

Mechanics of solid polymers, Lecture #12, July 10th 2009

Today's Plan

Rubber elasticity # 1

- I. Thermodynamics
- II. Experiment
- III. Statistical mechanical theory
- IV. Summary

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Rubber and elastomers

• Ex : Natural rubber



Hevea brasiliensis tree



Natural Rubber shoes



Rubber tire



To help elastomers bounce back even better it helps to crosslink them. (1844) Vulcanization



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Introduction

• Rubber can be stretched to many times their original length and can bounce back into their original shape without permanent deformation: non linear elasticity, or hyperelasticity.

• We aim at

- Understand the origin of rubber elasticity.
- Understand the unusual behaviour of a rubber when heated under tension.
- Be able to predict the stiffness of rubber from a simple picture of its molecular structure: statistical theory.
- Apply hyperelastic models to uniaxial extension and biaxial extension

I. Thermodynamics



- -dW = fdI pdV
- Reversible transformation: dQ = TdS
- A = U -T S Helmotz free energy

$$dA = dU - TdS - SdT = dQ - dW - TdS - SdT$$
 (reversible transformation)
= fdI - pdV - SdT (isochoric and isothermal transformation)

$$dA = fdI$$

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Thermodynamics



Typical values for fe/f

Conclusion : Rubber elasticity (hyperelasticity) is driven by entropy

Observations



Force depends linearly on temperature

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II. Experiment



Experiments : understanding





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Entropic change as a function of stretch



Figure by MIT OCW. [MIT M. Buehler, http://ocw.mit.edu]

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Rubber band

rubber bands, Richard Feynman



http://www.youtube.com/watch?v=baXv_5z7HVY

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III. Statistical mechanical theory

- Entropy of a single chain.
- Entropy of a collection of N random chains per unit volume
- Calculation of entropy variation of this assembly
- Determination of its force and stiffness
- Assumptions (ideal network):
 - Chains are constituted with n segments rotating freely
 - No excluded volume
 - The chain segments between crosslinks can be represented by Gaussian statistics
 - Affine deformation

Affine network model



• If one end of the chain is at (0,0,0), then the probability of the other end being at point (x,y,z) is :

$$p(x, y, z)dxdydz = \left(\frac{b}{\sqrt{\pi}}\right)^3 \exp(-b^2r^2)dxdydz$$

where $r^2 = x^2 + y^2 + z^2$ $b^2 = \frac{3}{2nl^2}$ *I* = bond length *n* = number of links

• The entropy is given by Bolzman law:

S = kInW

where W is the total number of possible conformations, and $W \propto p(x,y,z)$

$$S \propto C - k b^2 r^2$$

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Affine network model

• If we stretch the chain, so that the end is at a new location (Q'):

Q'(x'= $\lambda_1 x$, y'= $\lambda_2 y$, z'= $\lambda_3 z$)

• Then associated change in entropy is given by:

$$\Delta S = k \ln\left(\frac{W'}{W}\right) = k \ln\left(\frac{p'}{p}\right)$$
$$\Delta S = -kb^2 \left[(\lambda_1^2 - 1)x^2 + (\lambda_2^2 - 1)y^2 + (\lambda_3^2 - 1)z^2 \right]$$

• In the unstressed state, we have

$$\langle x^2 \rangle = \frac{\langle r^2 \rangle}{3}$$

- So, on average : $\langle \Delta S \rangle = -k \left(\frac{3}{2nl^2} \right) \frac{\langle r^2 \rangle}{3} \left[(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \right]$
- Where :

$$\left\langle r^2 \right\rangle = \int_{0}^{\infty} r^2 p(r) dr = nl^2$$



• The total entropy change is given by multiplying the entropy of a single chain segment by N :

$$\left\langle \Delta S_{tot} \right\rangle = -\frac{1}{2} Nk \left[\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right) \right]$$

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Z

Application to uniaxial tension

$$\left\langle \Delta S_{tot} \right\rangle = -\frac{1}{2} N k \left[\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right) \right]$$

•
$$\lambda_1 = \lambda_2$$

•
$$\lambda_1 \lambda_2 \lambda_3 = 1$$
 (constant volume)

• Therefore:
$$\langle \Delta S_{tot} \rangle = -\frac{1}{2} N k \left| \left(\frac{2}{\lambda_3} + {\lambda_3}^2 - 3 \right) \right|$$

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

We have : $f = \frac{kTN}{l_0}\left(\lambda_3 - \frac{1}{\lambda_3^2}\right)$

And :

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

1

Chain segments density



ared with $\frac{\mathbf{F}}{S_0} \approx AT g\left(\frac{l}{l_0}\right)$

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Elastic moduli

• For small deformation : $\lambda_3=1 + \epsilon_{33}$ where $\epsilon_{33} << 1$

$$\sigma = \frac{F}{S_0} = \frac{kTN}{V_0} \left(\lambda_3 - \frac{1}{\lambda_3^2} \right)_T \longrightarrow \sigma_{33} \approx \frac{kTN}{V_0} 3\varepsilon_{33}$$

- Young's modulus $\sigma_{33} = E\varepsilon_{33}$ with E = 3NkT
- Shear modulus

$$G = \frac{E}{2(1+\nu)} = NkT$$

rewritten :

$$G = \frac{\rho RT}{M_c}$$

 ρ specific mass $R = 8.314 \text{ J} \text{K}^{-1} \text{ mol}^{-1}$ ideal gaz constant M_c molar mass between entanglements

Comments

• Correction for chains ends

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

M_c molar mass between entanglements *M* molar mass

• Free rotation ?

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

+ excluded volume, long range interactions ...

• Affine deformation ?



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Comments

- isolated chain \rightarrow network: validity ?
- Results



Problem : For large deformation, no hardening !

 \rightarrow Langevin statistic for large deformations

IV. Rubber elasticity #1 : summary

- The elasticity of rubbers is predominantly entropy-driven. The stiffness increases with increasing temperature.
- The elastic force can be thought of as consisting of an entropic and an energetic part. The energetic contribution to the elastic force is generally small.
- Based on statistical theory and by considering changes in entropy due to deformation, we arrived at the following expression in uniaxial tension :

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

• Corrections are needed for large deformations : Langevin statistic, and phenomenological approaches.

Applications

Rubber band and protein



http://www.youtube.com/watch?v=IKpXlbeHwh4

Rubber bands heat engine



http://www.youtube.com/watch?v=OW6aEmOsXv0

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Thank you for your attention

Lecture# 13 will be given on July 17th