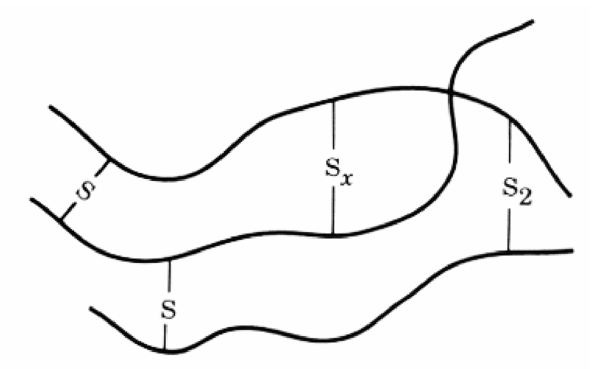
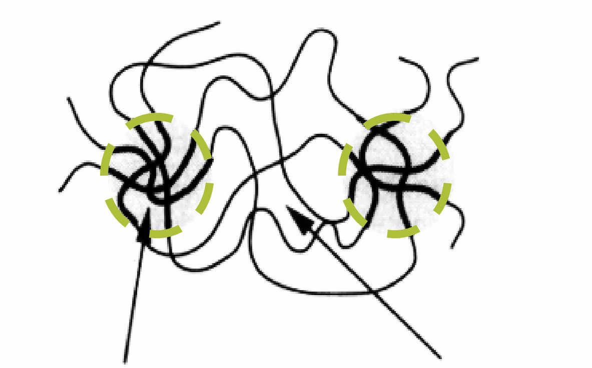
Chapter 3

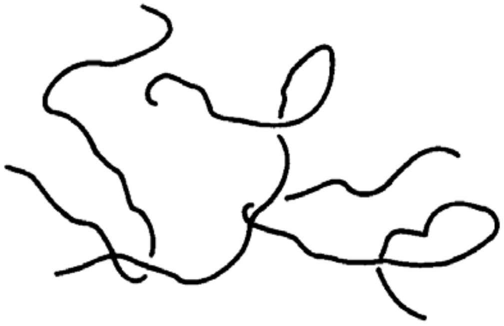
Rubber Elasticity

Rubber

- rubber (지우개?) = elastomer (탄성체, better term)
- A rubber should (requirement, ASTM)
  - stretch to > 100%
    - flexible chain (T_g < room temp)
  - snap back to its original length instantly and spontaneously
    - chemical crosslinking ~ vulcanization (가황) by sulfur or peroxide
    - physical crosslinking ~ thermoplastic elastomer (TPE) and glasses

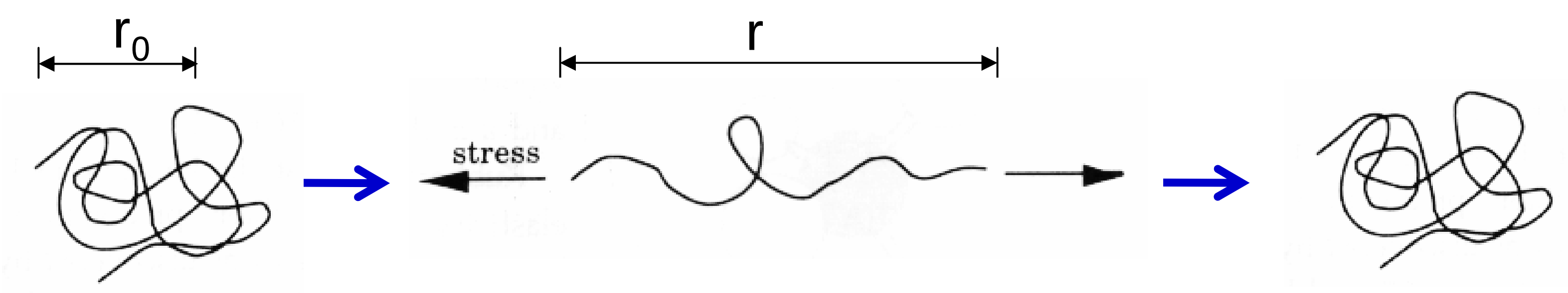




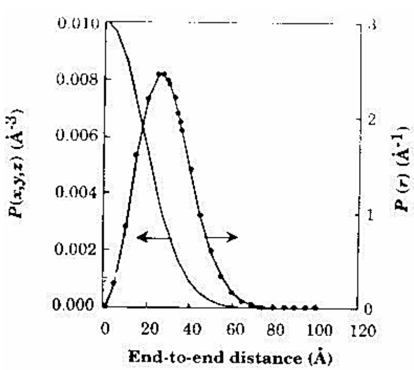


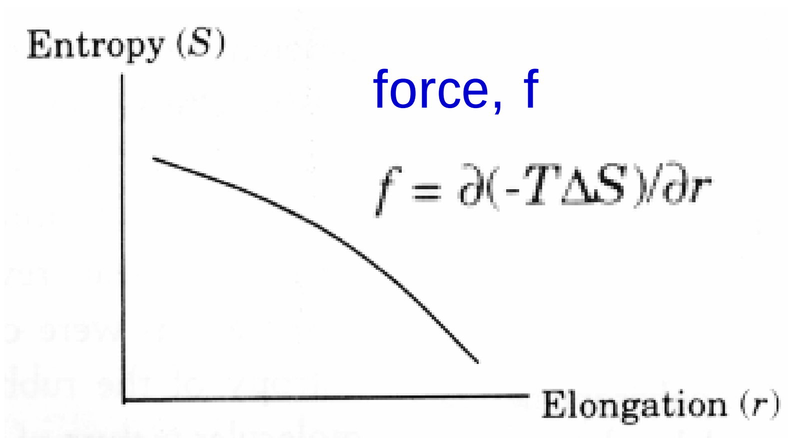
Rubber is an entropy spring.

- Rubbers (thermoelastic effect)
  - contract when heated
  - give out heat (get hot) when stretched
- rubber spring ~ entropy-driven elasticity



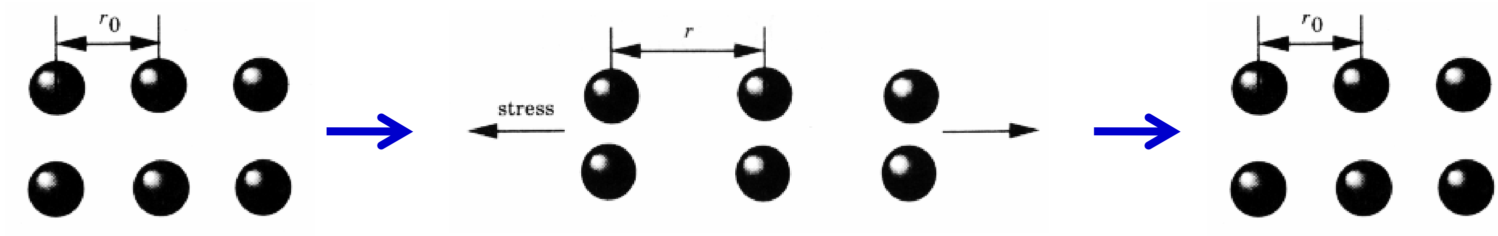
$r_0 = \langle r_i^2 \rangle^{½}$

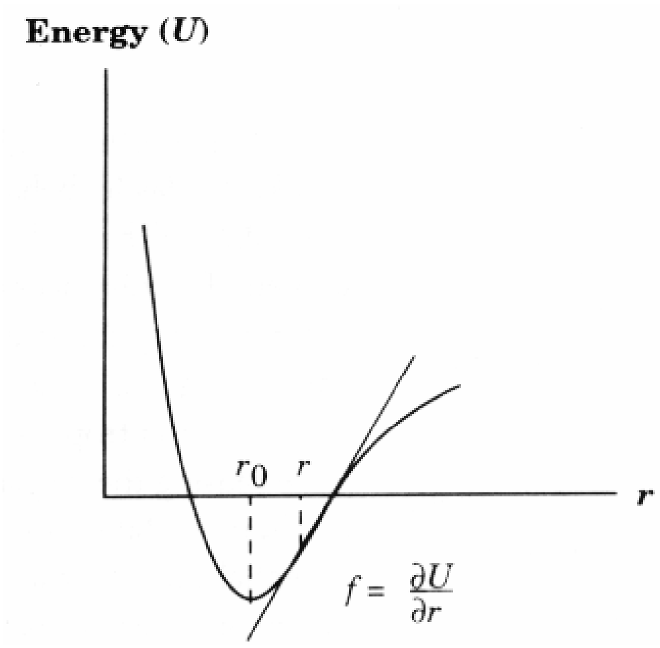




Rubber is an entropy spring.

- metal spring ~ energy-driven elasticity



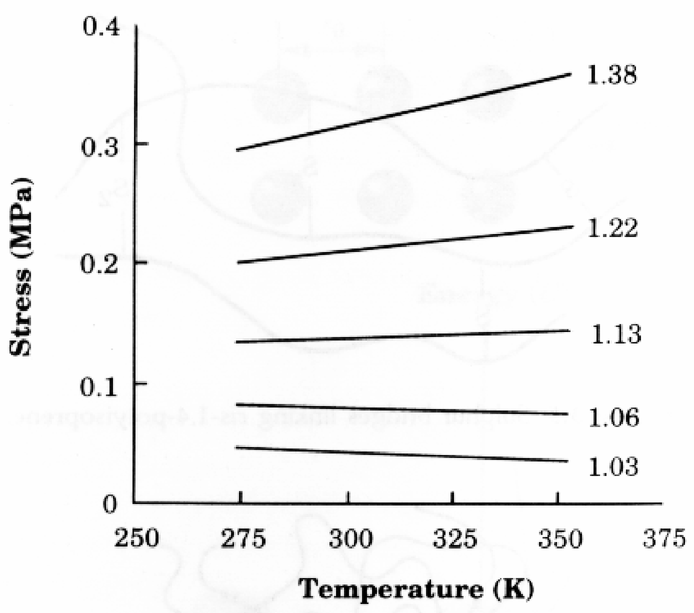


force, f

$$f = \frac{\partial U}{\partial r} = 2C(r - r_0) \qquad (3.2)$$

Thermodynamic theory

- Stress increases as temp increases.
  - At const length, rubbers contract when heated.
  - At low extension ratio ($\lambda = L/L_0$) below ~1.1, negative slope due to thermal expansion
- (retractive) force, f = (dG/dL)



$$G = H - TS = E + pV - TS \qquad (3.5)$$

$$dG = dE + p\,dV + V\,dp - T\,dS - S\,dT \qquad (3.6)$$

$$dE = T\,dS - p\,dV + f\,dL \qquad (3.4)$$

$$dG = f\,dL + V\,dp - S\,dT \qquad (3.7)$$

$$\left(\frac{\partial G}{\partial L}\right)_{p,T} = f \qquad (3.8)$$

$$\left(\frac{\partial G}{\partial T}\right)_{L,p} = -S \qquad (3.9)$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial L}\right)_{p,T}\right)_{p,L} = \left(\frac{\partial}{\partial L}\left(\frac{\partial G}{\partial T}\right)_{L,p}\right)_{p,T} \qquad (3.10)$$

$$\left(\frac{\partial f}{\partial T}\right)_{L,p} = -\left(\frac{\partial S}{\partial L}\right)_{p,T} \qquad (3.11)$$

$$G = H - TS$$

$$\left(\frac{\partial G}{\partial L}\right)_{p,T} = \left(\frac{\partial H}{\partial L}\right)_{p,T} - T\left(\frac{\partial S}{\partial L}\right)_{p,T} \qquad (3.12)$$

$$\left(\frac{\partial G}{\partial L}\right)_{p,T} = f \qquad (3.8)$$

$$f = \left(\frac{\partial H}{\partial L}\right)_{p,T} + T\left(\frac{\partial f}{\partial T}\right)_{p,L} \qquad (3.13)$$

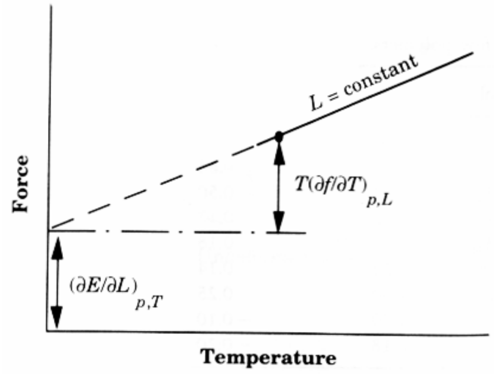
0 ← Rubber is incompressible. $\nu \approx 0.5$

$$\left(\frac{\partial H}{\partial L}\right)_{p,T} = \left(\frac{\partial E}{\partial L}\right)_{p,T} + p\cancel{\left(\frac{\partial V}{\partial L}\right)_{p,T}} \qquad (3.14)$$

$$\boxed{f = \left(\frac{\partial E}{\partial L}\right)_{p,T} + T\left(\frac{\partial f}{\partial T}\right)_{p,L}}$$

energetic   entropic part

thermodynamic equation of state for rubber elasticity



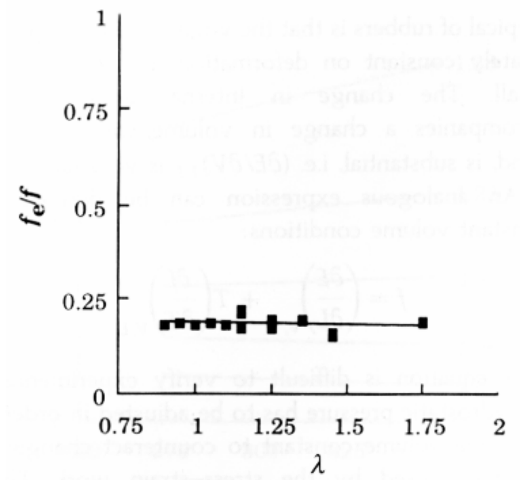
- Energetic part (f_e)
  - constitutes less than 20%

$$\frac{f_e}{f} = 1 - \frac{T}{f}\left(\frac{\partial f}{\partial T}\right)_{V,L} \qquad (3.21)$$

  - related to conformational energy change

$$\frac{f_e}{f} = T\left(\frac{\mathrm{d}(\ln\langle r^2\rangle_0}{\mathrm{d}T}\right) \qquad (3.23)$$

Table 3.1

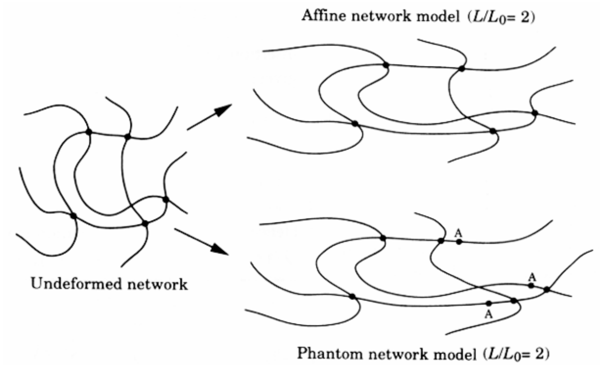


- ideal gas and ideal rubber
  - for ideal gas
    - $\partial E/\partial V = 0$
    - $P = T\partial S/\partial V$
  - for ‘ideal rubber’
    - $\partial E/\partial L$ ~ small
    - $f \approx T\partial S/\partial L$

- stretching in adiabatic condition
  - $dQ = TdS = -dW$ $(dE = 0)$
  - Stretching to $\lambda = 5$ adiabatically gives a temperature increase of 5 K.

Statistical mechanics theory

- assumptions 📖45
  - Gaussian (unperturbed) chains betw Xlinks
  - affine deformation (vs phantom network)
  - isotropic and incompressible
- entropy of a chain

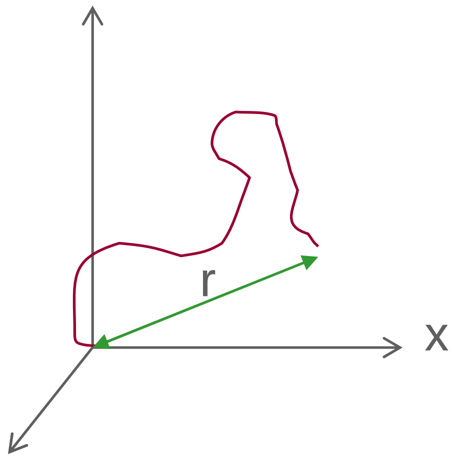


$$P(x, y, z)\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = \left(\frac{3}{2\pi\langle r^2\rangle_0}\right)^{3/2} \times \exp\left[-\frac{3(x^2+y^2+z^2)}{2\langle r^2\rangle_0}\right]\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \quad (3.24)$$

S = k ln P

$$S = k\ln(P(x, y, z)\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z) = k\left(\frac{3}{2}\ln\left(\frac{3}{2\pi\langle r^2\rangle_0}\right) - \left(\frac{3(x^2+y^2+z^2)}{2\langle r^2\rangle_0}\right) + \ln(\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z)\right) \quad (3.25)$$

$$S = C - k\frac{3r^2}{2\langle r^2\rangle_0} \quad (3.26)$$



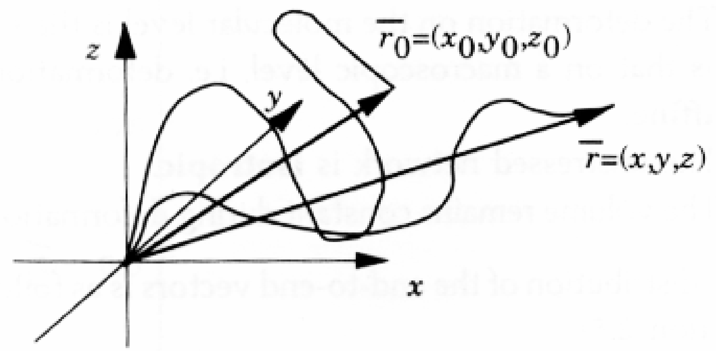
- entropy change upon deformation

extension ratio, $\lambda = L/L_0$

$$x = \lambda_1 x_0 \quad y = \lambda_2 y_0 \quad z = \lambda_3 z_0$$

$$S_0 = C - k\left(\frac{3(x_0^2 + y_0^2 + z_0^2)}{2\langle r^2\rangle_0}\right) \tag{3.27}$$

$$S = C - k\left(\frac{3(\lambda_1^2 x_0^2 + \lambda_2^2 y_0^2 + \lambda_3^2 z_0^2)}{2\langle r^2\rangle_0}\right) \tag{3.28}$$



$$\Delta S = S - S_0$$

$$= -3k\left(\frac{(\lambda_1^2 - 1)x_0^2 + (\lambda_2^2 - 1)y_0^2 + (\lambda_3^2 - 1)z_0^2}{2\langle r^2\rangle_0}\right) \tag{3.29}$$

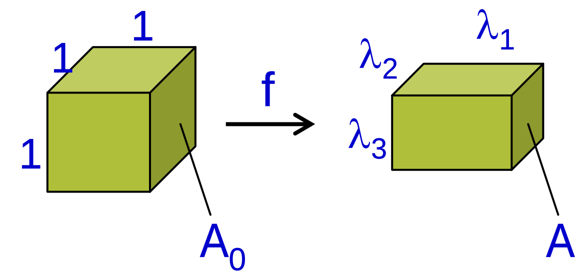
- For whole network with N chain segments

$$\Delta S_N = \sum_1^n \Delta S = -3k\left(\frac{(\lambda_1^2 - 1)\sum_1^n x_0^2 + (\lambda_2^2 - 1)\sum_1^n y_0^2 + (\lambda_3^2 - 1)\sum_1^n z_0^2}{2\langle r^2\rangle_0}\right) \tag{3.30}$$

$$\Delta S_N = -\tfrac{1}{2}nk(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

$$\Delta G = -T\Delta S_N = \tfrac{1}{2}nkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

- isotropic and incompressible deformation
  - $\lambda_1\lambda_2\lambda_3 = 1$
  - $\lambda_1 = \lambda \rightarrow \lambda_2 = \lambda_3 = 1/\lambda^{1/2}$
- force, f = dG/dL



$$f = \left(\frac{\partial(\Delta G)}{\partial L}\right)_{T,V} = \left(\frac{\partial(\Delta G)}{\partial \lambda}\right)_{T,V}\left(\frac{\partial \lambda}{\partial L}\right)_{T,V}$$

$$f = \frac{\partial}{\partial \lambda}\left(\tfrac{1}{2}\, nkT\left(\lambda^2 + \frac{2}{\lambda} - 3\right)\right)\frac{\partial}{\partial L}\left(\frac{L}{L_0}\right) = \frac{nkT}{L_0}\left(\lambda - \frac{1}{\lambda^2}\right)$$

true stress,

$\sigma = f/A = f/\ A_0\lambda_2\lambda_3 = f/\ A_0\lambda$

$$\sigma = \frac{NRT}{V_0}\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad (3.35)$$

$$\frac{N}{V_0} = \left(\frac{N\bar{M}_c}{V_0}\right)\left(\frac{1}{\bar{M}_c}\right) = \left(\frac{m_0}{V_0}\right)\left(\frac{1}{\bar{M}_c}\right) = \frac{\rho}{\bar{M}_c}$$

M_c ~ mol wt of one chain segment

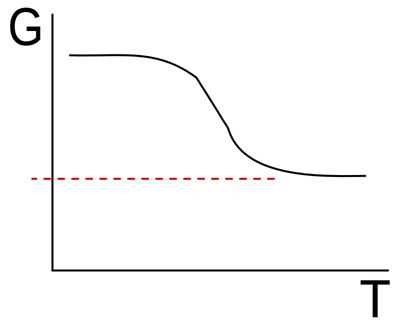
~ mol wt betw Xlinks

$$\boxed{\sigma = \frac{\rho RT}{\bar{M}_c}\left(\lambda^2 - \frac{1}{\lambda}\right)}$$

stat mechanical equation of state for rubber elasticity

modulus

- modulus, G = $\rho RT/M_c$
  - As Xlinking density ↑, M_c ↓, G ↑.
  - $G_N^0 = \rho RT/M_e$ for linear glassy polymers
    - M_e ~ entanglement mol wt



- phantom network model

$$\sigma = \left(1 - \frac{2}{\psi}\right)\frac{\psi \nu RT}{2}\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad (3.40)$$

    - ν ~ # of crosslinks, ψ ~ functionality of crosslink
  - When $\psi = 4$, $\sigma = ½\ \sigma$(affine deform'n model)
  - better accordance with SANS observations, which indicate less deformation than affine deformation.

Continuum mechanics approach

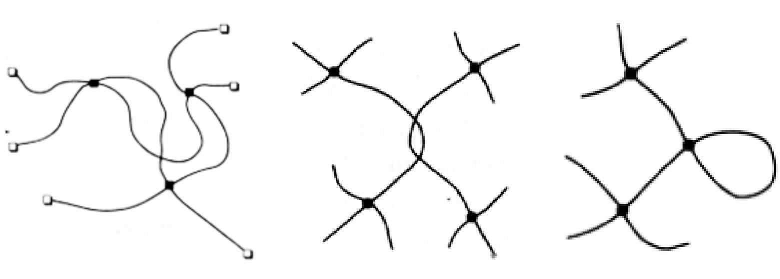
- application of linear elasticity to rubber elasticity
  - finite strain, e
  - $\lambda \approx 1 + 2e$

$$\sigma = 2\left(C_1 + \frac{C_2}{\lambda}\right)\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad (3.54)$$

Mooney-Rivlin Eqn

Deviation from theories

- network defects
  - chain ends, entanglements, loops
  - varies # of load-carrying chains



$$\sigma = \frac{\rho R T}{\bar{M}_c}\left(1 - \frac{2\bar{M}_c}{M}\right)\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad (3.51)$$

- At high λ, σ(exp't) is higher due to
  - non-Gaussian chain segments
    - stressed, extended, fewer conformations
  - strain-induced crystallization