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
\[ \nu = l \times c \]
Size of molecule Velocity of molecule

Molecular viscosity
Scientists typically use two measures of viscosity:
\[ \eta = \rho \nu \]
Molecular viscosity
kinematic viscosity
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

\[ \nu = l \times c \]

Recall: elasticity \( E = \frac{k_B T}{l^3} \)

Origin of viscosity of water

Dimensional analysis gives a relation between \( E \) and \( \eta \)

\[ \eta = E \times \tau \]

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)

\[ \tau = \frac{5 \times 10^{-7} \text{ cm}}{150000 \text{ cm/sec}} = 3 \times 10^{-13} \text{ sec} \]

Relaxation time for water

Compare this to

\[ \tau = \frac{\rho \nu}{E} \]

\( E = kT/l^3 = 2.5 \times 10^{10} \text{ g/(cm. sec}^2) \)
\( \rho = 1 \text{ g/cm}^3 \)
\( \nu = 0.01 \text{ cm}^2/\text{ sec} \)

\[ \tau = \frac{0.01}{2.5 \times 10^{10}} = 4 \times 10^{-13} \text{ sec} \]
**Viscosity of hot oil**

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

\[ \eta = E \times \tau \]
\[ \tau = \tau_0 \exp \left( \frac{U}{kT} \right) \]
\[ \eta = E \times \tau_0 \exp \left( \frac{U}{kT} \right) \]

*U*: same interaction energy as in week 1

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**Demo— sugar candy**

Sugar syrup thickens — i.e., gets more viscous on heating: Why?

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**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.

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**Xanthan Gum makes liquids thicker**

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

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**Polymers and Gelation**

Equations:

\[ E = \frac{kT}{\tau} \]
\[ \eta = E \times \tau \]

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

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**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

Food polymers: starches
Chains of polysaccharides

Food polymers: carbohydrates
Sugars, starches, pectin and gums

Wheat
Potatoes
75% starch
10% proteins
mostly long chain amyllose molecules

Starch-thickened sauces
Granules swell and leak polymers

Higher temperature
Examples: roux, gravy

Food polymers: proteins
Proteins are chains of amino acids

alanine
lysine
tryptophan
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 Alicia Foundation

Spherification—Mango spherification / Alicia 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 → 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: $D = 7 \times 10^{-10}$ m^2/sec

$t = \frac{L^2}{D} = \frac{(10 \times 10^{-4} \text{ m})^2}{7 \times 10^{-10} \text{ m}^2/\text{s}}$
$t = 0.1 \text{ sec}$

$D = 7 \times 10^{-10}$ m^2/\text{s}
$t = \frac{L^2}{D} = \frac{(10^{-9} \text{ m})^2}{7 \times 10^{-10} \text{ m}^2/\text{s}}$
$t = 1000 \text{ sec} = 20 \text{ min}$
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 $\sim N^{1/2}$

$U = k_B T$ for a gel

Elasticity related to Entropy of polymers
Stretching polymers reduces the number of states, reduces entropy

Entropy of polymers
Compressing polymers also reduces number of states, and 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

\[ E = \frac{k_B T}{l^3} \quad [E] = \frac{J}{m^3} \]

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

**Mesh size**

Calculate the spacing between cross-links

\[ l^3 = \frac{k_B T}{E} \]

**Melting of gels**

The cross-links in gelatin detach at high temperatures

**Viscoelasticity of polymers**

Degree of entanglement determines the behavior

\[ l^3 = \frac{k_B T}{E} \]

\[ \frac{4.2 \times 10^{-25} J}{20 kPa} \]

\[ = 2.1 \times 10^{-25} m^3 \]

\[ l = \sqrt[3]{2.1 \times 10^{-25} m^3} \]

\[ = 6 \times 10^{-10} m \]

\[ = 6 \text{ nm} \]
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

Relaxation time
Polymers can slowly untangle \( \rightarrow \) reptation

Relaxation time
Polymers can slowly untangle

This controls the elasticity, \( E \).

This controls the time constant, \( \tau \).
**Equation of the week**
Viscosity is related to elasticity by a time-scale

\[ \eta = E \times \tau \]

- \( \eta \) = viscosity [Pa s]
- \( E \) = elasticity [Pa]
- \( \tau \) = time-constant [s]

**Concentration Dependence**
Polymers become entangled at high densities

Higher concentration

This sets the elasticity, \( E \), and the relaxation time, \( \tau \).

Shorter polymers don’t entangle as much \( \rightarrow \) lower \( \eta \)

**Shear-rate Dependence**
Polymers can disentangle at high shear rates

Higher shear

Shear thinning

Example: ketchup

**Viscoelasticity in mouthfeel**
Elasticity and viscosity determine texture

Long times, slow changes

Short times, fast changes

Elastic gel

Viscous fluid

**Equation of the week**
Sample calculation for honey

\[ \eta = E \times \tau \]

\[ \tau = \frac{\eta}{E} = \frac{10^3 \text{Pa} \cdot \text{s}}{2 \times 10^4 \text{Pa}} \]

\[ \tau = 0.5 \text{s} \]

**Shear rate**
The rate of deformation sets the time scale.

Stress determined by viscous component
For a liquid, \( \text{viscosity} = \text{stress/ shear rate} \)
Solid gel

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

Viscosity of thickeners

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

\[\eta = E \times \tau\]

\[E = \frac{k_B T}{l^3}\]
\[\tau = \tau_0 \frac{L^2}{l^2}\]

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

Very strong concentration dependence