Today's Plan

Rubber elasticity # 2

I. Recall

II. Langevin statistic

III. Phenomenological approaches

IV. Summary

I. Recall

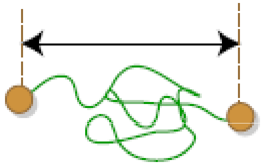
- The elasticity of rubbers is predominantly entropy-driven:

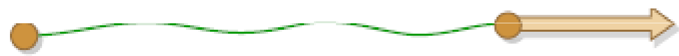
$$\boxed{f \approx -T\left(\frac{\partial S}{\partial l}\right)_T}$$

the force increases linearly with temperature

More disorder → **Less disorder**

Entropy - a natural law that expresses the driving force towards disorder





- Statistical mechanical theory

Based on gaussian statistical theory and by considering changes in entropy due to deformation, we arrived at the following expression in uniaxial tension :

$$\boxed{\sigma = \frac{F}{S_0} = \frac{kTN}{V_0}\left(\lambda_3 - \frac{1}{\lambda_3^2}\right)_T}$$

where N is the number junctions points in the network

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Comments on gaussian statistical mechanic

- Not all the crosslinks are effective

$$G = \frac{\rho RT}{M_c}\left(1 - \frac{2M_c}{M}\right)$$

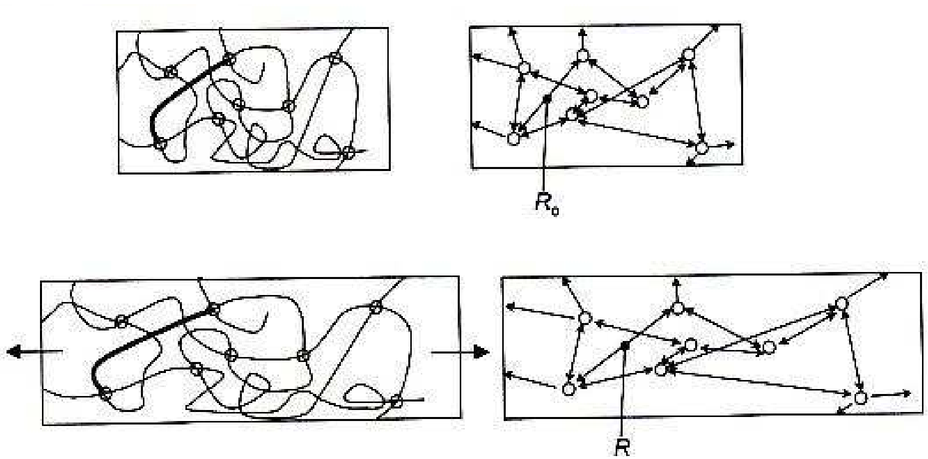
M_c molar mass between entanglements
M molar mass

- Free rotation ?

$$\langle r^2 \rangle = C_\infty n l^2 \qquad 2 < C_\infty < 10$$

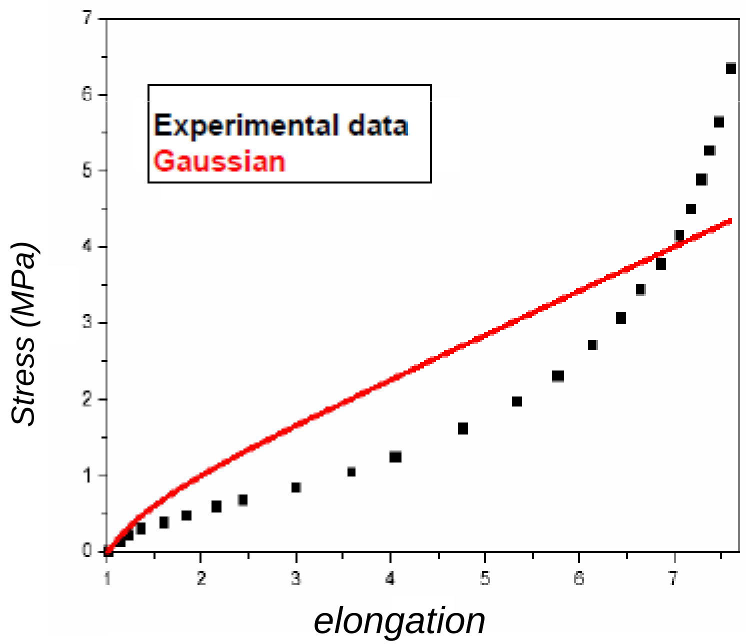
+ excluded volume, long range interactions …

- Affine deformation ?



Comments on gaussian statistical mechanic

- isolated chain → network: validity ?
- Validity of gaussian statistic ? (Total length of a chain can be > nl !)
- Results



Problem : For large deformation, no hardening !

→ Langevin statistic for large deformations and phenomenological approaches.

II. For large deformations : Langevin statistic

- Total length of a chain < nl

- Change of orientation : W(θ) = flcos(θ)

  → potential energy u= - W(θ)

- From Boltzman's statistic, probability of having a segment oriented by an angle θ is proportional to :

$$p(\theta) \propto \exp\left(-\frac{W(\theta)}{kT}\right) = \exp\left(\frac{Fl\cos\theta}{kT}\right)$$

- The average value of l in the direction of the applied force (x) is :

$$\langle l_x \rangle = \int_{u\min}^{u\max} lx(u)\,p(u)\,du$$

$$\frac{\langle l_x \rangle}{l} = \frac{\int_0^{\pi} \cos\theta \exp\left(\frac{Fl\cos\theta}{kT}\right)\sin\theta d\theta}{\int_0^{\pi} \exp\left(\frac{Fl\cos\theta}{kT}\right)\sin\theta d\theta}$$

Langevin statistic

- After integration: $$\frac{\langle l_x \rangle}{l} = \coth\left(\frac{Fl}{kT}\right) - \left(\frac{kT}{Fl}\right) = \mathrm{L}\left(\frac{Fl}{kT}\right)$$
  where L(x) *: Langevin function*
  $$\frac{n\langle l_x \rangle}{nl} = \frac{\langle r_x \rangle}{nl} = \mathrm{L}\left(\frac{Fl}{kT}\right)$$
  $$\mathrm{L}^{-1}\left(\frac{\langle r_x \rangle}{nl}\right) = \frac{Fl}{kT}$$
- After expansion of the inverse of Langevin function:
  $$\frac{Fl}{kT} = \left[3\left(\frac{\langle r_x \rangle}{nl}\right) + \frac{9}{5}\left(\frac{\langle r_x \rangle}{nl}\right)^3 + \frac{297}{175}\left(\frac{\langle r_x \rangle}{nl}\right)^3 + \ldots\right]$$
- For small deformations such as $\frac{\langle r_x \rangle}{nl} << 1$

one get : $\boxed{F = 3kT\frac{\langle r_x \rangle}{nl^2}}$ To be compared with $\longleftrightarrow$ $\frac{\mathbf{F}}{S_0} \approx AT\,g\left(\frac{l}{l_0}\right)$

Langevin statistic

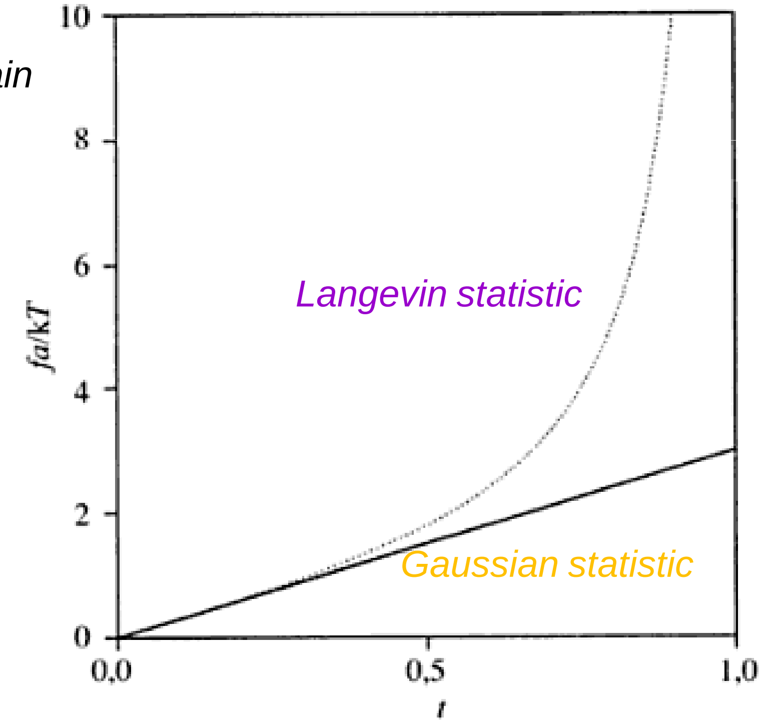
- 3D calculation taking into account the 3 perpendicular deformations leads to:

$$\sigma_{xx} = \lambda NkT\left[-\frac{1}{\lambda^2}+\frac{1}{3}\sqrt{n}\left[3\frac{\lambda}{\sqrt{n}}+\frac{9}{5}\left(\frac{\lambda}{\sqrt{n}}\right)^3+\frac{297}{175}\frac{5}{3}\left(\frac{\lambda}{\sqrt{n}}\right)^3+\ldots\right]\right]$$

n being the number of free links between 2 crosslinks

- Results

Force acting on a chain



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III. Phenomenological approaches

- Use of strain-energy functions

dA = dW for isochoric, isothermal and reversible transformation

We can imagine that the deformation is produced by independant changes in each of the component of strain, i.e:

$$dW = \frac{\partial A}{\partial e_{xx}} de_{xx} + \frac{\partial A}{\partial e_{yy}} de_{yy} + \frac{\partial A}{\partial e_{zz}} de_{zz} + \frac{\partial A}{\partial e_{yz}} de_{yz} + \frac{\partial A}{\partial e_{xz}} de_{xz} + \frac{\partial A}{\partial e_{xy}} de_{xy}$$

dW is work done by the external force per unit volume:

$$dW = \sigma_{xx} de_{xx} + \sigma_{yy} de_{yy} + \sigma_{zz} de_{zz} + \sigma_{yz} de_{yz} + \sigma_{xz} de_{xz} + \sigma_{xy} de_{xy}$$

This means that :

$$\sigma_{xx} = \frac{\partial A}{\partial e_{xx}} \quad \sigma_{yy} = \frac{\partial A}{\partial e_{yy}} \quad \sigma_{zz} = \frac{\partial A}{\partial e_{zz}} \quad \sigma_{yz} = \frac{\partial A}{\partial e_{yz}} \quad \sigma_{xz} = \frac{\partial A}{\partial e_{xz}} \quad \sigma_{xy} = \frac{\partial A}{\partial e_{xy}}$$

Note : In fact, various energy functions can be defined, corresponding to transformations at constant T and P, constant V and T, adiabatic transformations…We will refer to the energy-function as U.

Phenomenological approaches

- The form of the strain-energy functions

  - U must be an homogeneous quadratic function of the strain components
  - For isotropic solids, U must not depend on the choice of the direction of the coordinate axes: U is a function of strain invariants.

- The strain invariants

  Let's note the extensions ratio parallel to the 3 coordinate axes $\lambda_1, \lambda_2, \lambda_3$

$I_1 = 3 + 2\mathbf{e}_{rr} = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$

$I_2 = 3 + 4\mathbf{e}_{rr} + 2(\mathbf{e}_{rr}\mathbf{e}_{ss} - \mathbf{e}_{rs}\mathbf{e}_{sr}) = \lambda_1^2\lambda_2^2 + \lambda_1^2\lambda_3^2 + \lambda_2^2\lambda_3^2$

$I_3 = |\ \delta_{rs} + 2\mathbf{e}_{rs}\ | = \lambda_1^2\lambda_2^2\lambda_3^2 = 1$ (no change of volume deformation)

$\rightarrow$ U=f (I1,I2,I3)

$U = f(I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2,\ I_2 = 1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2)$

Phenomenological approaches

- If U is to vanish at zero strain, this implies that:

$$\boxed{U = \sum_{i=0,\, j=0}^{\infty} C_{ij} (I_1 - 3)^i (I_2 - 3)^j}$$

where $C_\infty=0$

- Example:
  - Neo Hookeen material $U = C_1(I_1 - 3) = C_1\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2\right)$

    which corresponds to gaussian statistic if we put $C_1=1/2NkT$

  - Mooney-Rivlin $U = C_1(I_1 - 3) + C_2(I_2 - 3)$

- The stress-strain relations

  Strain components are specified, and stress components are obtained using the strain-energy function.

Stress-strain relations

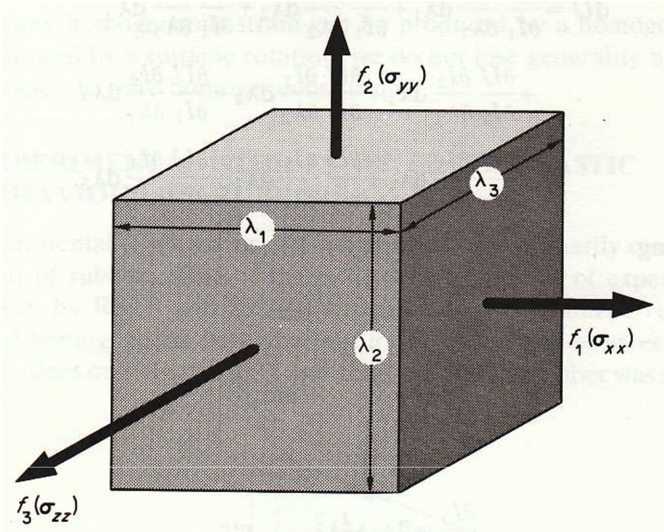

Figure 3.2. A cube of unit dimensions transforms to a rectangular parallelepiped of edges λ_1, λ_2 and λ_3 under the applied loads f_1, f_2 and f_3.

f = force per unit of underformed cross-section

The corresponding stress components in the deformed state are:

$$\sigma_{xx} = \frac{f_1}{\lambda_2\lambda_3} = \lambda_1 f_1 \qquad \sigma_{yy} = \frac{f_2}{\lambda_1\lambda_3} = \lambda_2 f_2 \qquad \sigma_{zz} = \frac{f_{"}}{\lambda_1\lambda_{é}} = \lambda_3 f_3$$

The work done (per unit of initial underformed volume) in an infinitesimal displacement from the deformed state where λ_i changes to $\lambda_i + d\lambda_i$ (i=1,2,3) is:

$$dU = f_1 d\lambda_1 + f_2 d\lambda_2 + f_3 d\lambda_3$$

$$dU = \frac{\sigma_{xx}}{\lambda_1} d\lambda_1 + \frac{\sigma_{yy}}{\lambda_2} d\lambda_2 + \frac{\sigma_{zz}}{\lambda_3} d\lambda_3$$

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Stress-strain relations

$$U = f(I_1, I_2, I_3),$$

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2,$$

$$I_2 = \frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \frac{1}{\lambda_3^2},$$

$$I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2.$$

Therefore

$$\begin{aligned} dU = {} & \frac{\partial U}{\partial I_1}\frac{\partial I_1}{\partial \lambda_1} d\lambda_1 + \frac{\partial U}{\partial I_1}\frac{\partial I_1}{\partial \lambda_2} d\lambda_2 + \frac{\partial U}{\partial I_1}\frac{\partial I_1}{\partial \lambda_3} d\lambda_3 \\ & + \frac{\partial U}{\partial I_2}\frac{\partial I_2}{\partial \lambda_1} d\lambda_1 + \frac{\partial U}{\partial I_2}\frac{\partial I_2}{\partial \lambda_2} d\lambda_2 + \frac{\partial U}{\partial I_2}\frac{\partial I_2}{\partial \lambda_3} d\lambda_3 \\ & + \frac{\partial U}{\partial I_3}\frac{\partial I_3}{\partial \lambda_1} d\lambda_1 + \frac{\partial U}{\partial I_3}\frac{\partial I_3}{\partial \lambda_2} d\lambda_2 + \frac{\partial U}{\partial I_3}\frac{\partial I_3}{\partial \lambda_3} d\lambda_3. \end{aligned}$$

Substituting

$$\frac{\partial I_1}{\partial \lambda_1} = 2\lambda_1, \qquad \text{etc.,}$$

$$\frac{\partial I_2}{\partial \lambda_1} = -\frac{2}{\lambda_1^3}, \qquad \text{etc.,}$$

and

$$\frac{\partial I_3}{\partial \lambda_1} = 2\lambda_1 \lambda_2^2 \lambda_3^2, \qquad \text{etc.,}$$

we have

$$\begin{aligned} dU = {} & 2\left\{\lambda_1 \frac{\partial U}{\partial I_1} d\lambda_1 + \lambda_2 \frac{\partial U}{\partial I_1} d\lambda_2 + \lambda_3 \frac{\partial U}{\partial I_1} d\lambda_3\right\} \\ & - 2\left\{\frac{1}{\lambda_1^3}\frac{\partial U}{\partial I_2} d\lambda_1 + \frac{1}{\lambda_2^3}\frac{\partial U}{\partial I_2} d\lambda_2 + \frac{1}{\lambda_3^3}\frac{\partial U}{\partial I_2} d\lambda_3\right\} \\ & + 2I_3\left\{\frac{1}{\lambda_1}\frac{\partial U}{\partial I_3} d\lambda_1 + \frac{1}{\lambda_2}\frac{\partial U}{\partial I_3} d\lambda_2 + \frac{1}{\lambda_3}\frac{\partial U}{\partial I_3} d\lambda_3\right\}. \end{aligned}$$

λ_1, λ_2 and λ_3 are independent variables.

Stress-strain relations

We can therefore equate the coefficients of $d\lambda_1$, $d\lambda_2$, and $d\lambda_3$ in these equations to find the stress components.

This gives

$$\boldsymbol{\sigma}_{xx} = 2\left\{\lambda_1^2 \frac{\partial U}{\partial I_1} - \frac{1}{\lambda_1^2}\frac{\partial U}{\partial I_2} + I_3 \frac{\partial U}{\partial I_3}\right\}, \qquad \text{etc.}$$

If the solid is incompressible $I_3 = 1$ and $U = f(I_1, I_2)$ only. In this case the stresses are now indeterminate with respect to an arbitrary hydrostatic pressure, $\mathbf{p}$, because this pressure does not produce any changes in the deformation variables λ_1, λ_2, λ_3. Then

$$\boldsymbol{\sigma}_{xx} = 2\left\{\lambda_1^2 \frac{\partial U}{\partial I_1} - \frac{1}{\lambda_1^2}\frac{\partial U}{\partial I_2}\right\} + \mathbf{p}.$$

In index notation the stresses are given as

$$\boxed{\boldsymbol{\sigma}_{ii} = 2\left\{\lambda_i^2 \frac{\partial U}{\partial I_1} - \frac{1}{\lambda_i^2}\frac{\partial U}{\partial I_2}\right\} + \mathbf{p},} \qquad \boldsymbol{\sigma}_{ij} = 0.$$

IV. Rubber elasticity #2 : summary

- The elasticity of rubbers is predominantly entropy-driven. The stiffness increases with increasing temperature.
- Upon loading, the chains become ordered. This leads to a reduction in entropy. Upon unloading, the MMs return to their initial state in the form of random balls, provided that the chains are sufficiently long and flexible.
- Based on statistical theory and by considering changes in entropy due to deformation, we arrived at the following expression in uniaxial tension :

$$\boxed{\sigma = \frac{F}{S_0} = \frac{kTN}{V_0}\left(\lambda_3 - \frac{1}{\lambda_3^2}\right)_T}$$

- Such expression has been improved by using Langevin statistic .
- Phenomenological theories that uses the concept of strain-energy functions have been studied (Rivlin , Neo Hookean..). Neo Hookean model corresponds to gaussian statistic.

Thank you for your attention !