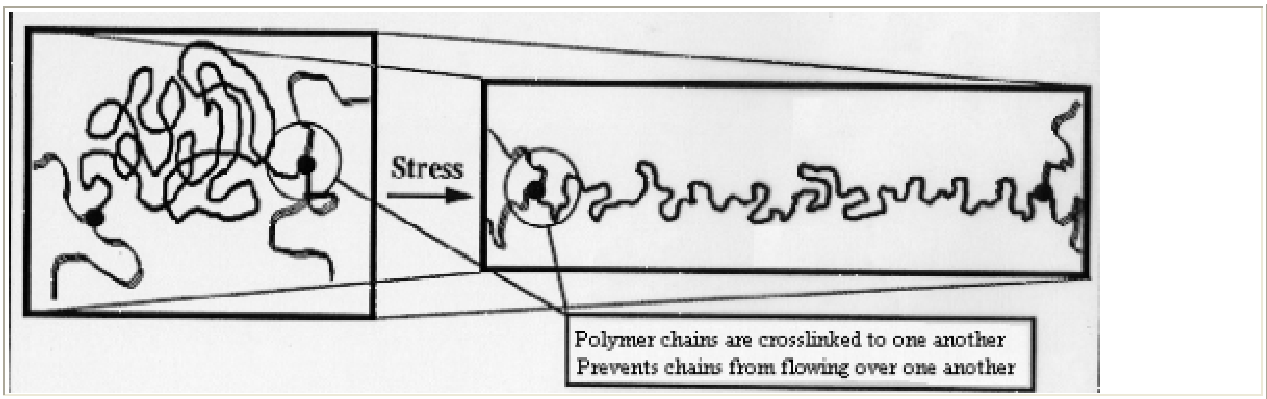
3.11 Recitation #9
November 4, 2003

Rubber Elasticity

The Entropic Spring

More Disorder → **Less Disorder**

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



Rubber bands are made from polymers, but the chains are crosslinked to provide a network.

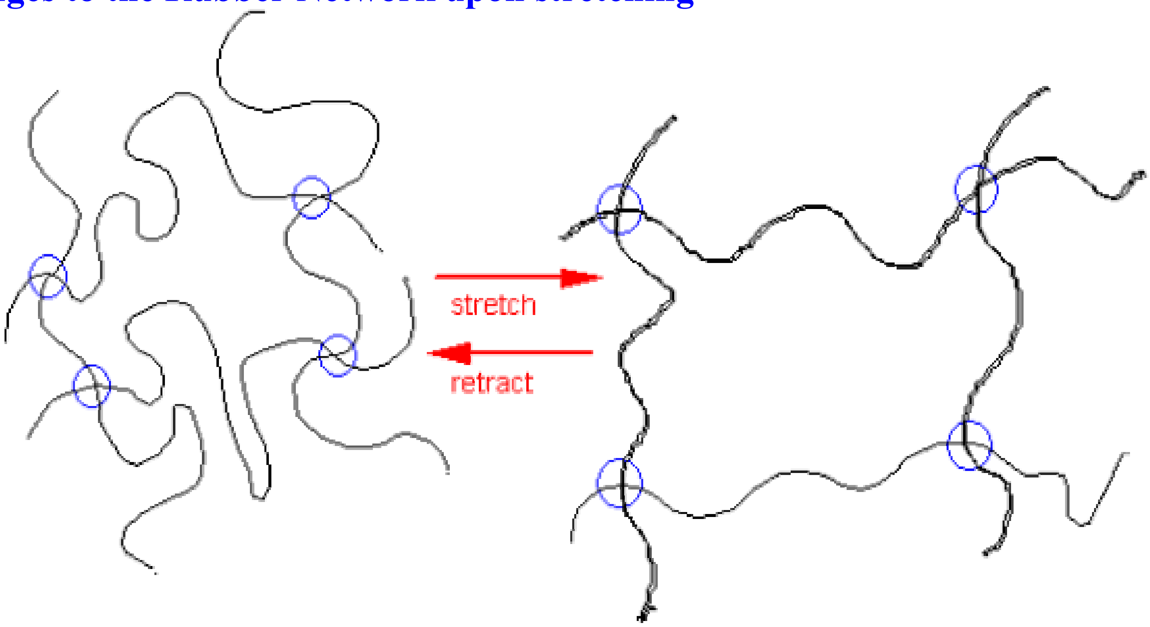
The amorphous phase in PE is also said to be rubbery – it is above its T_g but is constrained by the surrounding crystals and so cannot be said to be liquid-like.

For the rubber bands, it is the crosslinks which determine the properties.

The crosslinks provide a 'memory'.

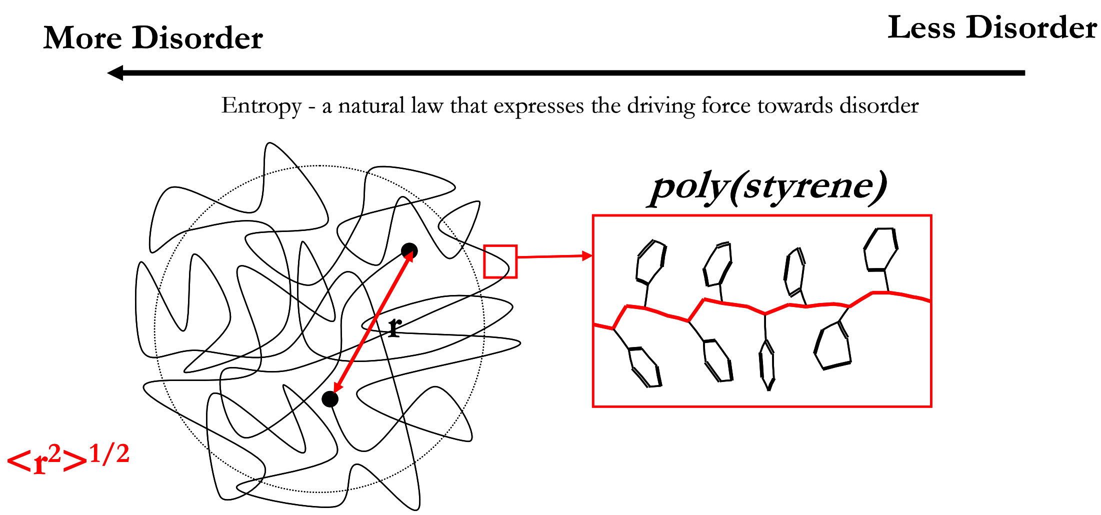
When the network is stretched, entropic forces come into play which favour retraction, returning the network to its original unstretched/equilibrium state.

Changes to the Rubber Network upon stretching



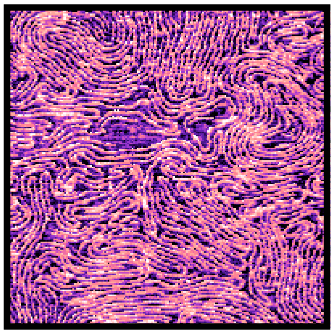
Loss of entropy upon stretching, means that there is a retractive force for recovery when external stress removed.

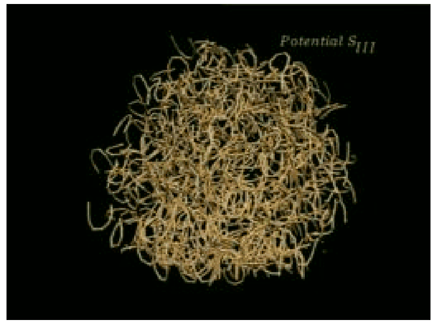
This is why a rubber band returns to its original shape.



Random Coil Configurations of Polymers:

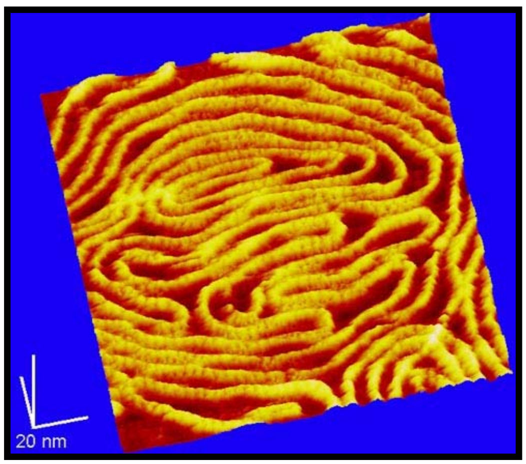
DNA **simulation**





*(*FEBS Lett. 371:279-282)*

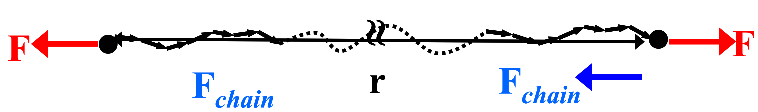
DNA



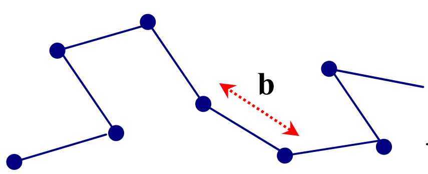
*(*Z. Shao, http://www.people.Virginia.EDU/~js6s/zsfig/figureindex.html)*

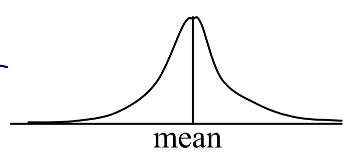
Let's look at Freely Jointed Chain Model

consider stretching a single random coil polymer chain :



Polymer Chain : Random walk in space. (Gaussian)





Can be thought of as a freely jointed chain. Joint length is **b**. An independently oriented segment. It is NOT usually a monomer length, usually 4 or 5 monomers long.

A simple reminder of polymer statistics.

Suppose the walk has N links:
End to end distance R(N)

From Rubber elasticity :
r = instantaneous chain end-to-end separation distance
(Draw on board--- squiggly lines with beginning and end separated by r)
$\langle r^2 \rangle = na^2$ root mean square end to end distance
a = statistical segment length—local chain stiffness
n = # of a's
Lc = contour length—length of fully extended chain.

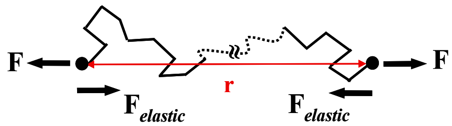
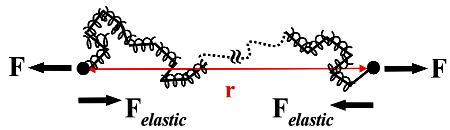
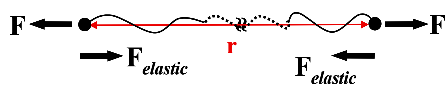
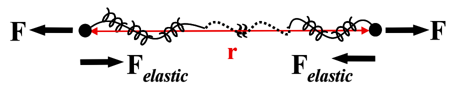
Probability of finding a free chain end a radial distance, r, away from a fixed chain end (origin) ~ omega = P(R) = $(4b^3r^2)$/sqrt(pi)*exp($-b^2r^2$)
where b = sqrt $(3/(2na^2))$

This is Gaussian form
Macrostate is defined by the length r.
Microstates are the different random walks. So..
$P(R) \sim e^{-3R^2/2Nb^2} \sim \Omega(R)$ (# of μstates with length R) (N=n and b=a)
Configurational Entropy (measure of disorder) = S = kb*ln[P(r)]
Helmholtz Free Energy = A or H = -Tkb*ln[P(r)]
Entropic elastic force, linear elasticity (hookean spring) f or F = -dA(r)/dr^2
Entropic chain stiffness = k = dF(r)/dr or second derivative of A.

➔a random walking polymer at finite T is a Hookean spring

Why is this useful?
Because these equations define the stretching of a single polymer chain.

The following chart defines several types of Elasticity Models for Single Polymer Chains—you may need to describe the difference between a couple of these on your problem set.

MODEL	**SCHEMATIC**	**FORMULAS**
Freely-Jointed Chain (FJC) (Kuhn and Grün, 1942 James and Guth, 1943)	 **(a,** n)	**Gaussian :** $F_{elastic} = [3k_BT/L_{contour}a]\,r$ **Non-Gaussian :** $F_{elastic} = (k_BT/a)\,L^*(r/L_{contour})$ *low stretches* : Gaussian, L*(x)= "inverse Langevin function"= $3x+(9/5)x^3+(297/175)x^5+(1539/875)x^7+\ldots$ *high stretches* **:** $F_{elastic}=(k_BT/a)(1-r/L_{contour})^{-1}$
Extensible Freely-Jointed Chain (Smith, et. al, 1996)	 **(a,** n, $k_{segment}$)	**Non-Gaussian :** $F_{elastic} = (k_BT/a)\,L^*(r/L_{total})$ where : $L_{total} = L_{contour} + nF_{elastic}/k_{segment}$
Worm-Like Chain (WLC) (Kratky and Porod, 1943 Fixman and Kovac, 1973 Bustamante, et. al 1994)	 **(p,** n)	**Exact** : *Numerical solution* **Interpolation Formula** : $F_{elastic} = (k_BT/p)[1/4(1-r/L_{contour})^{-2}-1/4+r/L_{contour}]$ low stretches : Gaussian, $F_{elastic} = [3k_BT/2pL_{contour}]\,r$ high stretches **:** $F_{elastic} = (k_BT/4p)(1-r/L_{contour})^{-2}$
Extensible Worm-Like Chain (Odijk, 1995)	 **(p,** n, $k_{segment}$)	**Interpolation Formula** : $F_{elastic} = (k_BT/p)[1/4(1-r/L_{total})^{-2} - 1/4 + r/L_{total}]$ low stretches : Gaussian high stretches : $r = L_{contour}[1-0.5(k_BT/F_{elastic}p)^{1/2} + F_{elastic}/k_{segment}]$

Freely Jointed Chain Equations:

Gaussian :
F*elastic* = [3kBT /L*contour***a**] **r**
Non-Gaussian :
F*elastic*= (kBT/**a**) *L**(**r**/L*contour*)
low stretches : Gaussian, L*(x)= "inverse Langevin function"=
3x+(9/5)x^3+(297/175)x^5+(1539/875)x^7+...
high stretches **: F*elastic***=(kBT/**a**)**(1-r**/L*contour*)-1

Worm-like chain Equations:
Exact : *Numerical solution*
Interpolation Formula :
F*elastic* = (kBT/**p**)[1/4(1-**r**/L*contour*)-2-1/4+**r**/L*contour*]
low stretches : Gaussian, **F*elastic*** = [3kBT /2pL*contour*] **r**
high stretches **: F*elastic*** = **(**kBT/4**p)(1-r**/L*contour*)-2

Example Problem:

In an atomic force microscopy experiment, a force is applied to a DNA strand with $L_{contour}$ = 100nm, to induce a low stretch. Determine the persistence length if the global stiffness of the chain is 1.23 μN/m. (HINT: Which elasticity model is often used to model DNA?) Assume experiment is conducted at room temperature = 20°C.

DNA is often modeled using the Worm-Like Chain model. For the extensible or inextensible Worm-Like Chain model, the low stretch regime follow a Gaussian equation:

$$F_{elastic} = [3k_bT/2pL_{contour}]r$$

This equation resembles that for a Hookean linear elastic spring with spring constant of $[3k_bT/2pL_{contour}]$ which can be considered the global stiffness of the chain. Thus,

$$1.23\mu N = 3(1.38106e\text{-}23\ J/K)(293K) / 2p(100nm)$$

Solving for p, persistence length: p = 49.2nm

If extra time, I will talk a bit about the stress vs. strain equations for Gaussian constant volume deformation (discussed Monday in class).