Dynamic Light Scattering Study of Polymer Chain Dimensions

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MIT 3.014 Module A

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3.014 Lab Module A

Purpose: to measure polymer dimensions using dynamic light scattering (DLS) and to relate the particle size to the number of monomers.

Additional goals:

- Learn about light scattering
- Introduction to polymer behavior
- Gain laboratory experience

Why do we care?

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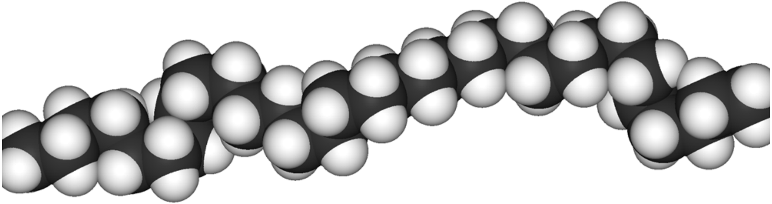
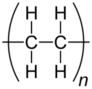
Outline

Introduction to Polymers

Introduction to Polymers

Polymers are long molecules composed of repeating units known as monomers.

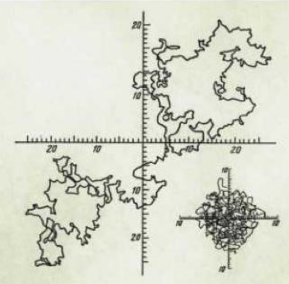




Molecular weights are very high – typically between 10,000 and 10,000,000 g/mol!

Polymers in Solution

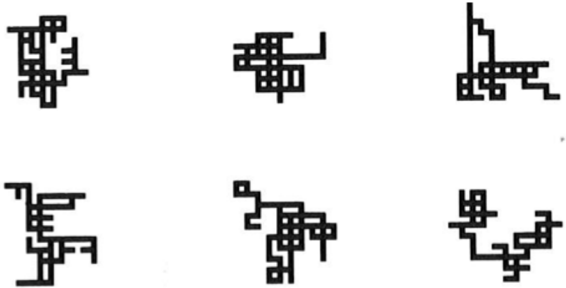
In solution, polymers generally form coils:



They swell in good solvents and shrink in poor solvents.

Random Walk Model

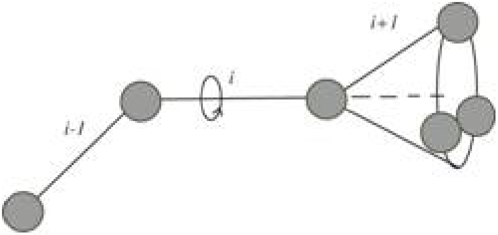
Mathematician's random walk:
- each step is independent from the previous step
- path can cross over itself



100 step simulation

Random Walk Model

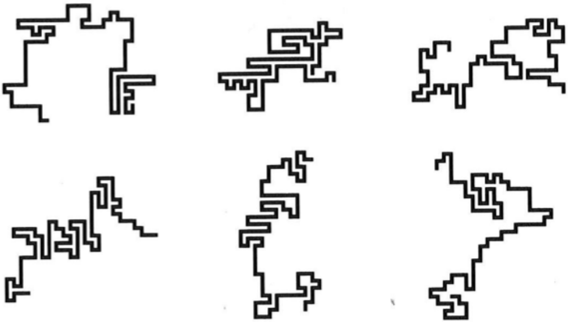
Chemist's random walk:
- some restrictions on bond angle



- path cannot cross over itself

Random Walk Model

"Self-avoiding random walk" leads to effective swelling:



100 step simulation

Scaling laws

Mathematician's model: $\left\langle R^2 \right\rangle^{1/2} = N^{1/2} l$

Self-avoiding model: $\left\langle R^2 \right\rangle^{1/2} = N^{1/2} C_\infty^{1/2} l$

$\left\langle R^2 \right\rangle^{1/2}$ is the RMS end-to-end distance, N is the number of steps, l is the step length, and $C_\infty^{1/2}$ depends on the polymer.

Types of Solvent

In general, $\langle R^2 \rangle^{1/2} \sim N^{\nu}$

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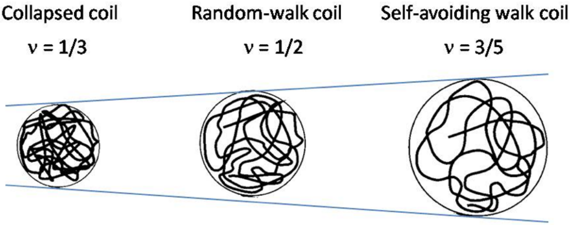
Good solvent: $\nu > 1/2$ (generally around $3/5$)

Bad solvent: $\nu < 1/2$

“Theta" solvent: $\nu = 1/2$



Choice of Solvent

Hildebrand solubility parameter:

$$\Delta H_m \sim (\delta_1 - \delta_2)^2$$

In this lab:

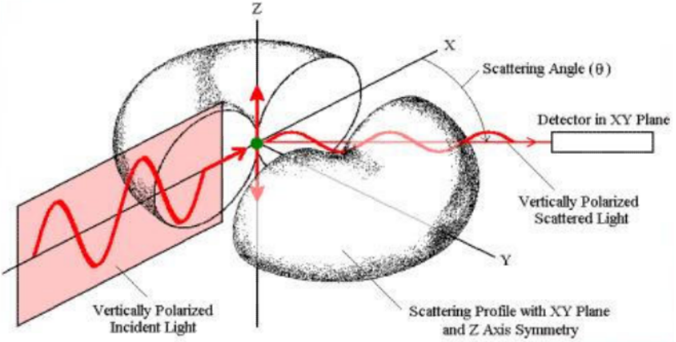
$$\delta_{PS} = 18.5 \times 10^3 J^{1/2} m^{-3/2}$$
$$\delta_{THF} = 18.5 \times 10^3 J^{1/2} m^{-3/2}$$
$$\delta_{acetone} = 19.7 \times 10^3 J^{1/2} m^{-3/2}$$

Low values of ΔH_m predict favorable mixing.

Scattering

Intuitive viewpoint: light deflected by particles in its trajectory

Technical viewpoint:



Rayleigh Scattering

Particle size is $<<$ light wavelength.

$$I \sim 1/\lambda^4$$

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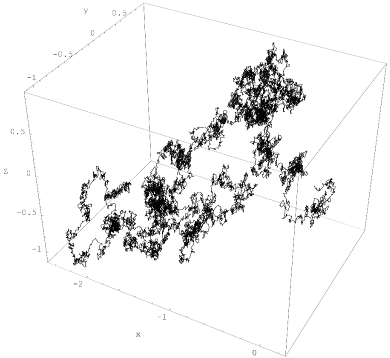
Particle size is $<<$ light wavelength.

$$I \sim 1/\lambda^4$$

- Blue scattered more than red – this is why the sky looks blue!
- Looking at the sun, you see yellow and red, the colors that are scattered less
- At sunset, light moves through more atmosphere, creating a greater yellow/red color gradient

Dynamic Light Scattering (DLS)

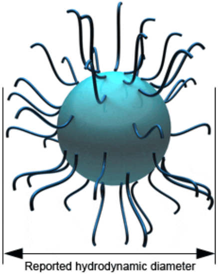
- Light is scattered from particles solution
- Particles move due to “Brownian motion," which depends on particle size, solution viscosity, temperature, and particle density



Stokes-Einstein Equation

$$R_h = \frac{kT}{6\pi\eta_s D}$$

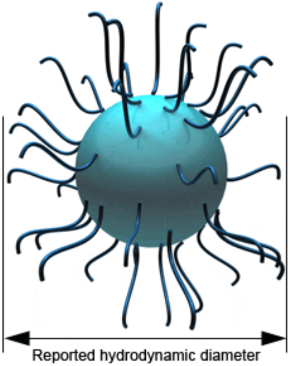
Terminology:
k = Boltzmann constant
T = temperature
η_s = solvent viscosity
D = Diffusion coefficient of particles
R_h = “Hydrodynamic radius"



The larger the particle, the slower the diffusion.

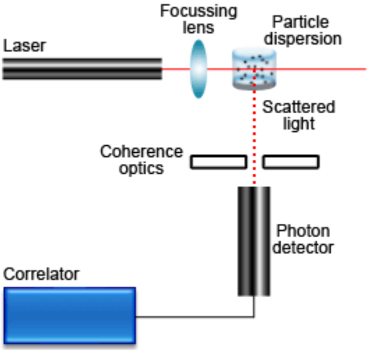
Hydrodynamic Radius

Radius of particle in solution, including solvent molecules that may be clustered around particle

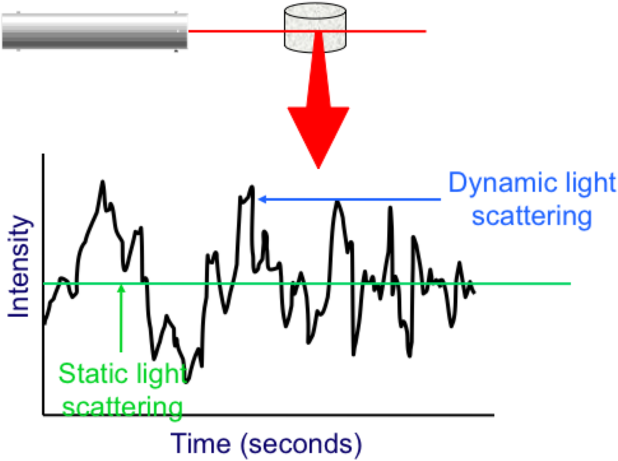


Overview of DLS

- Direct laser at dilute solution of particles
- Measure intensity fluctuations
- Infer diffusion coefficient from speed of intensity fluctuations
- Calculate hydrodynamic radius from diffusion coefficient



Intensity Curves



Correlation

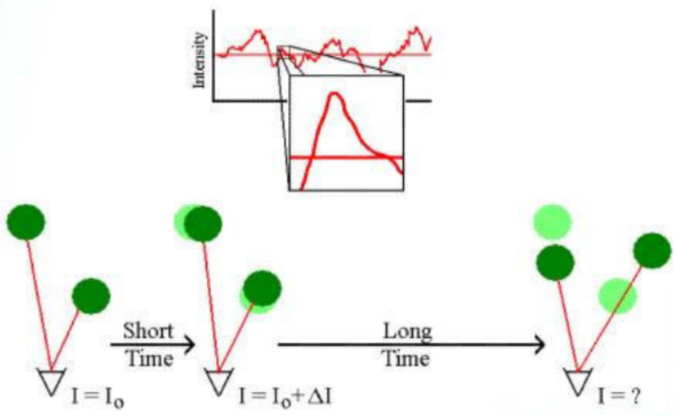
Basic idea: fit an exponential correlation curve to the intensity graph, and determine how long it takes for the correlation curve to decay.

$$G(\tau) = \int_0^\infty I(t)I(t+\tau)\,dx$$

If the particles are large, the signal will be changing slowly and the correlation will persist for a long time.

If the particles are small and moving rapidly then the correlation will disappear more rapidly.

Correlation



DLS Summary

- Particles in a dilute solution move due to Brownian motion
- Light scattered from particles is detected, creating an intensity curve
- Rate of correlation curve decay is related to diffusion coefficient of particles
- Diffusion coefficient determines particle size (hydrodynamic radius)

Lab Goals

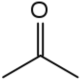
Goals of 3.014 module A:

- Make dilute polymer solutions
- Measure hydrodynamic radius of particles using DLS
- Derive scaling law of polymer chains in solution

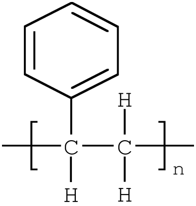
Materials

Tetrahydrofuran (THF)

Acetone



Polystyrene



Lab Safety

Acetone and tetrahydrofuran (THF) are both extremely flammable. Additionally, THF is moderately reactive, causes irritation to skin, eyes, and respiratory systems, and affects the central nervous system. Solvents should only be handled within a fume hood. Additionally, the following safety equipment should be worn when handling chemicals:

- Long pants, closed-toed shoes
- Lab coat
- Goggles
- Heavy (blue) nitrile gloves

Solutions

Polystyrene M_w (g/mol)	Target Concentration (g/mL)	Solvent
90,000	0.01	THF & THF/Acetone
152,000	0.009	THF
200,000	0.007	THF & THF/Acetone
390,000	0.006	THF
575,000	0.004	THF & THF/Acetone
900,000	0.003	THF
2,000,000	0.001	THF

All solutions will be 5mL, so you will need to calculate the appropriate amount of polymer to use.

Procedure

- Make dilute polymer solutions
- Go to 8-206 in small groups for DLS
- Clean up
- Derive scaling law of polymer chains in THF and THF/Acetone mixture

Analysis

$$R_0 \propto N^{\nu}$$

$$\log(R_0) = \nu \log(N)$$

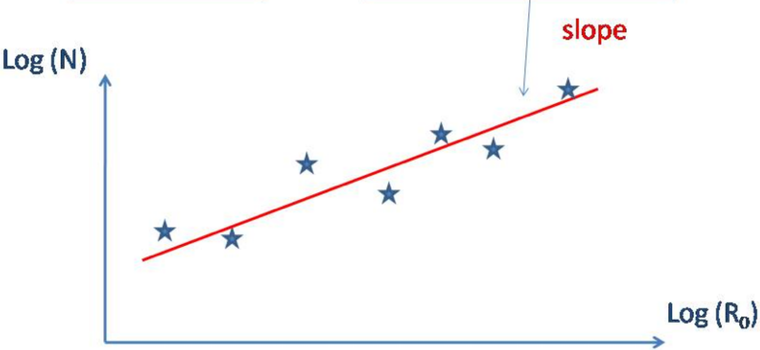


Image Credits and Thanks

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