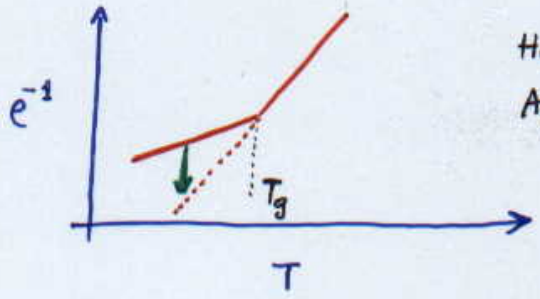
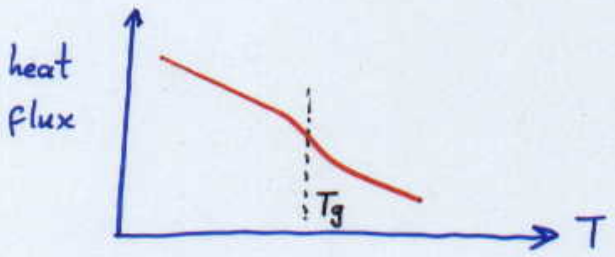
GLASS

- Amorphous SOLID
- Local motions : free volume, cooperativity
- Non-equilibrium - Ageing

- Low temperatures, high frequencies

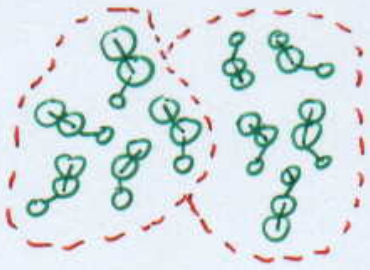


Heating/Cooling rate dependence
Ageing



"Soft metals" : $G_0 \sim 10^8$ Pa (or higher)

Cooperativity : $P \sim \exp\left(-\frac{z\,\Delta E}{kT}\right)$ $z \simeq 5\text{-}10$ conformers

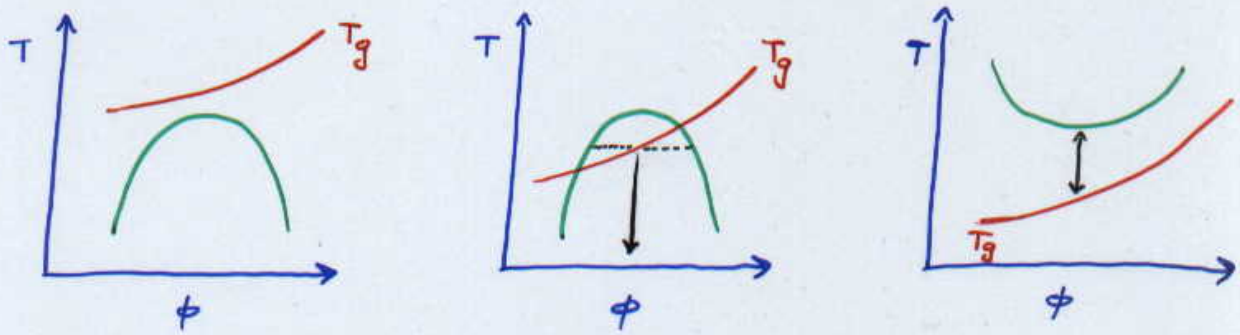


Glass transition is NOT a thermodynamic transition

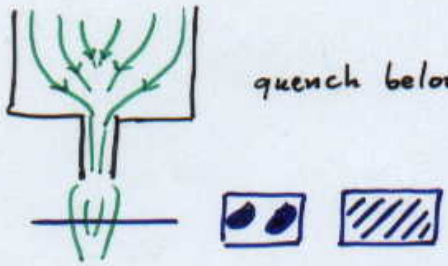
Liquid-like order (amorphous) is FROZEN

$T < T_g$: Solid $T > T_g$: Liquid or solid

Practical Aspects BLENDS A/B



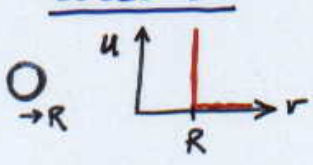
Fox-Flory: $\frac{1}{T_g} = \frac{\phi_A}{T_{gA}} + \frac{1-\phi_A}{T_{gB}}$



quench below T_g

PS: 50-110°C

COLLOIDS



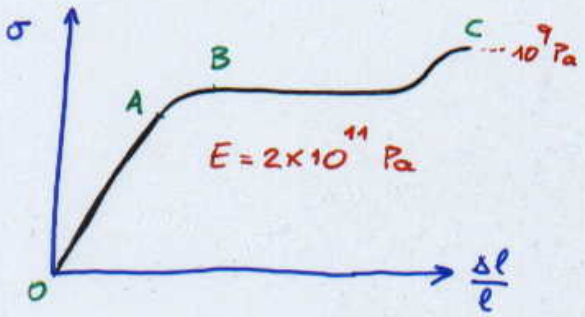
"GAS" LIQUID CRYSTAL GLASS (GEL)

CAN ACHIEVE MUCH LOWER G_0

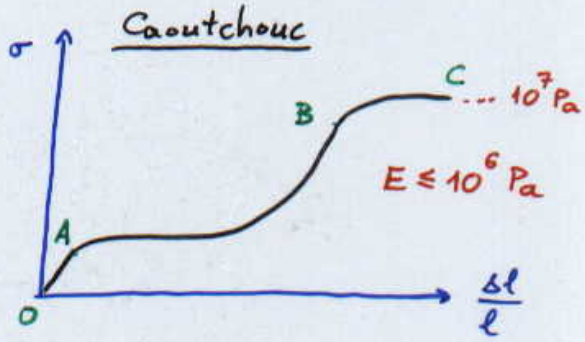
RUBBER

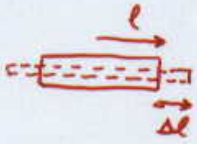
{ SOLID (permanent or temporary)
{ Network

Steel



Caoutchouc





$$\sigma = \frac{F}{A} = E \frac{\Delta l}{l}$$

{ OA Linear reversible
{ AB Non linear reversible
{ BC Irreversible - flow
{ C Catastrophic failure

Single chain — Gaussian

$$P(R) \sim \exp\left[\frac{-3R^2}{2Nl^2}\right]$$

$$F = \frac{3kT}{Nl^2} R$$

$$U = -TS \qquad S = k \ln P \qquad f = \frac{\Delta U}{\Delta R}$$

$$G = \frac{3kT}{Nl^2}$$

Entropic origin

Vulcanization : Rubber

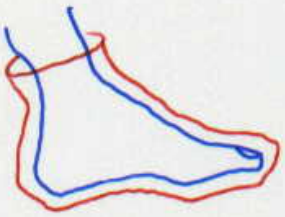
→ stretch

$$\sigma = 3kT_v \frac{\Delta l}{l}$$

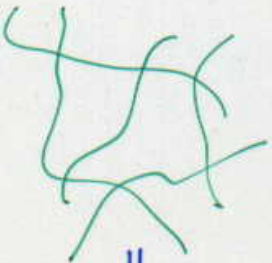
$$E = 3kT_v$$

The Indian boot

South American Indians
~ 2500 yrs ago

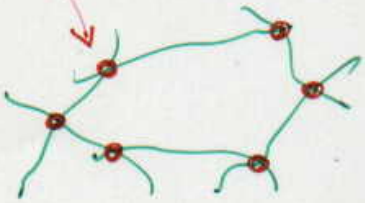


Hevea tree
↓ milky juice (syrop)
↓ Latex
(~coagulation)



Latex (liquid)

oxygen



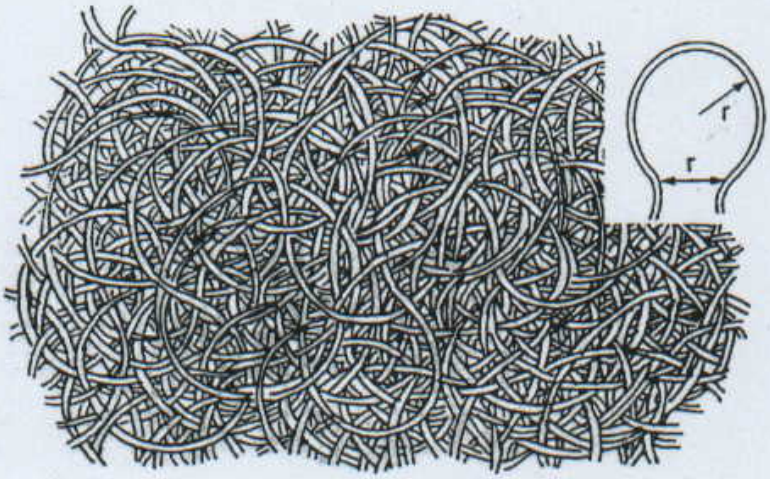
Solid (gel)

Goodyear (1839) Natural Rubber (sulfur – hevea tree)

SOFT MATTER ⇒ { WEAK EXTERNAL ACTION
CAUSES
HUGE TRANSFORMATIONS OF MATTER

MELT

- Liquid
- Large scale motion
- Physical: temporary network
- Entanglements



Coopevativity: $P \sim \exp\left[-\frac{z\Delta E}{kT}\right]$ $\quad z = O(10^3)$

High temperatures $T > T_g$ liquid ; Low frequencies $T = T_g + 50\text{-}100^\circ C$

Equilibrium (annealing)

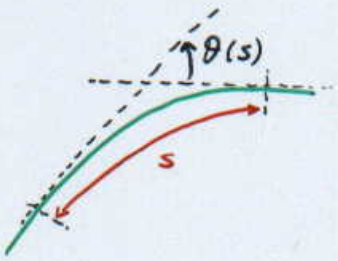
Size matters: MW effects

Determine VISCOSITY, self-diffusion.

Flexibility, Entanglements

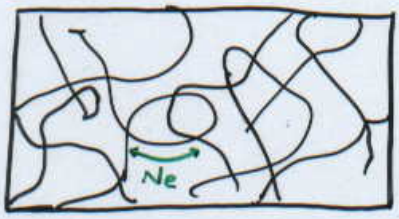
TUBE MODEL - Reptation (de Gennes, Doi-Edwards)

Flexibility : Persistent length



$$\langle \cos\theta(s) \rangle = \exp\left[-\frac{s}{\ell}\right]$$

Entanglements : Network Ne typically 50-500



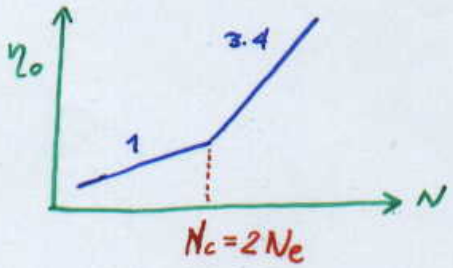
$N < N_e$ unentangled chains

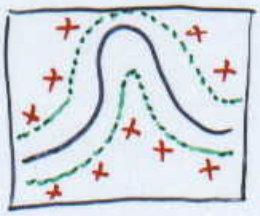
$\eta_0 \sim N$

$N > N_e$ temporary physical network (rubber-like)

$G_0 \sim \frac{1}{N_e}$

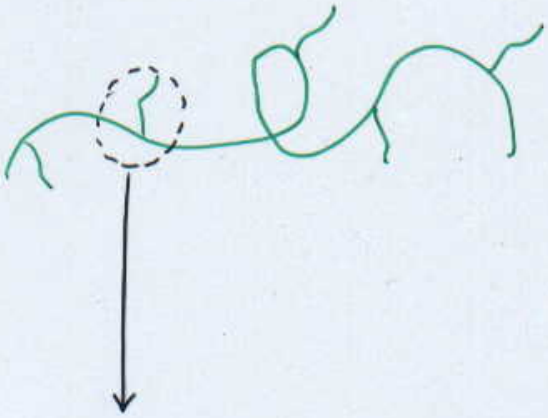
$\eta_0 \sim N^{3.4}$



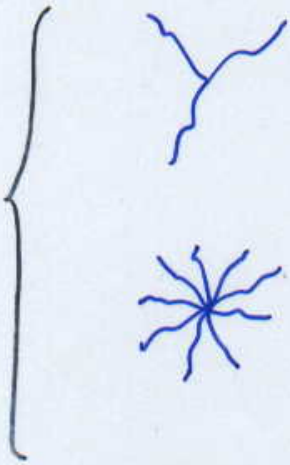


Tube concept- Reptation

Practical Aspects: POLYETHYLENE



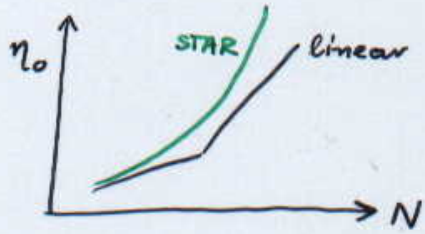
Branching effects



STAR POLYMERS

Arm relaxation – Tube fluctuations

$\eta_o \sim \exp\left[\frac{N}{N_e}\right]$ independent of arm number!



MACROMOLECULAR ARCHITECTURE

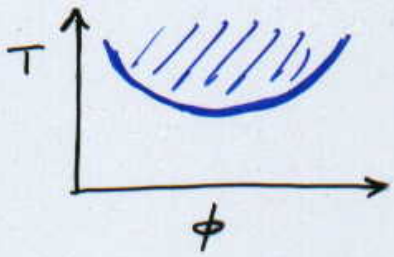
H-shaped

combs

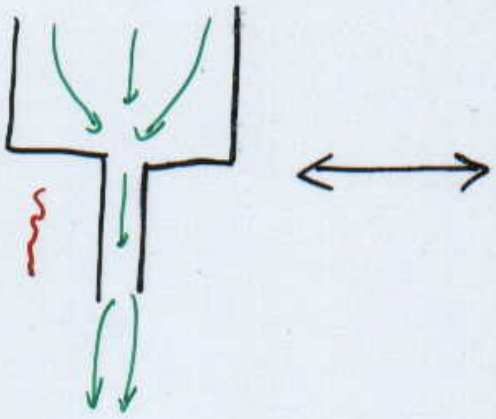
pom-pom

Application: Processing

Question: POLYMER BLEND UNDER SHEAR
MIXING or DEMIXING ?



SMA/PMMA (DSM / ICI)



$\nabla u \sim 10^{2} - 10^{4}\ s^{-1}$

$\nabla u \sim 10^{0} - 10^{2}\ s^{-1}$

State of the Art — Han (NIST); Higgins (Imperial); Weiss (UConn); Hashimoto (Kyoto) Mewis (KU Leuven)

Challenge — Binary blend; Small ΔT_g; High ∇u