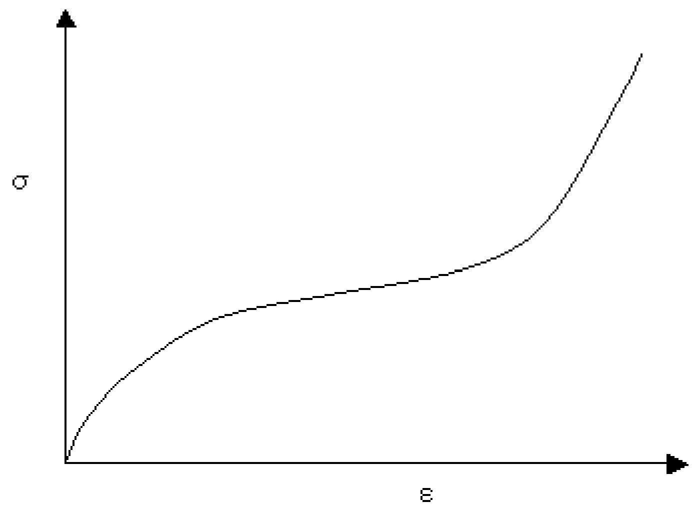
S-shaped Curves

S-shaped stress-strain curves occur in rubbery materials (lightly cross-linked polymers). Materials with S-shaped stress-strain curves are particularly susceptible to elastic instabilities, which are of interest in analysing phenomena such as aneurysms in arteries. The curves have the form:



An S-shaped stress-strain curve

The initial part of this curve, where the stiffness decreases with increasing load can be predicted theoretically, by considering the rubber as an entropy spring, (shown in detail in The Stiffness of Rubber TLP). This treatment assumes that all extension occurs via conformational changes (i.e. that there is no bond stretching) and also assumes that the chain is composed of a series of joined links which are equally likely to lie in any direction (the random walk assumption).

Using the random walk assumption, the probability distribution for the end-to-end length of a polymer chain with a certain number of links can be obtained, and the Boltzmann expression ($S = k \ln W$) can be used to determine the change in entropy on extending the chain and moving it to a less probable conformation. The total entropy change can be found by multiplying the result for one chain by the total number of chain segments N_t.

If we assume that the extension occurs without significant change in the enthalpy, pressure, volume or temperature, then the change in Gibbs free energy (⊗*G*) can be related to the entropy change (⊗*S*) via the equation $\Delta G \approx -T\Delta S$. If deformation occurs only in the *x* direction then the force required for deformation is

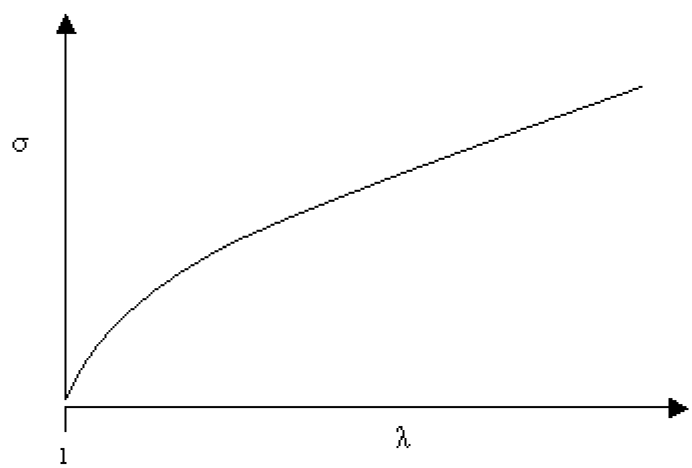
$$F = \frac{\partial \Delta G}{\partial x}$$

and an expression for the stress required for a given extension (with the rubber in uniaxial tension) can be obtained.

If *N* is the number of chain segments per unit volume and ⌊ is the extension ratio of the rubber, then the nominal stress for a rubber loaded in uniaxial tension is:

$$\sigma = kTN\left[\lambda - \frac{1}{\lambda^2}\right]$$

where *k* is the Boltzmann constant and *T* is the temperature.
This gives a stress strain curve of the form:



The theoretically predicted stress-extension curve for rubbery materials

Thus the theory predicts that the stiffness of rubber varies a little (particularly at low extensions), but that it tends to a limiting value at higher extensions. At lower extensions, the theoretical stress-extension curve is fairly similar to the S-shaped curves obtained experimentally. At extensions of $\lambda = 4$ the experimental and theoretical curves diverge, with much larger stiffness seen experimentally than predicted theoretically. This occurs because at larger extensions the assumptions of the model are no longer valid: the polymer chains are mostly aligned with the applied stress and so applying higher stress stretches strong intra-molecular bonds.

Source:http://www.doitpoms.ac.uk/tlplib/bioelasticity/s-shaped-curves.php