professor at Technion in Israel, who chose the name inspired by a verse in the Bible "The mountains flowed before the Lord" in a song by prophet Deborah
  - For man – in his relatively short lifetime – the mountains are solid, but for the Lord with an infinite observation time, the mountains flow.



τ = Maxwell relaxation time (time for material to "reach" equilibrium after perturbation)

T= Observation time

High De: material is more like elastic solid

Low De: material is more like a viscous fluid

Examples of viscoelastic materials

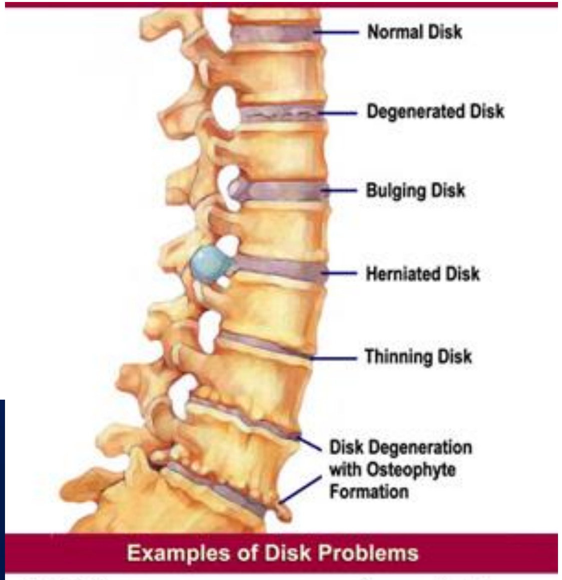
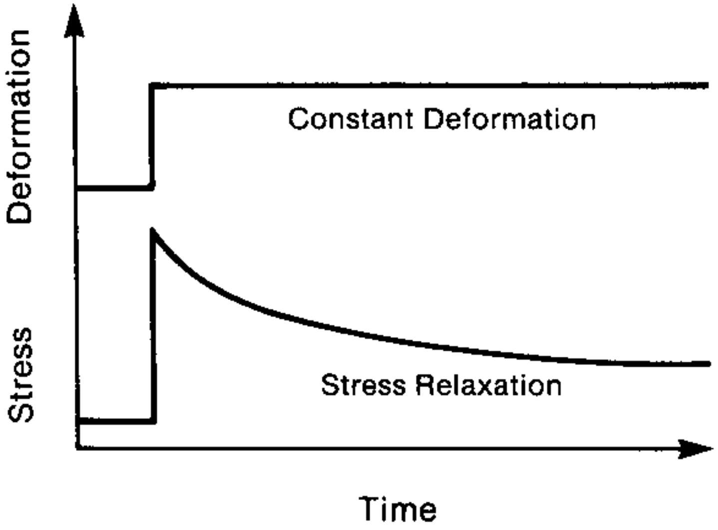


Figure 2.

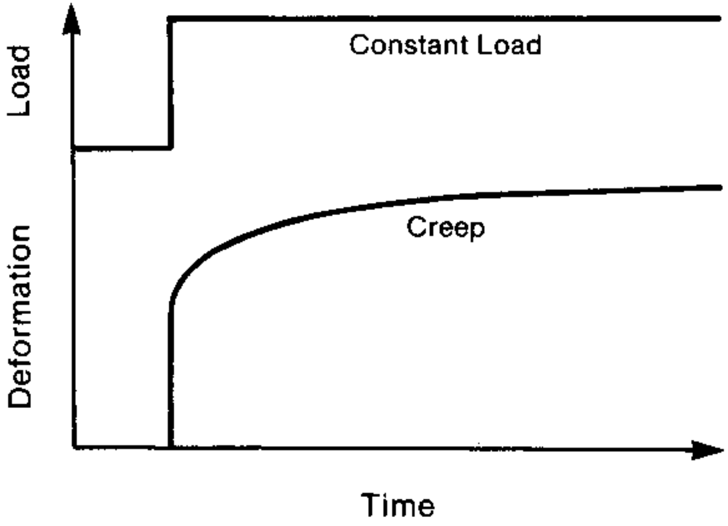
Stress Relaxation



When a body is deformed (or strained) and that deformation (or strain) is held constant, stresses in the body reduce with time.

Figure from Fung "Biomechanics" 2nd ed.

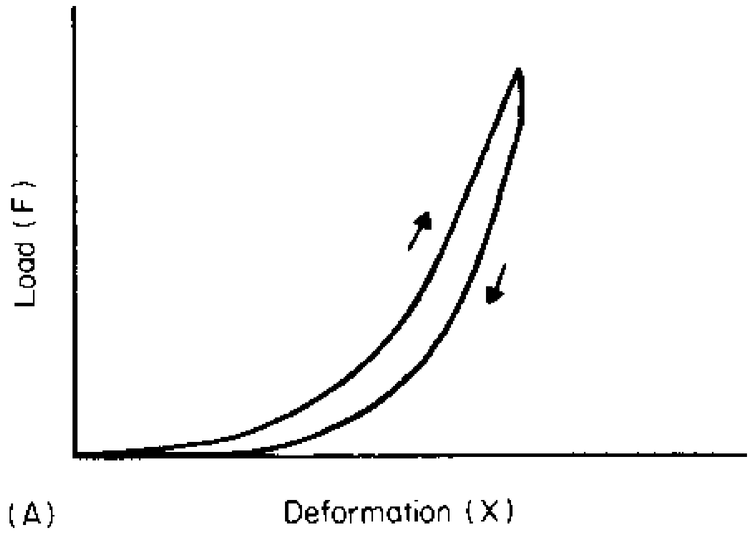
Creep



When a body is loaded (or stressed) and the stress is held constant, the body continues to deform (or strain) with time.

Figure from Fung "Biomechanics" 2nd ed.

Hysteresis



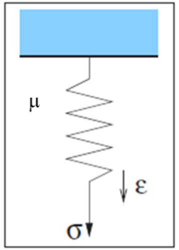
When a body subjected to cyclic loading, load-displacement (or stress-strain) behavior for increasing loads is different than behavior for decreasing loads.
The area between the curves represents energy loss (dissipation).

Figure from Fung "Biomechanics" 2nd ed.

Viscoelasticity

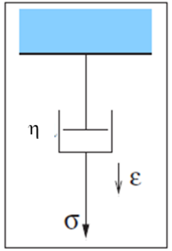
- Behavior exhibited by a material (or tissue) that has both viscous and elastic elements in its response to a deformation (or strain) or load (or stress)

- Represented by:
  - **Spring** for elastic element
    - Assumed to linearly elastic



$$\sigma = \mu\varepsilon \quad (\text{or } \sigma = E\varepsilon)$$

  - **Dashpot/damper** for viscous element
    - Follows Newtonian fluid constitutive law



$$\sigma = \eta \frac{d\varepsilon}{dt}$$

Lumped parameter models

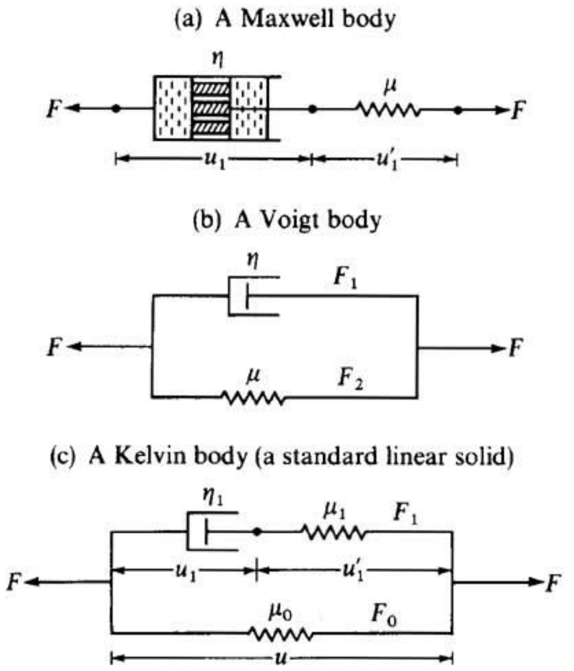


Figure 2.11:1 Three mechanical models of viscoelastic material. (a) A Maxwell body, (b) a Voigt body, and (c) a Kelvin body (a standard linear solid).

The Maxwell, Voigt and Kelvin (SLS) models are all composed of combinations of linear springs (μ or E) and dashpots (η).

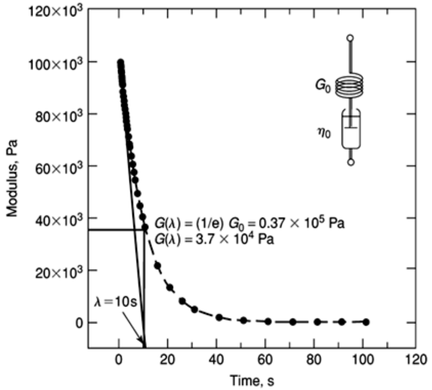
A **linear spring** with spring constant μ theoretically produces a **deformation proportional** to the **load**.

A **linear dashpot** with coefficient of viscosity η produces a **velocity proportional** to the **load**.

Maxwell model

- Represented by a **purely viscous damper (*η*)** and a **purely elastic spring (*E*)** connected in **series**
- The model can be represented by the following differential equation (DEQ):

$$\frac{d\epsilon_{Total}}{dt} = \frac{d\epsilon_D}{dt} + \frac{d\epsilon_S}{dt} = \frac{\sigma}{\eta} + \frac{1}{E}\frac{d\sigma}{dt}$$



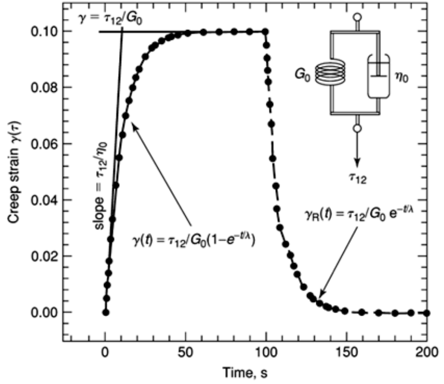
Stress relaxation experiment

- Predicts/models a stress that decays exponentially with time to zero with permanent deformation
- Model **doesn't accurately predict creep** (constant stress). Predicts that strain will increase linearly with time. Actually strain rate decreases with time

Voigt model

- Represented by a **Newtonian damper (*η*)** and **Hookean elastic spring (*E*)** in **parallel**
- The model can be expressed as a linear first order DEQ

$$\sigma(t) = E\varepsilon(t) + \eta\frac{d\varepsilon(t)}{dt}$$



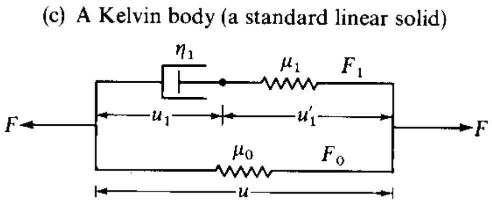
Creep and recovery response

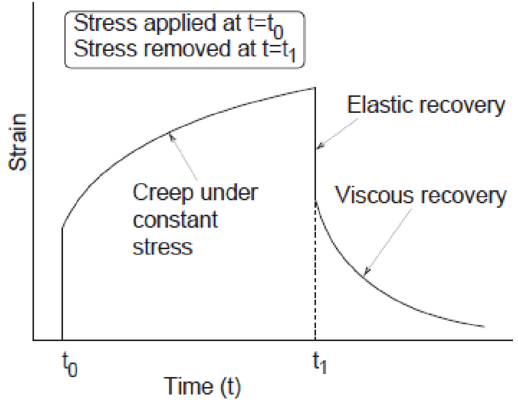
- Represents a solid undergoing reversible viscoelastic strain
- Models a solid that is very stiff but will creep (e.g. crystals, glass, apparent behavior of cartilage). At constant stress (creep), predicts strain to tend to σ/E as time continues to infinity
- The model is **not accurate for predicting stress-relaxation** in a material/tissue

Standard Linear Solid (SLS) model

- Represented by a **Hookean spring** in **parallel** to a **Newtonian damper** + **Hookean spring arm**
- The model can be expressed as a linear first order DEQ:

$$\sigma + \frac{\eta_1}{\mu_1}\dot{\sigma} = \mu_0\varepsilon + \eta_1\left(1+\frac{\mu_0}{\mu_1}\right)\dot{\varepsilon}$$





Creep and recovery response

- Represents a solid undergoing an elastic and a reversible viscoelastic strain
- At constant stress (creep), predicts an initial strain from the spring which will creep over time until the parallel spring carries all the applied load
- The model is a **linear approximation** of **viscoelastic materials/tissues** that are **time dependent** but **completely recover** from applied loads

Summary: creep and relaxation responses

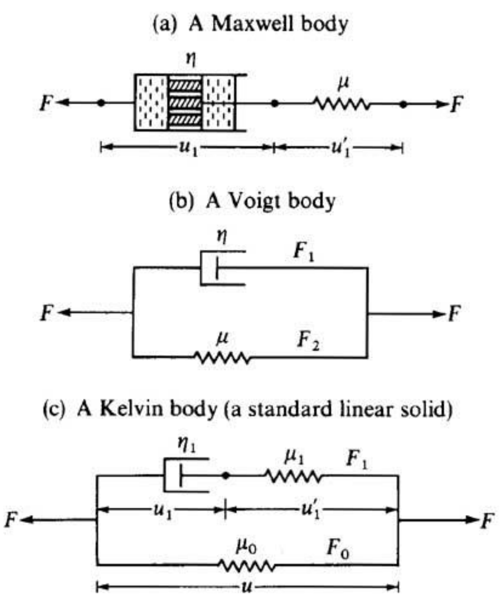


Figure 2.11:1 Three mechanical models of viscoelastic material. (a) A Maxwell body, (b) a Voigt body, and (c) a Kelvin body (a standard linear solid).

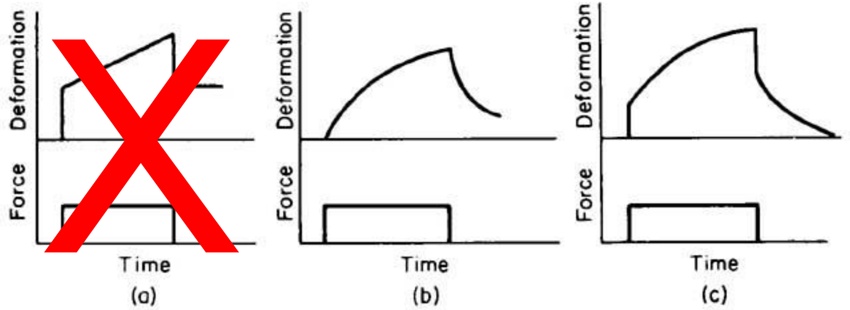


Figure 2.11:3 Creep functions of (a) a Maxwell, (b) a Voigt, and (c) a standard linear solid. A negative phase is superposed at the time of unloading.

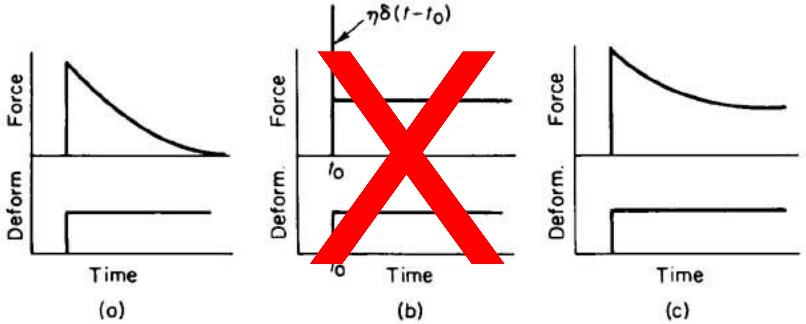
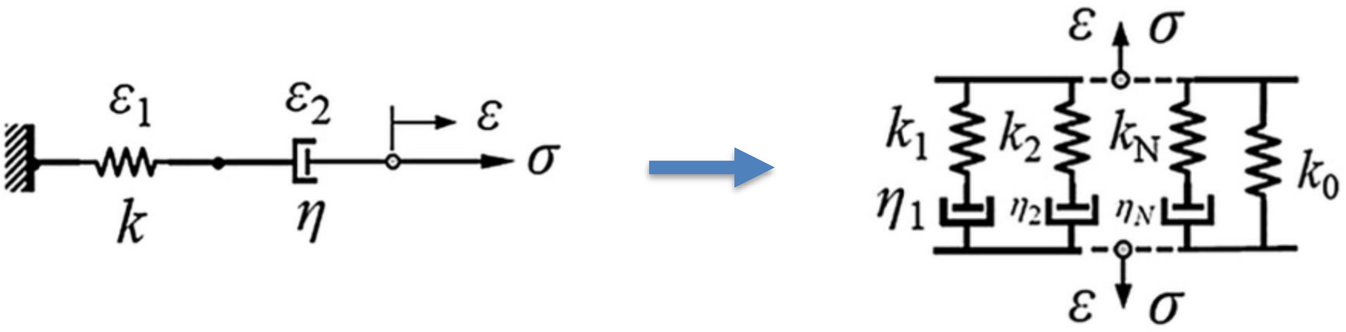


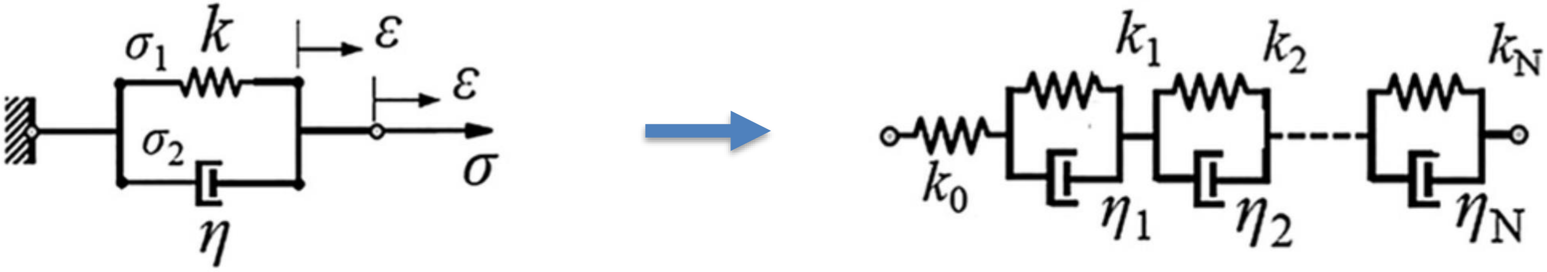
Figure 2.11:4 Relaxation functions of (a) a Maxwell, (b) a Voigt, and (c) a standard linear solid.

Generalized Models

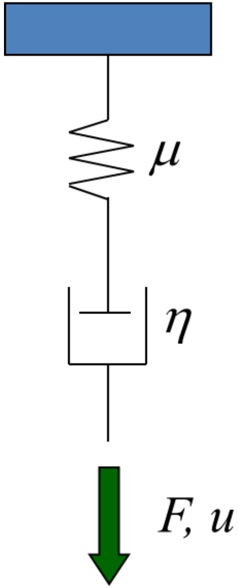
- **Generalized Maxwell** model consists of **Maxwell elements** in **parallel** to a **pure spring**



- **Generalized Voigt** model consists of **Voigt elements** in **series** to a **pure spring**



Maxwell model creep



$$\dot{u} = \dot{u}_s + \dot{u}_d \qquad \dot{u} = \frac{\dot{F}}{\mu} + \frac{F}{\eta}$$

$$solve\ for\ u(t)\ if\ F(t) = 1(t)$$

$$\int \dot{u}\, dt = \int \left(\frac{\dot{F}}{\mu} + \frac{F}{\eta} \right) dt \quad t > 0$$

$$u(t) = \frac{1(t)}{\mu} + \frac{t}{\eta} \quad t > 0$$

$$c(t) = \frac{1(t)}{\mu} + \frac{t}{\eta} \quad t > 0$$

Creep functions

- Solving the DEQs for the Maxwell, Voigt, and Kelvin models for displacement $\varepsilon = c(t)$, when the stress $\sigma(t)$ is a unit step function $1(t)$
- We obtain a set of results known as the *creep functions*
- These functions represent the elongation (strain) in the viscoelastic material which is produced by a sudden application of unit stress at time = 0

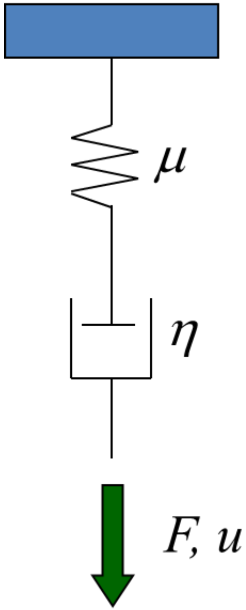
$$c(t) = (1/\mu + t/\eta)1(t) \qquad \textbf{Maxwell}$$

$$c(t) = 1/\mu\ (1-e-(\mu/\eta)t)1(t) \qquad \textbf{Voigt}$$

$$c(t) = 1/E_R\ [\ 1 - (1-\tau_\varepsilon/\tau_\sigma)e-t/\tau_\sigma]1(t) \qquad \textbf{SLS}$$

where $\tau_\varepsilon = \eta_1/\mu_1$, $\tau_\sigma = (\eta_1/\mu_0)(1 + \mu_0/\mu_1)$, and $E_R = \mu_0$

Maxwell model relaxation



$$\frac{\dot{F}}{\mu} + \frac{F}{\eta} = \dot{u}$$

$$solve\ for\ F(t)\ if\ u(t) = 1(t)$$

$$\frac{\dot{F}}{\mu} + \frac{F}{\eta} = 0 \quad \Rightarrow \quad \dot{F} + \frac{\mu}{\eta} F = 0 \quad t > 0$$

$$F(t) = Ce^{-\frac{\mu}{\eta}t}$$

$$solving\ for\ C\ from\ initial\ condition\ F(0^+) = \mu$$

$$k(t) = \mu e^{-\frac{\mu}{\eta}t} \quad t > 0$$

Relaxation Functions

- Solving the DEQs for stress [$\sigma(t) = k(t)$] when the applied strain is a unit step function $\varepsilon(t) = 1(t)$ yields the *relaxation functions*
- These represent the resisting stress as a function of time

$$k(t) = \mu e^{-(\mu/\eta)t} 1(t)$$ **Maxwell**

$$k(t) = \eta\delta(t) + \mu 1(t)$$ **Voigt**

$$k(t) = E_R\,[\,1 - (1 - \tau_\sigma/\tau_\varepsilon)e^{-t/\tau\varepsilon}]\,1(t)$$ **SLS**

where $\tau_\varepsilon = \eta_1/\mu_1$, $\tau_\sigma = (\eta_1/\mu_0)(1 + \mu_0/\mu_1)$, and $E_R = \mu_0$

Linear model summary

Maxwell

- Good for predicting stress-relaxation
- Poor at predicting creep
- Used for soft solids with non-recoverable deformations

Voigt

- Good for predicting creep with small elastic deformation
- Not accurate with predicting stress relaxation
- Used for polymers, rubber, cartilage when the load is not too high

Standard Linear Solid

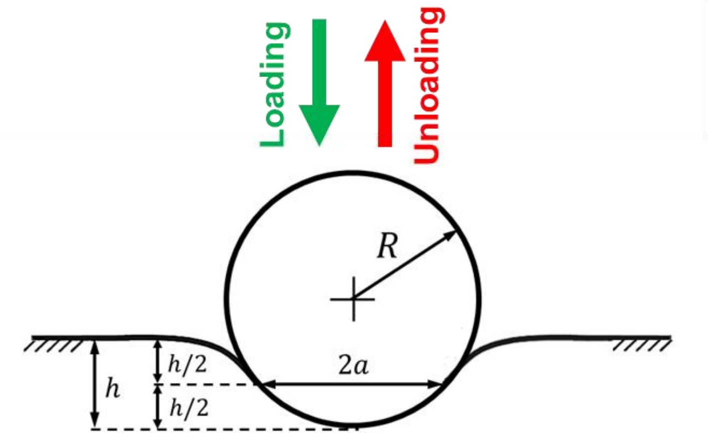
- Predicts both creep and stress-relaxation
- Fully recoverable & initial elastic displacement

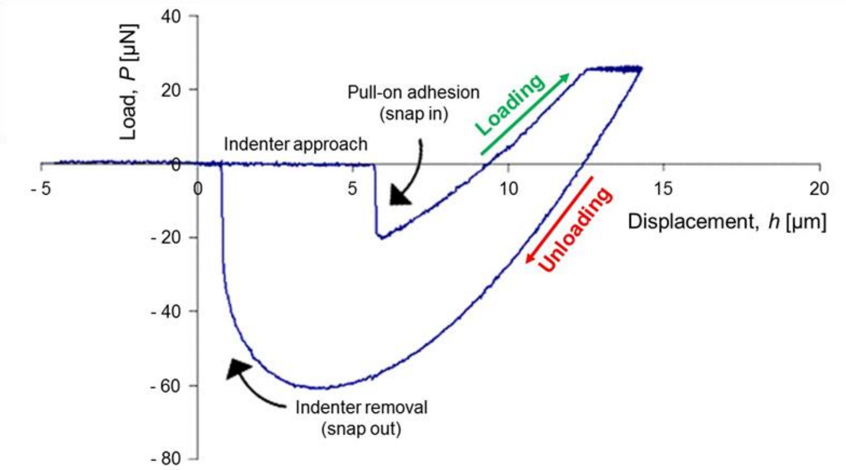
Generalized

- Used for fitting experimental data to an arbitrary level of accuracy

Nano-indentation

- A **popular technique** to **characterise material mechanical properties** at the **micro-scale**
- Typically, a probe is brought in contact with a surface, pushed into the material and then retracted, recording load (P) and displacement (h) over time (t)





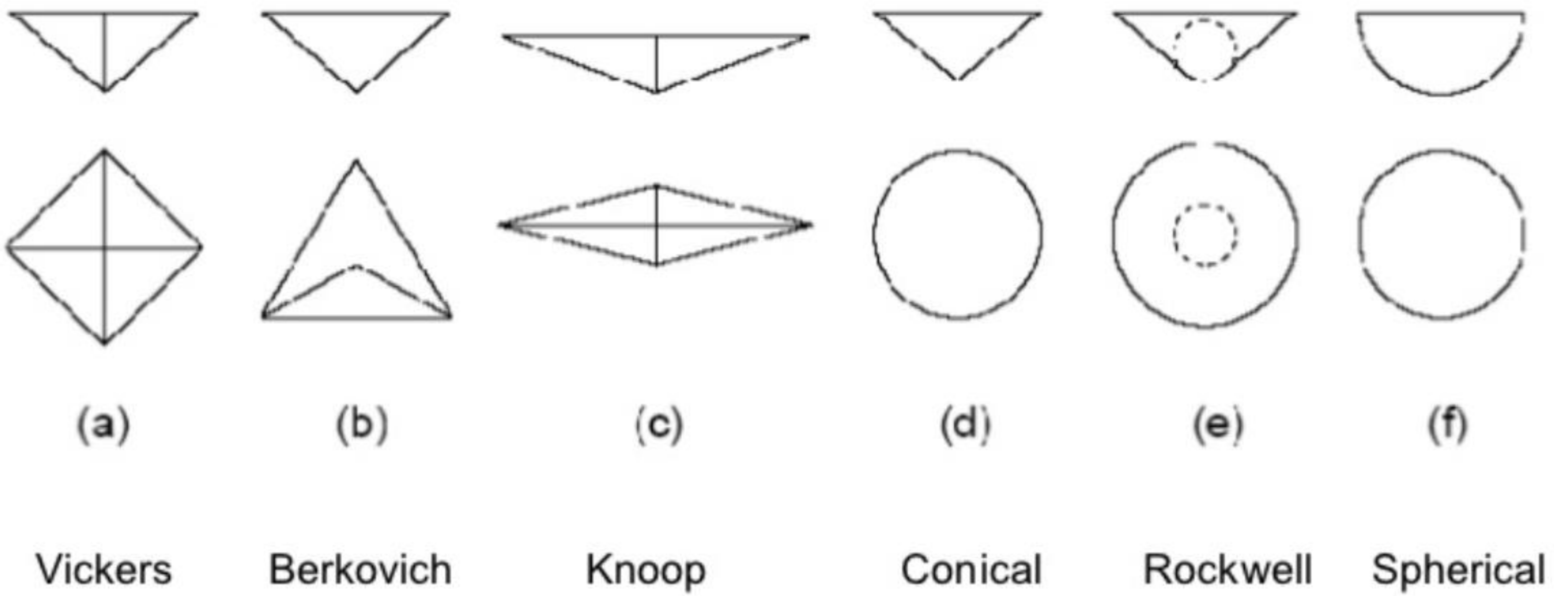
- The **P-h-t data** are then **analysed** with a **range of models**, such as elastic, elastoplastic, viscoelastic or poroviscoelastic, to **derive material mechanical properties**

Why nanoindentation?

- Ideal for **probing local gradients and heterogeneities** (typical of e.g. natural materials) and investigating their hierarchical multi-scale organization
- **Does not require extensive sample preparation** prior to testing (in contrast with most classical techniques, e.g. tensile testing which requires "dog-bone" shaped samples)
- Allows the measurement of **very small forces and displacements** (generally in the range of μN ÷ mN and nm ÷ μm, respectively)
- Requires **small volumes of materials**, and is thus particularly suitable for valuable samples
- Very small forces are applied, thus the technique is **well suited for soft biomaterials** (e.g. hydrogels), which due to their pliable and highly hydrated nature, are a challenge to characterise using macro-scale techniques

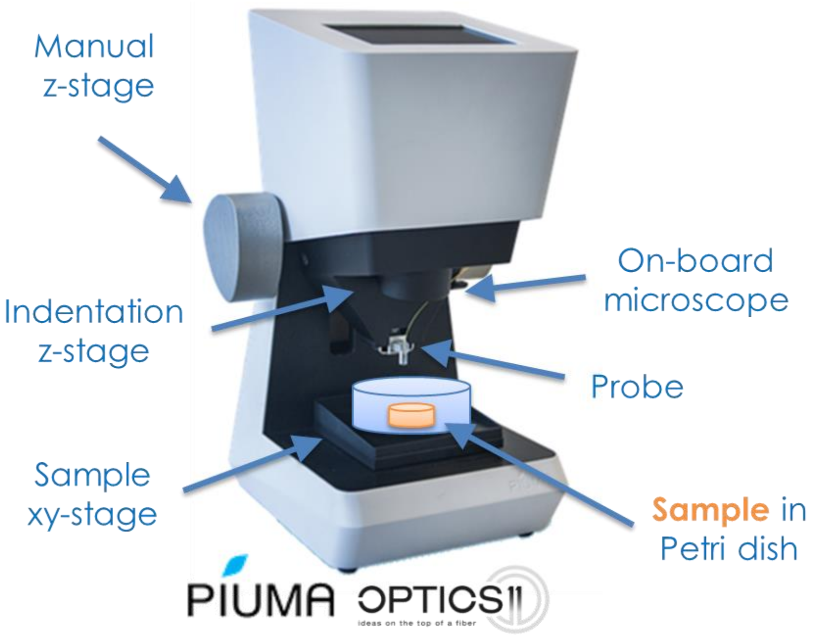
Why nanoindentation?

- A **variety of deformation modes** can be **studied** at typical **cell length-scales** by **changing** experimental **time scales, indenter tip geometry** and **loading conditions**



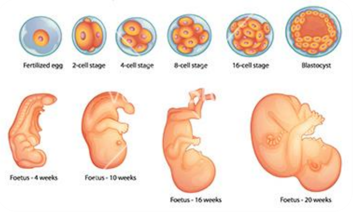
Why nanoindentation?

- Most commercial nano-indentation systems come with an **automated x-y stage** that allows **spatial mapping** of sample **local mechanical properties**

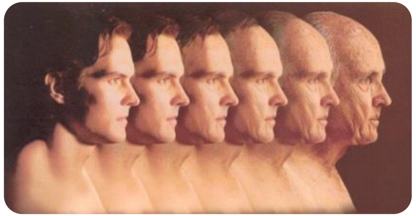


Why nanoindentation?

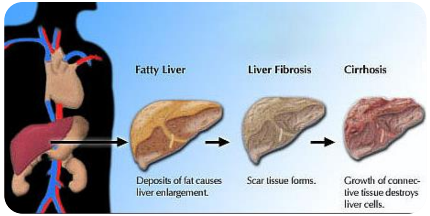
- The mechanical behavior of **biological tissues** generally changes with



development



ageing



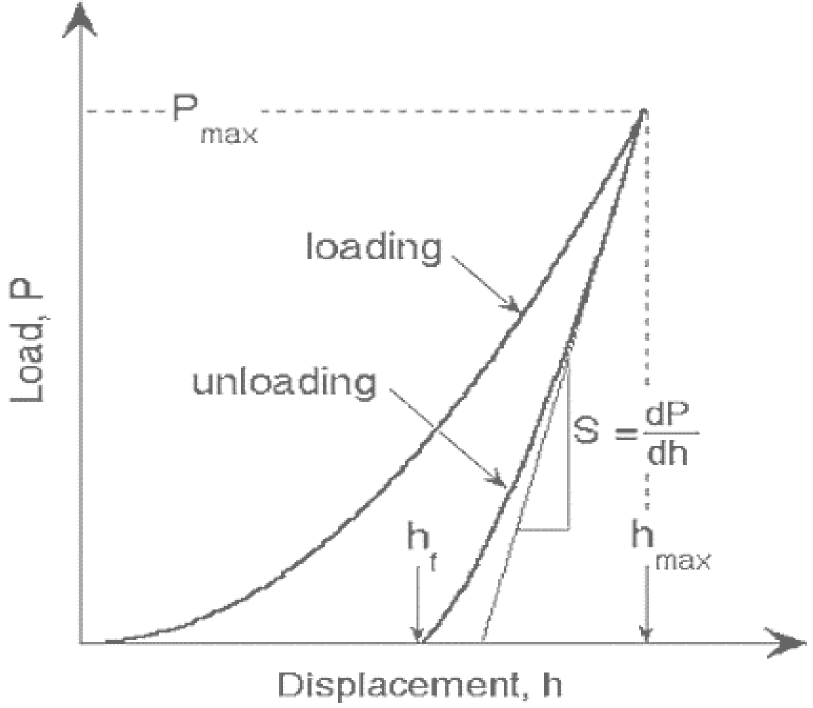
disease

- Thus, nanoindentation can also be attractive in the biomedical context as a **potential diagnostic tool** or for **engineering smart cell culture scaffold** based on **intelligent materials**

ELASTIC PROPERTIES

Elastic properties: unloading curve analysis
Oliver-Pharr model

- Introduced in 1992 and revised in 2004, it is based on an elastic–plastic contact model and uses three key parameters from the indentation test:
  - the **peak indenter force** (P_{max})
  - the **peak indenter displacement** (h_{max})
  - the **unloading slope** or **stiffness** ($S = \partial P / \partial h$)



Elastic properties: unloading curve analysis
Oliver-Pharr model

- The Oliver–Pharr method begins by **fitting** the **unloading portion** of the indentation load–depth data to the **power-law relation** shown below:

$$P = \alpha(h - h_f)^m$$

- Once the three fitting parameters *a*, *m* and h_f are obtained, the **contact stiffness *S***, which is defined as the slope of the unloading curve at the maximum indentation depth, can be **computed from**

$$S = \left.\frac{dP}{dh}\right|_{h=h_m} = Bm(h_m - h'_f)^{m-1}$$

- The **contact depth** of the spherical indentation h_c can be calculated by following the Oliver–Pharr method as

$$h_c = h_m - 0.75\frac{P_m}{S}$$

Elastic properties: unloading curve analysis
Oliver-Pharr model

- The **contact area A_c** can be **computed directly from** the **contact depth h_c** and the **radius of the indenter tip R**

$$A_c = \pi(2Rh_c - h_c^2)$$

- The contact stiffness S and the contact area Ac are then used to **calculate the reduced** (or effective) **modulus**

$$E_r = \frac{\sqrt{\pi}}{2\beta}\frac{S}{\sqrt{A_c}}$$

where **β** is a **dimensionless correction factor** which accounts for the deviation in stiffness due to the lack of axisymmetry of the indenter tip, with β=1.0 for axisymmetric indenters, β=1.012 for a square-based Vickers indenter, and β=1.034 for a triangular Berkovich punch

- **β = 1** for **spherical indenter tips**

- After obtaining the reduced modulus E_r, the **indentation modulus** from the Oliver–Pharr method can be finally determined by

$$E_{op} = \frac{1-v_s^2}{(1/E_r)-((1-v_i^2)/E_i)}$$

where v_s is **Poisson's ratio of the specimen**, E_i and v_i are respectively the **elastic modulus** and **Poisson's ratio** of the **indenter**. For **ordinary single phase materials**, the **indentation modulus** obtained **is** the **elastic modulus** of the **specimen**.

- **If** the **indenter elastic modulus** E_i is **much larger** than **that of the specimen** (e.g., SMAs, hydrogels, soft (bio)materials), the **indenter** can be **treated** as a **rigid body** and E_{op} can be **simplified** as

$$E_{op} = (1 - v_s^2)E_r$$

Elastic properties: loading curve analysis
Hertz model

- The analysis of the **loading portion** of nano-indentation data collected with a spherical tip is generally based on the **Hertz model**, assuming a **linear elastic** and **isotropic material response**.
- The **load** $\boldsymbol{P}$ is expressed as:

$$P = \frac{4}{3} E_{eff} R^{1/2} h^{3/2}$$

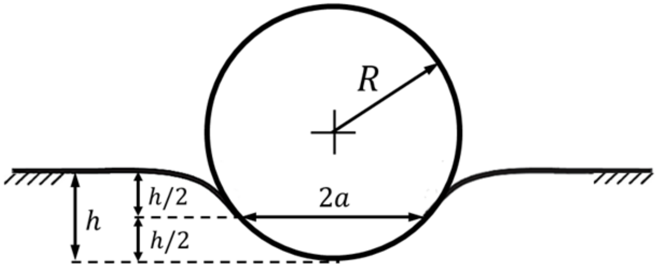
where $\boldsymbol{R}$ is the **radius** of the **spherical indenter tip**, $\boldsymbol{h}$ is the **penetration depth** and $\boldsymbol{E_{eff}}$ denotes the **effective composite elastic modulus** of the indenter and specimen system given by:

$$\frac{1}{E_{eff}} = \frac{1-\upsilon^2}{E} + \frac{1-\upsilon'^2}{E'}$$

E' and υ' respectively refer to the modulus and Poisson's ratio of the indenter, while the other terms refer to those of the sample

Elastic properties: loading curve analysis
Hertz model

- For a **rigid spherical indenter**, Sneddon showed that the **elastic displacements** of a **plane surface above** and **below** the **circle of contact** are **equal** and given by $h/2$, with:



$$h = \frac{a^2}{R}$$

where $\boldsymbol{a}$ denotes the **contact radius during indentation**. Combining previous equations yields:

$$\frac{P}{\pi a^2} = \frac{4}{3\pi} E_{eff} \left(\frac{a}{R}\right)$$

The **left side** is generally referred to as the **indentation stress (σ_{ind})** or mean contact pressure, while $\boldsymbol{a/R}$ on the right side represents the **indentation strain (ε_{ind})**

Elastic properties: loading curve analysis
Hertz model

- In case of **soft materials**, where $E' \gg E$, it can be approximated that:

$$\frac{1}{E_{eff}} \approx \frac{1 - \upsilon^2}{E}$$

- Consequently, the **sample elastic modulus** can be derived as:

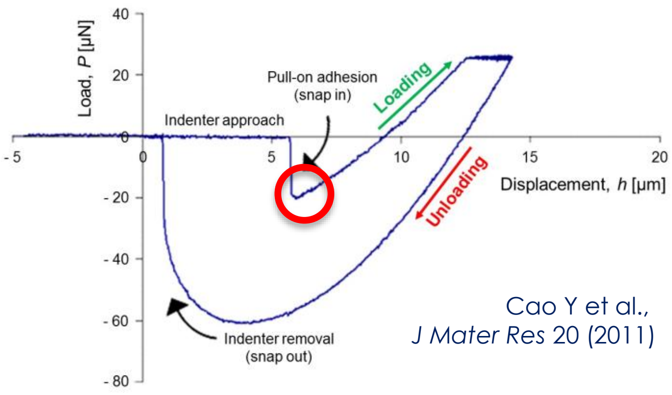
$$E = \frac{3(1 - \upsilon^2)P}{4R^{1/2}h^{3/2}}$$

Loading analysis issue: initial contact point

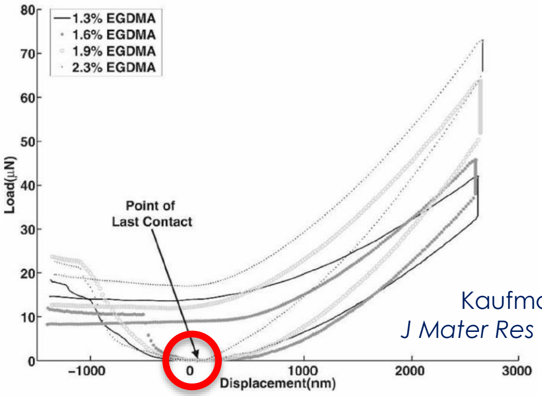
Commercial load-controlled nano-indenters → Load-based contact point determination → ⚠

Even **small trigger load** can **cause** a **significant pre-stress** on **soft samples**

Ideal tests should **start out of sample contact** ⇒ need of **displacement-controlled experiments** and **post-measurement identification** of the **initial contact point**



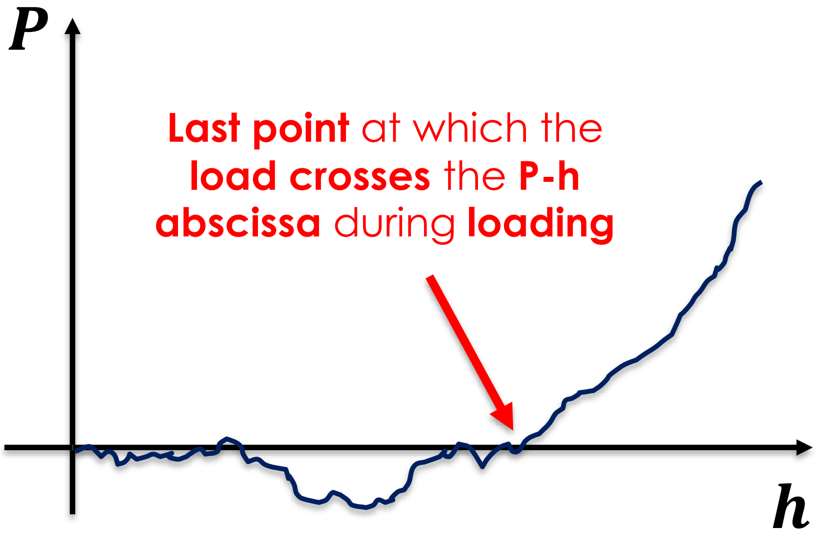
Cao Y et al.,
J Mater Res 20 (2011)



Kaufman et al.,
J Mater Res 23 (2008)

Loading analysis issue: initial contact point

- A possible solution…



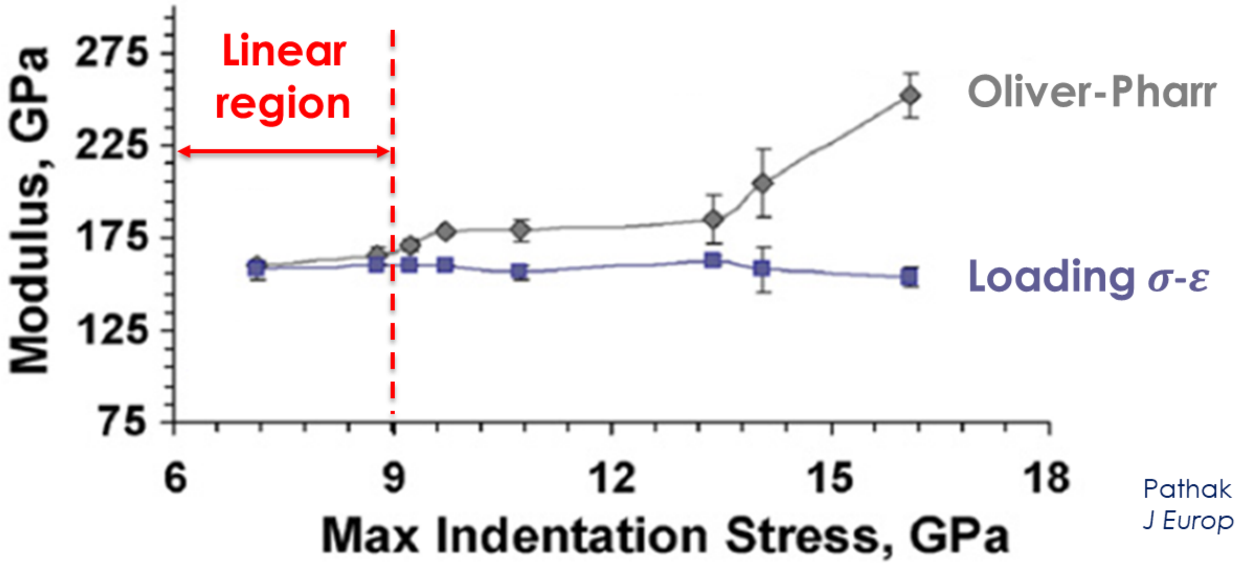
Unique identification of the **contact point** both when

- ✓ **Snap into contact** is **poorly evident**
- ✓ **Noise around zero load** is present

Tirella A et al., *JBMR A* 102 (2014)   Mattei G et al., *J Biomech* 47 (2014)   Mattei G et al., *JMBBM* (2015)

Advantages of loading curve analysis

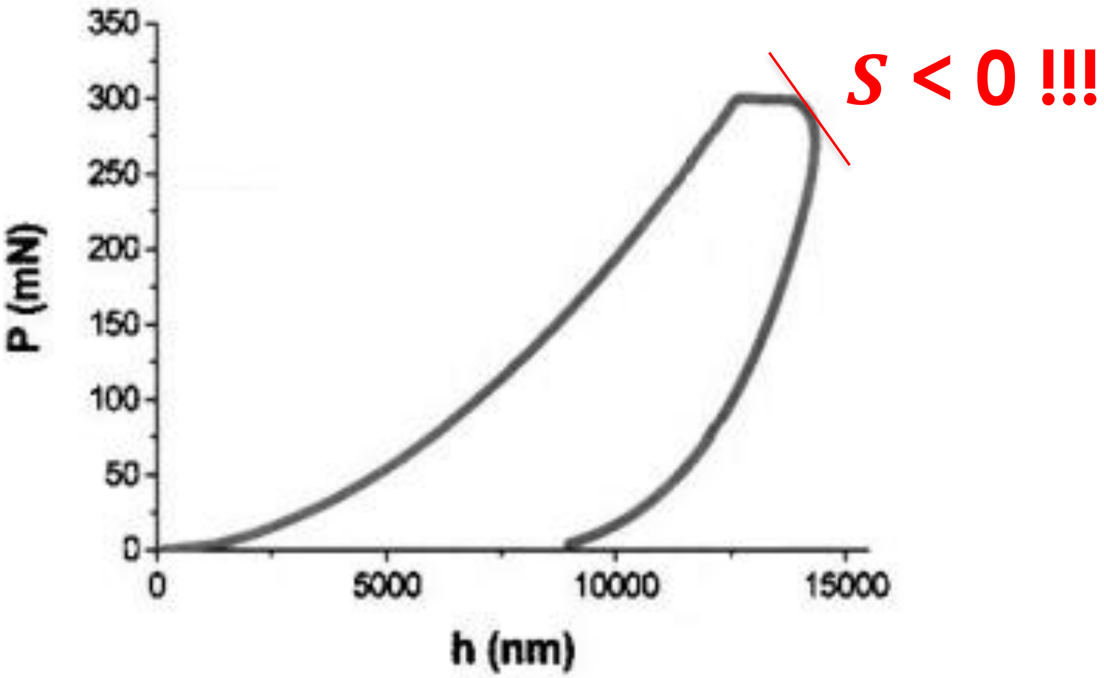
- **Mechanical properties** representative of those of the **virgin material**, returning a **constant modulus** value regardless of the maximum load (or displacement) chosen for the measurements.



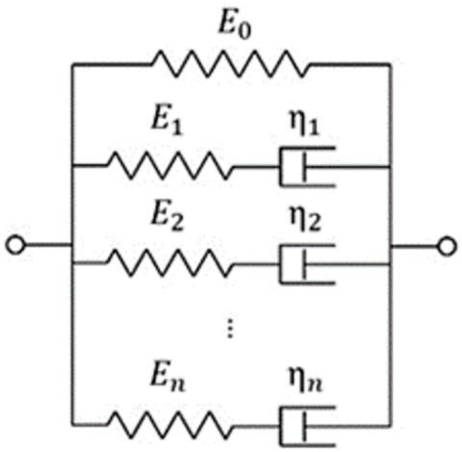
Pathak et al.,
J Europ Cer Soc 28 (2008)

Advantages of loading curve analysis

- Moreover, during unloading it is assumed that only the elastic displacements are recovered, thus **methods based on the unloading curve** are **unsuitable** for testing **viscoelastic materials.**

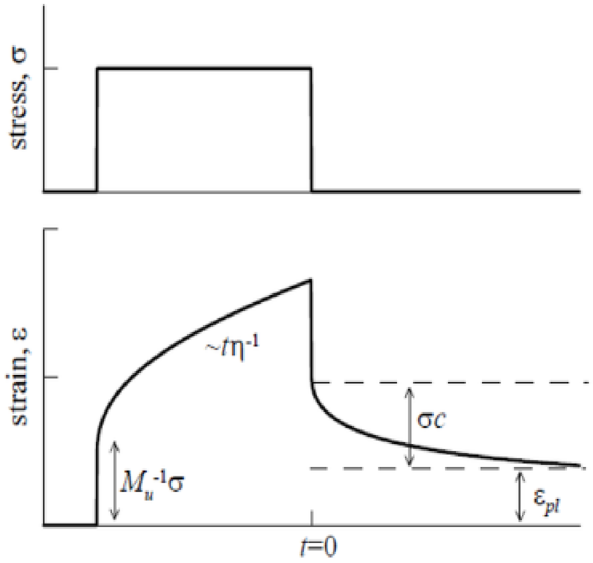


VISCO-ELASTIC PROPERTIES



Creep

- A **creep test** is based on **applying a constant load** and **measuring** the **change in displacement over time** due to viscoelastic phenomena
- **Hertz-type viscoelastic theory** can be used to obtain the **effective creep compliance** of a material under a step load (P_0, constant over time) imposed by a spherical indenter, obtaining:

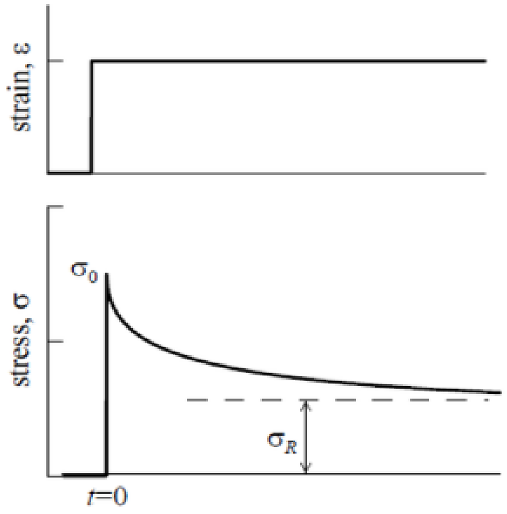


$$J_{eff}(t) = \frac{4}{3}\frac{R^{\frac{1}{2}}}{P_0}\, h(t)^{\frac{3}{2}}$$

In case of **soft materials** where $E' \gg E$, the **creep compliance** becomes:

$$J(t) = \frac{4}{3(1-\upsilon^2)}\frac{R^{\frac{1}{2}}}{P_0}\, h(t)^{\frac{3}{2}}$$

- **Stress-relaxation** can be considered the dual of creep test. It consists of **measuring** the **load relaxation over time** in **response** to a **constant step indentation input** (h_0). Assuming $E' \gg E$, the **relaxation modulus** can be expressed as:



$$E(t) = \frac{3(1-\upsilon^2)P(t)}{4R^{1/2}{h_0}^{3/2}}$$

Notably, in general $E(t) \neq 1/J(t)$,
except for $t = 0$ where $E(0) = 1/J(0)$.

Useful references

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