Chapter 9

Rubber Elasticity

Rubber

- rubber (지우개?) = elastomer (탄성체, better term)
- A rubber
  - stretches to 100's of %

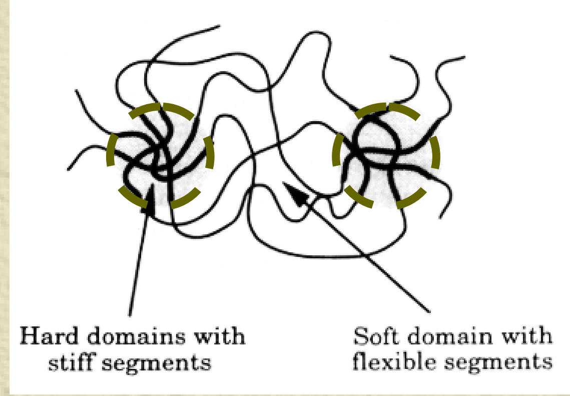
    ← flexible chain (T_g < room temp)
  - snaps back to its original length instantly

    ← crosslinked (chemically)

    ✓vulcanization (가황) 🕮p432

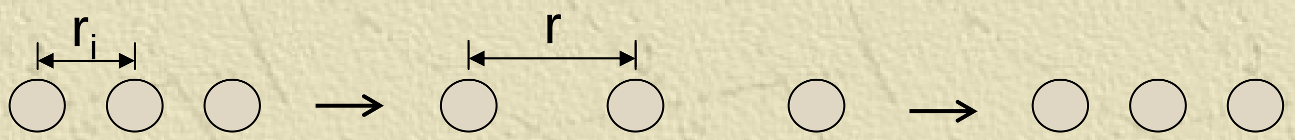
    ✓physically crosslinked in TPE

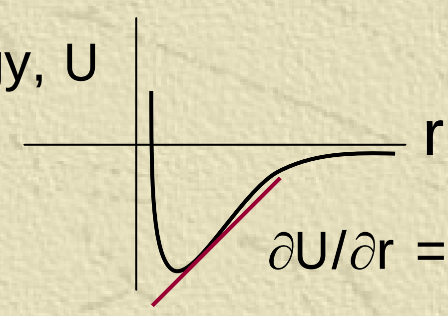
    - TPE ~ thermoplastic elastomer 🕮p483



Rubber is an entropy spring.

- metal spring ~ energy-driven elasticity





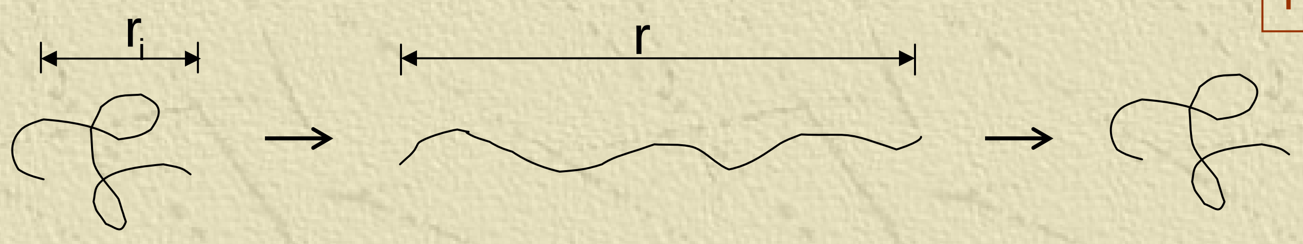
$F = U - TS$

For ideal gas,

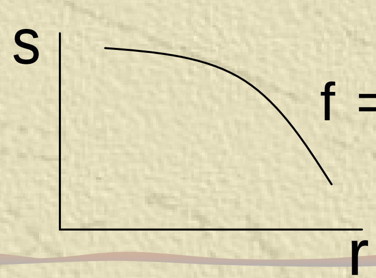
$\partial U/\partial V = 0$

$P = T\partial S/\partial V$

- rubber ~ entropy-driven elasticity



$r_i = \langle r_i^2 \rangle^{½}$



$f = \partial(-T\Delta S)/\partial r$

✓ ideal rubber

📖Fig 9.7 p439

Rubber elasticity equations

- Statistical Thermodynamics
  - Helmoltz free energy, $F = U - TS$ 🕮eqn (9.5)
  - (retractive) force, f

    $f = \partial F/\partial r = \partial U/\partial r - T\,\partial S/\partial r = -kT\,\partial \ln\Omega/\partial r$ 🕮eqn (9.6), (9.20)
  - For one chain;
    - Ω ~ # of conformations → probability of a conformation
    - W(r) ~ probability finding the other end at betw r & r+dr 🕮Fig 9.9

      $W(r)dr = [\Omega dr / \int \Omega dr]\, 4\pi r^2$ 🕮eqn (9.22)
    - Ω for Gaussian W(r) 🕮Fig 9.10

      $\partial \ln\Omega/\partial r = -2\beta^2 r$ where $\beta = 3/(2\langle r_0^2\rangle)$ 🕮eqn (9.26)
    - f from eqn (9.20) & (9.26)

      $f = 3kTr/\langle r_0^2\rangle$ 🕮eqn (9.27) $f \propto r$ ~ a spring

Stat thermo 2

- For n chains;
  - deformation from r_i to r
    - $r_0 \rightarrow r$ for 1 chain, $r_i \rightarrow r$ for many chains
      practically, $r_0 = r_i$
    - affine deformation

    $\langle r^2\rangle / \langle r_i^2\rangle = (1/3)(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)$ eqn (9.28)

  - work done, using eqn (9.27)

    $-W = \Delta F = [3nRT/\langle r_0^2\rangle] \int r\,dr$ ($\int$ from r_i to r) eqn (9.30)

  - Integrating and using eqn (9.28)

    $\Delta F = (nRT/2)(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)$ eqn (9.31)

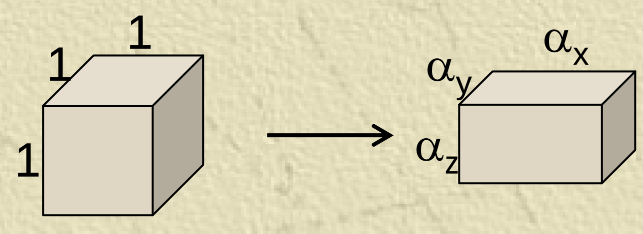
  - When incompressible ($\nu = 0.5$), $\alpha_x\alpha_y\alpha_z = 1$, $\alpha_y = \alpha_z = 1/\alpha_x^{1/2} = 1/\alpha^{1/2}$

    $\Delta F = (nRT/2)(\alpha^2 + 2/\alpha - 3)$ eqn (9.33)

  - stress, σ

    $\sigma = \partial F/\partial\alpha = nRT(\alpha - 1/\alpha^2)$

    eqn (9.34)

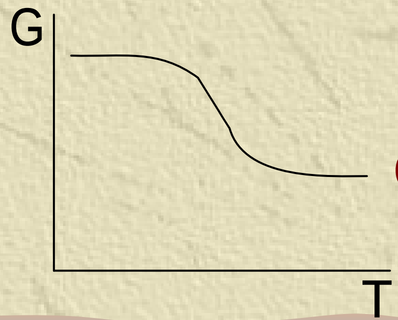


extension ratio, $\alpha = 1 + \varepsilon$

Equation of state (EOS) for rubber elasticity

Stat thermo 3

- constitutive eqn (구성방정식, relation betw σ and ε)
  - extension ratio, α
    - $\alpha = 1 + \varepsilon$
    - $\alpha^{-2} = (1 + \varepsilon)^{-2} = 1 - 2\varepsilon + \text{---} \quad \approx 1 - 2\varepsilon$ for small ε
  - modulus, E from eqn (9.34)
    - $E = \sigma/\varepsilon = [nRT\ (1 + \varepsilon - (1 - 2\varepsilon)) / \varepsilon = 3nRT$
  - For rubber, $\nu = 0.5$
    - $G = E / 2(1 + \nu) = E/3 = nRT = (\rho RT/M_c)$
    - n ~ # of chains → # of chain fragments
    - M_c ~ mol wt betw Xlinks



$G = \rho RT/M_c$

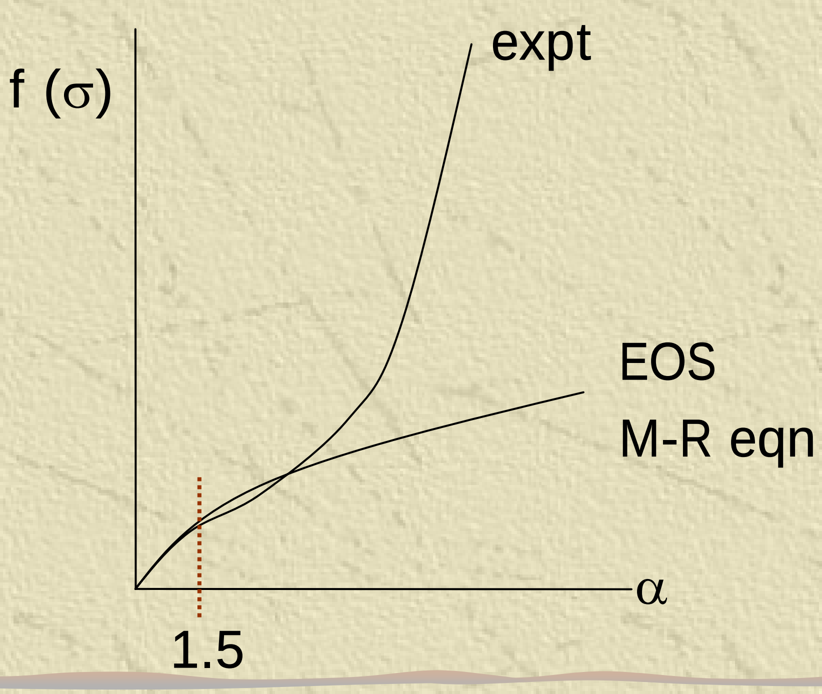
$G_N^0 = \rho RT/M_e$ for linear polymers
M_e ~ entanglement mol wt
🕮 Fig 9.21 p464

Continuum mechanics eqn

- Continuum Mechanics approach
  - Mooney-Rivlin eqn

$$\sigma = (2C_1 + 2C_2/\alpha)\,(\alpha - 1/\alpha^2) = G\,(\alpha - 1/\alpha^2)$$ 📖 eqn (9.49)

- Comparison with experiments



Rubber becomes compressible, anisotropic, and strain-induced crystallizes.

📖Fig 9.5 p436