Week 5 Lecture

Viscosity, viscoelasticity, gelation

Viscosity

Demo: Ice melts to become water--Water flows

Demo: A cube of gelatin gel deforms under shear

What happens if you warm the gel-can you still push it?

Liquid cannot sustain a shear—it flows when sheared

Resistance to flow depends on viscosity

Viscosity of oil

Oil is more viscous than water
Demo: Takes a longer time to flow through funnel

Demo—you did this in the lab :
Drop a ball bearing or chickpea in a tube
filled with water, oil, and honey
Which liquid does the ball fall slowest, fastest?
Rank the time of fall in increasing order

Viscosity

A material is a liquid if the molecules can move around each other.

The fundamental quantity that governs this is the *time* that it takes for molecules to move around their neighbors.

If it takes a long time for them to move by each other, the material is very viscous.

If it takes a short time, the material is less viscous.

Molecular viscosity

$$\nu = \underset{\nwarrow \text{ Size of molecule}}{l} \times \underset{\nearrow \text{ Velocity of molecule}}{c}$$

Molecular viscosity

Scientists typically use two measures of viscosity:

$$\nu = l \times c$$ kinematic viscosity

$$\eta = \rho \nu$$ Dynamic viscosity

For lay people, the best measure of viscosity is the time it takes something to flow.

Of course, these three concepts (kinematic and dynamic viscosity, and flow time) are related.

Molecular viscosity

length^2/time $\nu = l \times c$ length^2/time

length length/time

$$\text{molecular viscosity: } \nu = l \times c$$

$$\text{Recall: elasticity: } E = \frac{k_B T}{l^3}$$

Origin of viscosity of water

Dimensional analysis gives a relation between E and η

$$\eta = E \times \tau$$

Viscosity = Elasticity times a relaxation time

All fluids are solids at short enough times

Times depend on the fluid

Short-time elasticity of a liquid

http://www.youtube.com/watch?v=f2XQ97XHjVw

Origin of viscosity of water

$\eta = E \times \tau$ Dynamic viscosity

$\eta = \rho \times \nu$ kinematic viscosity

Just different measures of viscosity

Relaxation time for water

Question: What is the time that molecules move by each other?

Answer:

$$\tau = \frac{l}{c}$$

l = molecular size = 5 Angstroms
c = 1500 meters/second (room Temperature)

$$\tau = \frac{5 \times 10^{-8}\text{cm}}{150000 \text{ cm/sec}} \approx 3 \times 10^{-13}\text{sec}$$

Relaxation time for water

Compare this to

$$\tau = \frac{\rho \nu}{E}$$

E = kT/ l^3 = 2.5 x 10^{10} g /(cm. sec^2)
ρ = 1 g/cm^3
ν = 0.01 cm^2/ sec

$$\tau = \frac{0.01}{2.5 \times 10^{10}} \approx 4 \times 10^{-13}\text{sec}$$

Viscosity of hot oil

Hot oil flows faster than cold oil
Viscosity decreases with increasing temperature
Molecules move around each other more easily

$$\eta = E \times \tau$$

$$\tau = \tau_0 \exp\left(U/kT\right)$$

$$\eta = E \times \tau_0 \exp\left(U/kT\right)$$

U : same interaction energy as in week 1

Demo— sugar candy

Sugar syrup thickens –i.e. gets more viscous on heating– Why?

Name	Temp	Description	Usage
Thread	223-235* F	The syrup drips from a spoon, forms thin threads in water	Glacé and candied fruits
Soft ball	235-245* F	The syrup easily forms a ball while in the cold water, but flattens once removed	Fudge and fondant
Firm ball	245-250* F	The syrup is formed into a stable ball, but loses its round shape once pressed	Caramel candies
Hard ball	250-266* F	The syrup holds its ball shape, but remains sticky	Divinity and marshmallows
Soft crack	270-290* F	The syrup will form firm but pliable threads	Nougat and taffy.
Hard crack	300-310* F	The syrup will crack if you try to mold it	Brittles and lollipops
Caramel	320-350* F	The sugar syrup will turn golden at this stage	Pralines

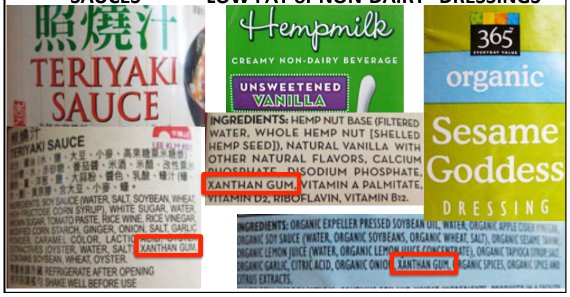
Thickeners—viscosity depends on concentration

- Very small amount of material increases viscosity a lot—example adding flour to a cream sauce or to a gravy
  - Related to thickeners being polymers and gelation

Xanthan Gum makes liquids thicker

- **Xanthan Gum (E415)**: makes food thick and creamy; also stabilizes foods to help solids and liquids stay together

SAUCES **LOW FAT or NON-DAIRY** **DRESSINGS**



Polymers and Gelation

Equations: $E = \frac{k_B T}{l^3}$ $\eta = E \times \tau$

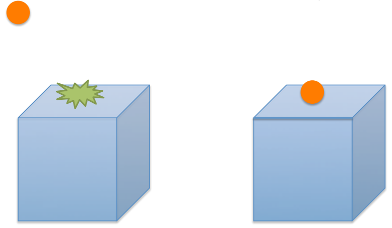
Key concepts:
Viscoelasticity and time-dependence
Elasticity of polymer gels
Viscosity of polymer solutions

Viscoelastic gels

Example: olive oil with gelatin

Viscoelasticity of corn starch (or silly putty)

How does time scale affect viscoelasticity?

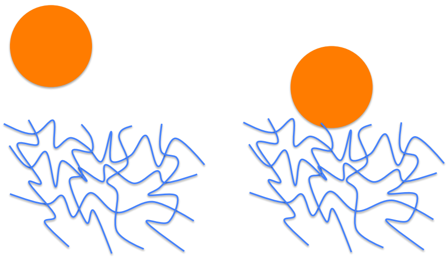


Short time: elastic

Long time: viscous

Viscoelasticity of corn starch

How does time scale affect viscoelasticity?

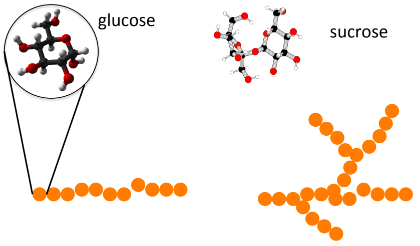


Short time: elastic

Long time: viscous

Food polymers: starches

Chains of polysaccharides



Food polymers: carbohydrates

Sugars, starches, pectin and gums

Wheat

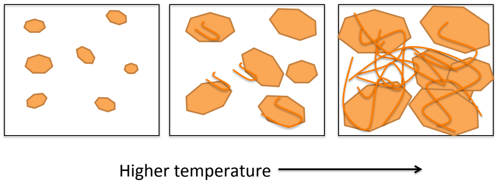
75% starch
10% proteins

Potatoes

mostly long chain amylose molecules

Starch-thickened sauces

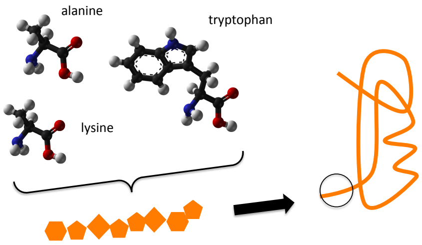
Granules swell and leak polymers



Examples: roux, gravy

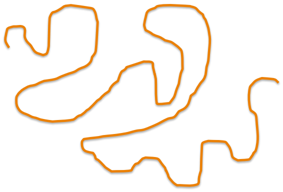
Food polymers: proteins

Proteins are chains of amino acids



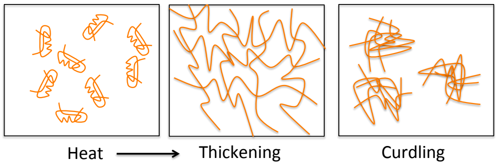
Food polymers: hydrocolloids

Xanthan gum, guar gum, locust bean gum



Protein-thickened sauces

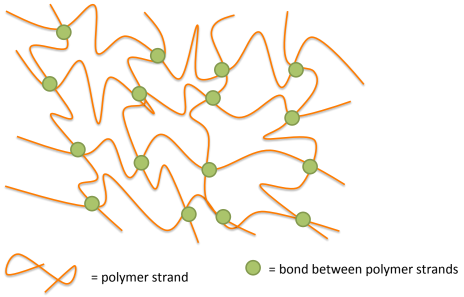
Heat denatures the proteins, which then entangle



Examples: meat stock, sabayon, hollandaise

Polymers can cross-link to form a gel

Methods: entanglement or ions



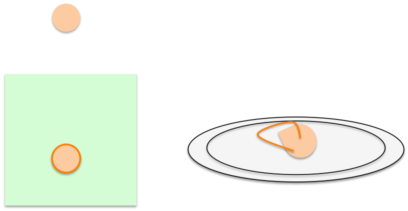
Spherification: an example of gelation

Green pea ravioli / el Bulli and Alícia Foundation

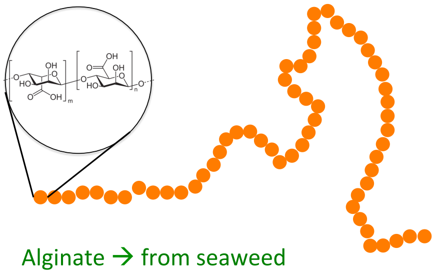
Spherification—Mango spherification / Alícia Foundation

Spherification: an example of gelation

Form thin layer of gel around droplet
Crosslinks are ionic



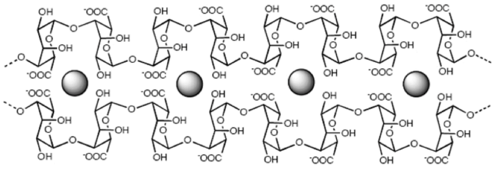
Alginate is a polysaccharide



Alginate → from seaweed

Example of gelation

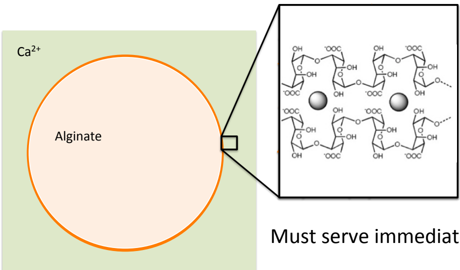
Calcium ions join together separate alginate strands



$Ca^{2+} + 2Alg^{-} \rightarrow CaAlg_2$

Spherification: Direct

Alginate drop forms gels with Ca^{2+} in solution

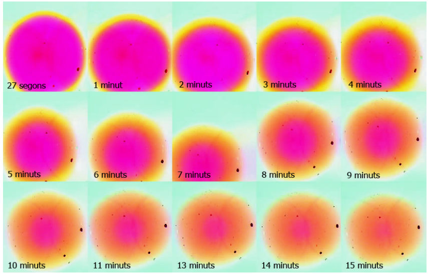


Must serve immediately

These can *not* be stored

Internal view of spherification

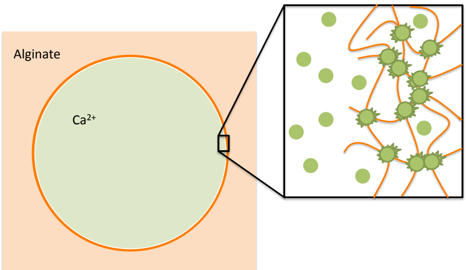
Shell thickens with time in the Ca^{2+} bath



(F. Sapiña y E. Martinez, Universitat de València)

Spherification: Inverse

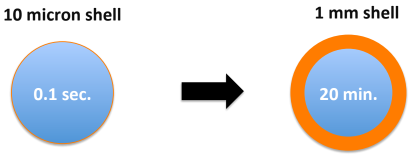
Ca^{2+} solution forms gels with aqueous alginate



These *can* be stored

Time scale for spherification

Diffusion of Ca^{2+} ions in water: $D = 7 \times 10^{-10}$ m²/sec

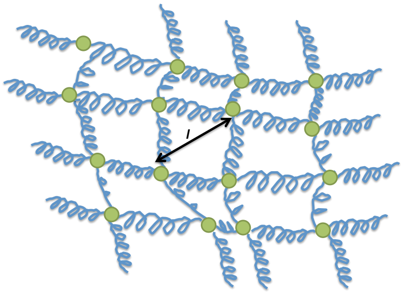


$$t = \frac{L^2}{D} = \frac{(10\times10^{-6}\,\mathrm{m})^2}{7\times10^{-10}\,\mathrm{m}^2/\mathrm{s}}$$
$$t = 0.1\,\mathrm{sec}$$

$$t = \frac{L^2}{D} = \frac{(10^{-3}\,\mathrm{m})^2}{7\times10^{-10}\,\mathrm{m}^2/\mathrm{s}}$$
$$t = 1000\,\mathrm{sec} = 20\,\mathrm{min}$$

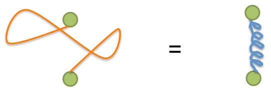
Polymers can cross-link to form a gel

Between cross-links, polymers behave like springs



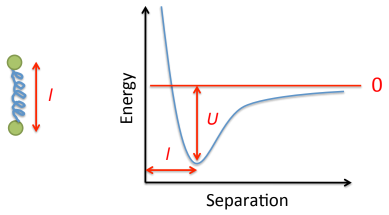
Elasticity of polymers

Polymers have a natural cross-link spacing
Polymer with N monomers
Has an equilibrium length ~ N $^{1/2}$



Elasticity of polymers

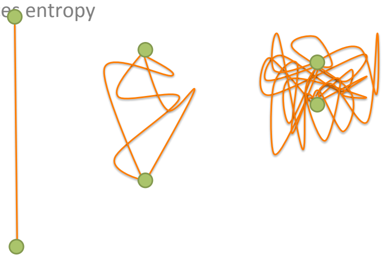
Polymers have a natural cross-link spacing



$U \approx k_B T$ for a gel

Elasticity related to Entropy of polymers

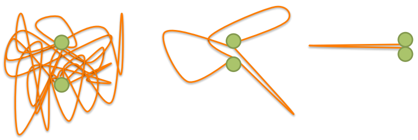
Stretching polymers reduces the number of states, reduces entropy



More states,
Higher entropy →

Entropy of polymers

Compressing polymers also reduces number of states, and entropy



Fewer states,
Lower entropy →

Equation of the week

Elasticity of a gel depends on cross-link spacing

$$E = \frac{k_B T}{l^3}$$

E = elasticity [Pa]
k_B = Boltzmann constant [J/K]
T = temperature [K]
l = mesh spacing [m]

Equation of the week

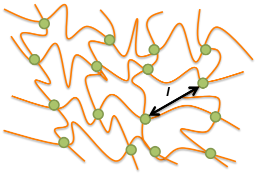
Elasticity of a gel depends on cross-link spacing

$$E = \frac{k_B T}{l^3} \qquad [E] = \frac{\mathrm{J}}{\mathrm{m}^3}$$

E = elasticity [Pa]
k_B = Boltzmann constant [J/K]
T = temperature [K]
l = mesh spacing [m]

Mesh size

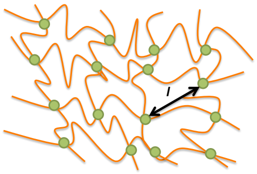
Calculate the spacing between cross-links



$$l^3 = \frac{k_B T}{E}$$

Mesh size

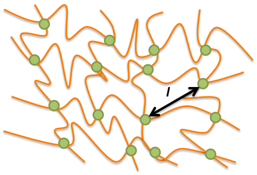
Calculate the spacing between cross-links



$$l^3 = \frac{k_B T}{E}$$

Mesh size

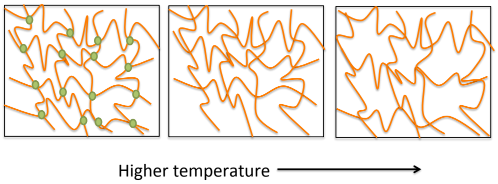
Calculate the spacing between cross-links



$$\begin{aligned} l^3 &= \frac{k_B T}{E} \\ &= \frac{4.2\times10^{-21} J}{20\mathrm{kPa}} \\ &= 2.1\times10^{-25}\,\mathrm{m}^3 \\ l &= \sqrt[3]{2.1\times10^{-25}\,\mathrm{m}^3} \\ &= 6\times10^{-9}\,\mathrm{m} \\ &= 6\ \mathrm{nm} \end{aligned}$$

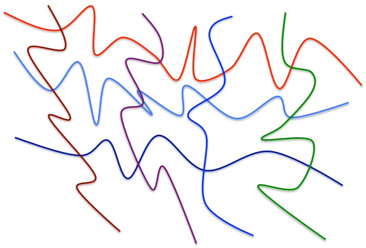
Melting of gels

The cross-links in gelatin detach at high temperatures



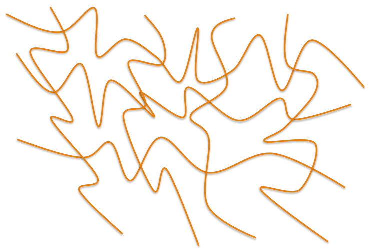
Viscoelasticity of polymers

Degree of entanglement determines the behavior



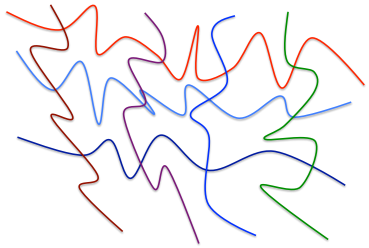
Viscoelasticity of polymers

Lose identity of individual polymers when entangled



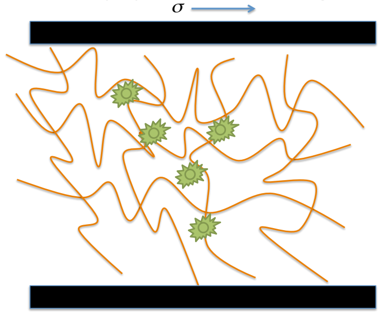
Viscoelasticity of polymers

Degree of entanglement determines the behavior



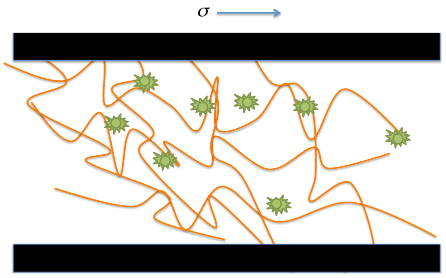
Entanglement is like elasticity

At short times, polymers can't disentangle



Elasticity of Polymers

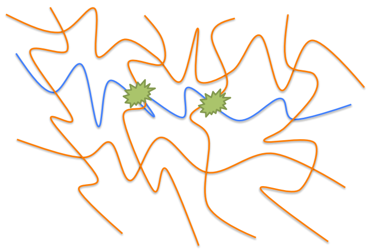
Polymers are constrained under sudden shear



This controls the elasticity, E.

Relaxation time

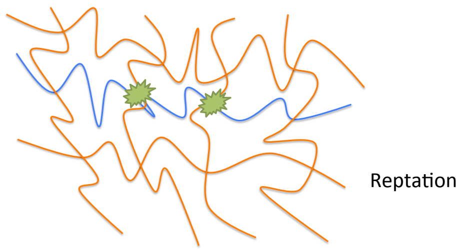
Polymers can slowly untangle → reptation



This controls the time constant, τ.

Relaxation time

Polymers can slowly untangle



This controls the time constant, τ.

Equation of the week

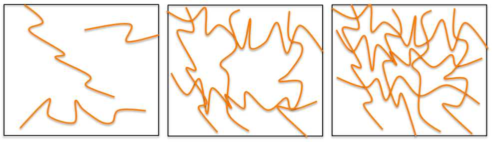
Viscosity is related to elasticity by a time-scale

$$\eta = E \times \tau$$

η= viscosity [Pa s]
E = elasticity [Pa]
τ = time-constant [s]

Concentration Dependence

Polymers become entangled at high densities



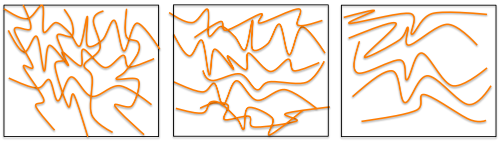
Higher concentration ⟶

This sets the elasticity, *E*, and the relaxation time, τ.

Shorter polymers don't entangle as much → lower η

Shear-rate Dependence

Polymers can disentangle at high shear rates



Higher shear ⟶

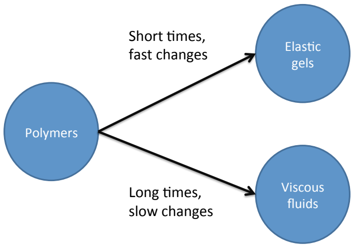
Shear thinning

Example: ketchup

Animation courtesy
Naveen Sinha

Viscoelasticity in mouthfeel

Elasticity and viscosity determine texture



Equation of the week

Sample calculation for honey

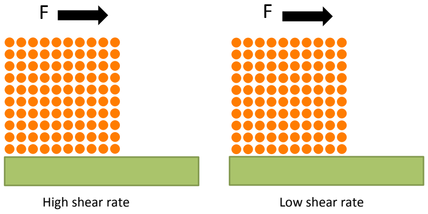
$$\eta = E \times \tau$$

$$\tau = \frac{\eta}{E} = \frac{10^3\,\mathrm{Pa \cdot s}}{2 \times 10^3\,\mathrm{Pa}}$$

$$\tau = 0.5\mathrm{s}$$

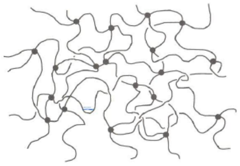
Shear rate

The rate of deformation sets the time scale.



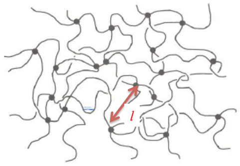
Stress determined by viscous component
For a liquid, viscosity = stress/ shear rate

Solid gel



Thickener is a polymer
Polymer forms network in the water
This forms the solid gel

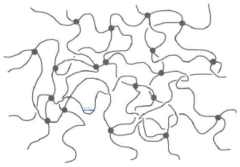
Solid gel



Thickener is a polymer
Polymer forms network in the water
This forms the solid gel

$$l^3 = \frac{kT}{E}$$
$$= \frac{4.2\times10^{-21}}{1000}$$
$$= 4.2\times10^{-24}$$
$$l = \sqrt[1/3]{4.2\times10^{-24}}$$
$$= 1.6\times10^{-8}\,\text{meters}$$
$$= 16 \;\; \text{nanometers}$$

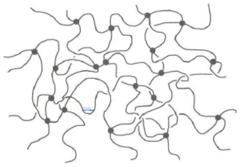
Viscosity of thickeners



The bonds are not permanent
Molecules can move
Molecules must disentangle to move

Spaghetti demo

Viscosity of thickeners

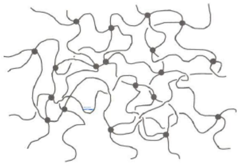


$$\eta = E\times\tau$$

$$E = \frac{k_B T}{l^3} \qquad \tau = \tau_0 \frac{L^2}{l^2}$$

Viscosity of thickeners

$$\eta = E\times\tau$$



$$E = \frac{k_B T}{l^3} \qquad \tau = \tau_0 \frac{L^2}{l^2}$$

$$\eta = kT\tau_0 \frac{1}{l^5} \sim C^{5/3}$$

Very strong concentration dependence