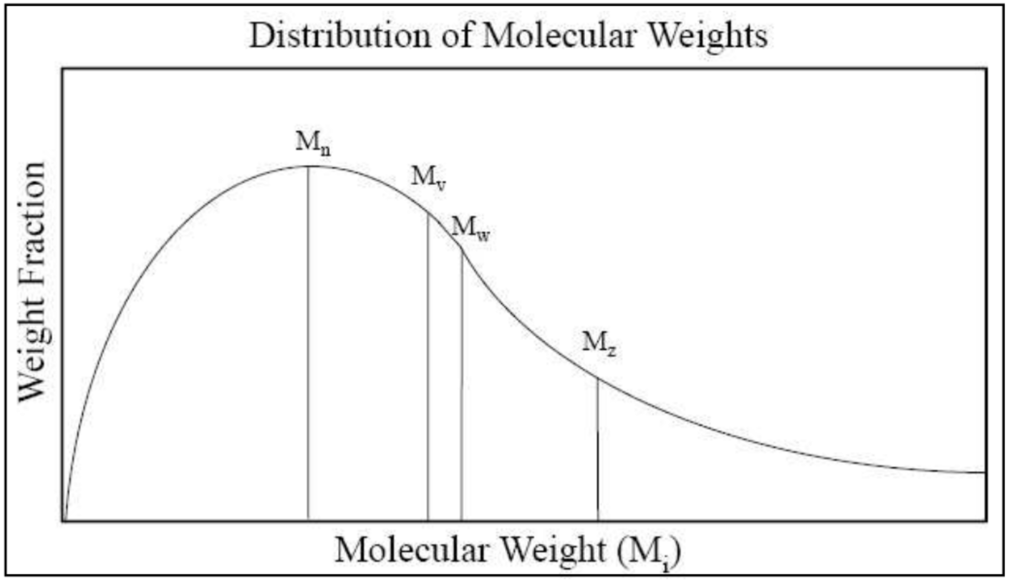
Molecular Weight Determination



Outline

How we can determine the molecular weight?

Osmometry
Viscometry
Gel Permeation Chromatography
Light scattering

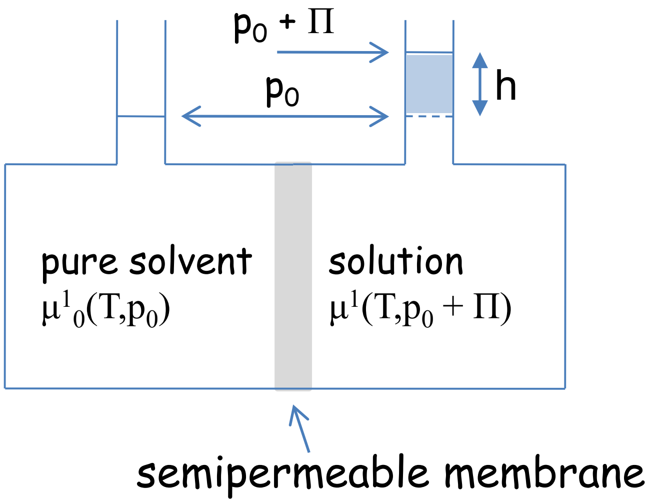
Scanning Probe Microscopies (STM/AFM)

Osmometry

Based on collegative properties (depending on number of molecules in solution but not their chemical structure)

Osmotic Pressure
of a dilute, uncharged solution

$$\Pi = \rho\, g\, h$$



Van t'Hoff equation:

for ideal, infinite diluted solution

- of small molecules:

$$\Pi\, V = nRT \qquad \text{with } n = \frac{cV}{M} \rightarrow \frac{\Pi}{c} = \frac{RT}{M}$$

- of polymers:

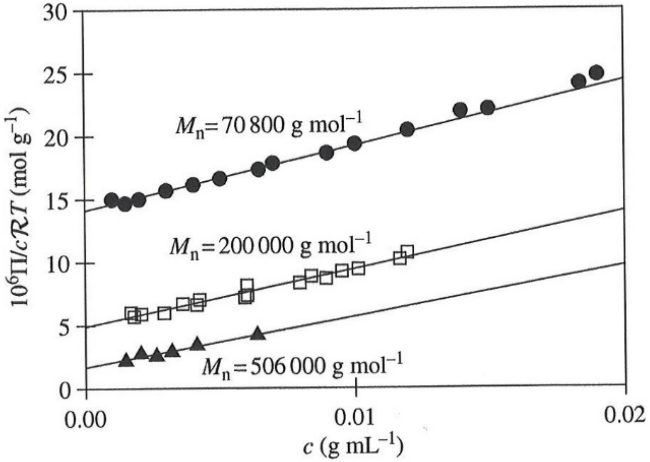
$$\boxed{\frac{\Pi}{c} = \frac{RT}{\overline{M}_n}}$$

Π: Osmotic pressure
T: Temperature
c : concentration of polymer solution
R: gas constant
M: molecular weight
ρ: solvent density
g: gravitational acceleration

Osmometry

But at finite concentrations, interactions between the solvent and the solute result in a deviation of van't Hoff law:

$$\boxed{\frac{\Pi}{c} = \frac{RT}{\overline{M_n}} + A_2 c + A_3 c^2 + \;\dots\dots}$$

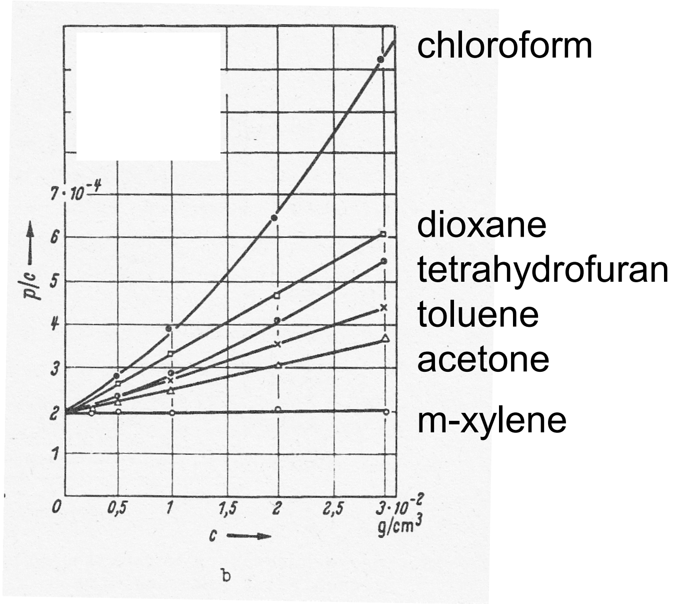


$A_1 = RT/\overline{M}_n$	
A_2, $A_{3\dots}$	virial coefficients, depending on solvent, molecular weight and temperature contribution to osmotic pressure from interaction between species i and j
A_2	Interaction between polymer – polymer, polymer – solvent or solvent - solvent
A_3,A_4…	Multiple interactions

Poly(α-methylstyrene) samples in toluene at 25°C
from: I. Noda, N. Kato, T. Kitano and M. Nagasawa, Macromolecules, 16, 668 (1981)

Extrapolation to c=0 gives $\overline{M}_n$ exactly

Osmometry



Π/c – c curves polymethylmethacrylate in different solvents

The sign of the second virial coefficient A_2 indicates repulsion or attraction between chains.

$A_2 > 0$: repulsion between polymers
→ Increase of osmotic pressure

$A_2 < 0$: attraction between chains

$A_2 = 0$ ideal behavior

Viscometry

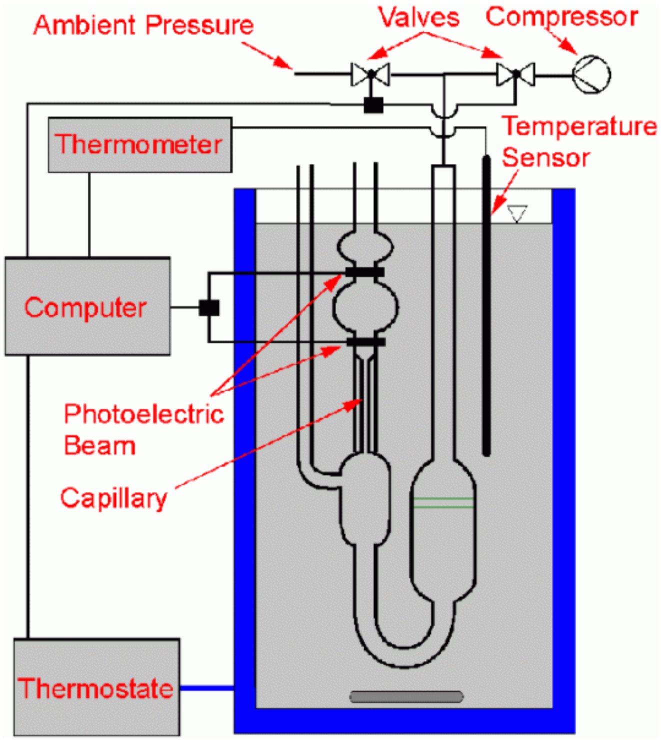
$$\boxed{\eta \frac{\delta v_x}{\delta y} = \sigma_{yx}}$$

shear stress
Newton's law

η: viscosity [Pa s] = 10 Poise, 1P = dyne s cm^{-2}
$\dot{\gamma} = dv_x/dy$ strain rate

velocity gradient

Viscosity η: measure for the resistance of the fluid to flow



The earliest methods for measuring viscosity were based on using capillary tubes and measuring the time it took for a volume of liquid to pass through the length of the tube.

→ How the Molecular Weight can be estimated?

Defining Viscosity in Polymer Solutions

As with other polymer solution properties, the solutions used for viscosity measurements will be nonideal and therefore η_{sp}/c depends on the concentration

→ extrapolation to zero concentration
→ a power series of concentration with virial coefficients

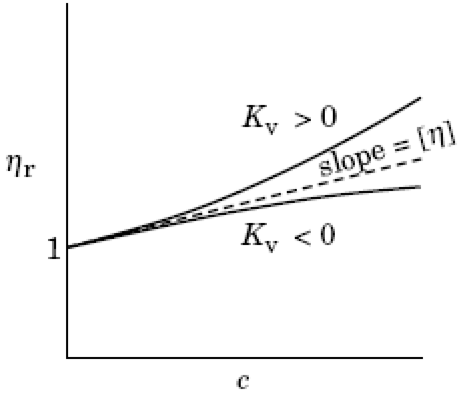


Figure 3.31 illustrates how η_r changes with c. The linear coefficient $[\eta]$ is called the **intrinsic viscosity**. It can be obtained as the slope in the plot of η_r as a function of c in the low concentration limit:

η: viscosity of the solution
η_s:viscosity of the solvent
K_v: coefficient

relative viscosity η_r

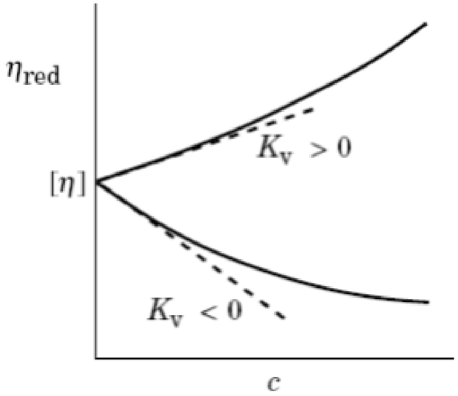
$$\eta_r \equiv \frac{\eta}{\eta_s} = 1 + [\eta]c + K_v c^2 + \dots .$$

specific viscosity η_{sp},

$$\eta_{sp} \equiv \eta_r - 1 = \frac{\eta - \eta_s}{\eta_s} = [\eta]c + K_v c^2 + \dots .$$

The reduced viscosity η_{red} refers to the ratio of η_{sp} to c:

$$\eta_{red} \equiv \frac{\eta_{sp}}{c} = \frac{\eta - \eta_s}{\eta_s c} = [\eta] + K_v c + \dots .$$



Reduced viscosity η_{red} plotted as a function of c. The intercept is $[\eta]$. The slope of the tangent at c = 0 gives K_v.

Intrinsic Viscosity

Intrinsic viscosity [η] is a measure of a solute's contribution to the viscosity of a solution.

Intrinsic viscosity reflects the capability of a polymer in solution to enhance the viscosity of the solution. The viscosity behavior of macromolecular substances in solution is one of the most frequently used approaches for characterization.

$$\eta = \eta_s\,(1 + [\eta]c + k_H[\eta]c^2 + \dots.)$$

K_H Huggins coefficient

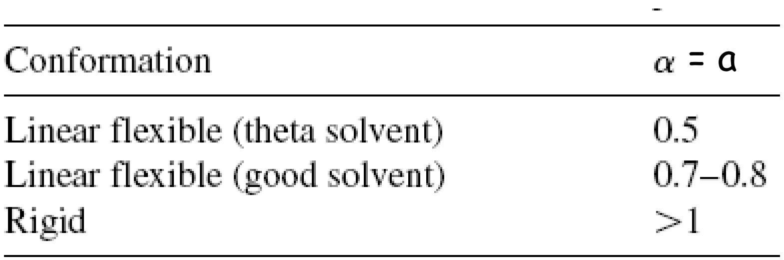
The intrinsic viscosity number is defined as the limiting value of the specific viscosity/concentration ratio at zero concentration.

$$[\eta] \equiv \lim_{c \to 0} \frac{\eta_r - 1}{c} = \lim_{c \to 0} \frac{\eta - \eta_s}{c\eta_s}$$

Intrinsic Viscosity and Molecular Weight

Mark-Houwink-Sakurada equation: $\boxed{[\eta] = K_M \overline{M_v}^{\,a}}$

K_M is a constant of the unit L/g, and a is called Mark-Houwink-Sakurada exponent. K_M and a are different from polymer to polymer and depend on the solvent as well as the temperature.



Conformation	α = a
Linear flexible (theta solvent)	0.5
Linear flexible (good solvent)	0.7–0.8
Rigid	>1

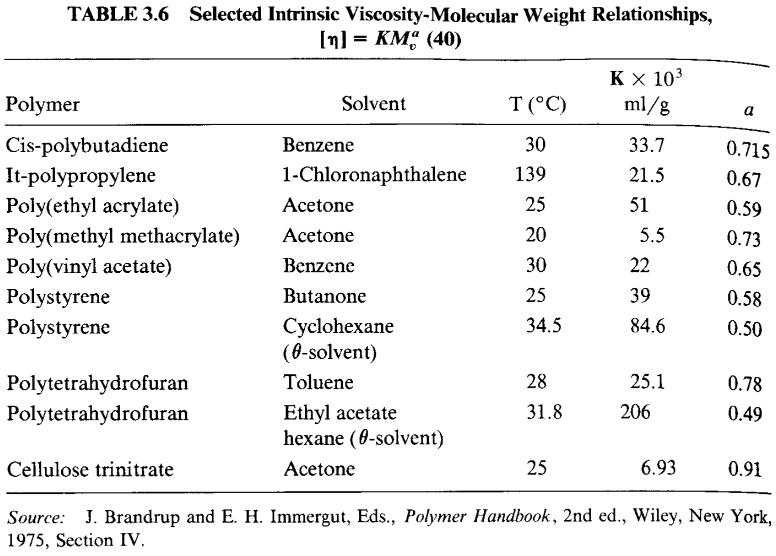


TABLE 3.6 Selected Intrinsic Viscosity-Molecular Weight Relationships, $[\eta] = KM_v^a$ (40)

Polymer	Solvent	T (°C)	K × 10^3 ml/g	*a*
Cis-polybutadiene	Benzene	30	33.7	0.715
It-polypropylene	1-Chloronaphthalene	139	21.5	0.67
Poly(ethyl acrylate)	Acetone	25	51	0.59
Poly(methyl methacrylate)	Acetone	20	5.5	0.73
Poly(vinyl acetate)	Benzene	30	22	0.65
Polystyrene	Butanone	25	39	0.58
Polystyrene	Cyclohexane (θ-solvent)	34.5	84.6	0.50
Polytetrahydrofuran	Toluene	28	25.1	0.78
Polytetrahydrofuran	Ethyl acetate hexane (θ-solvent)	31.8	206	0.49
Cellulose trinitrate	Acetone	25	6.93	0.91

Source: J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, Section IV.

[η] determination: Huggins equation and Kramer equation

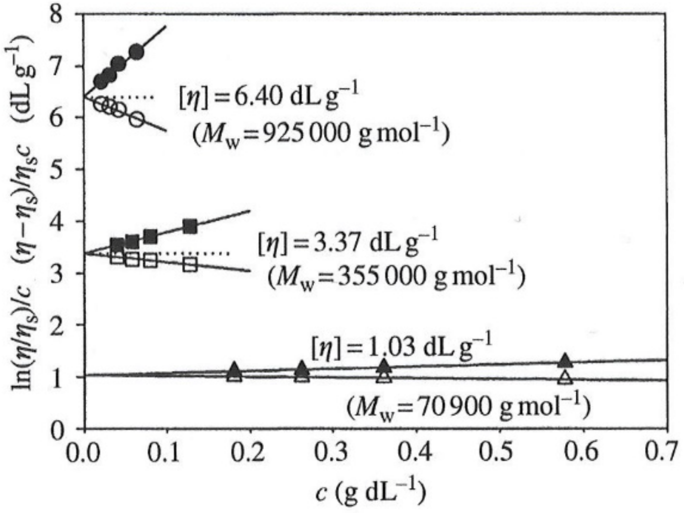
Dilute solution viscosity measurements at multiple concentrations yield the intrinsic viscosity by using two equation forms for the extrapolation to zero concentration

First extrapolation form:
Huggins equation

$$\frac{\eta - \eta_s}{\eta_s c} = [\eta] + k_H[\eta]^2 c + \ldots.$$

Second extrapolation form:
Kramer equation

$$\frac{\ln\left(\frac{\eta}{\eta_s}\right)}{c} = [\eta] + \left(k_H - \frac{1}{2}\right)[\eta]^2 c + \ldots.$$



Determination of [η] for three different polybutadiene samples in tetrahydrofuran at 25°C. Huggins filled symbols, Kramer open symbols. All three polymers $K_H = 0.37$

Poiseuille Equation

The measurement is based on the capillary flow. At slow flow the velocity profile in the capillary is of a parabolic cone:

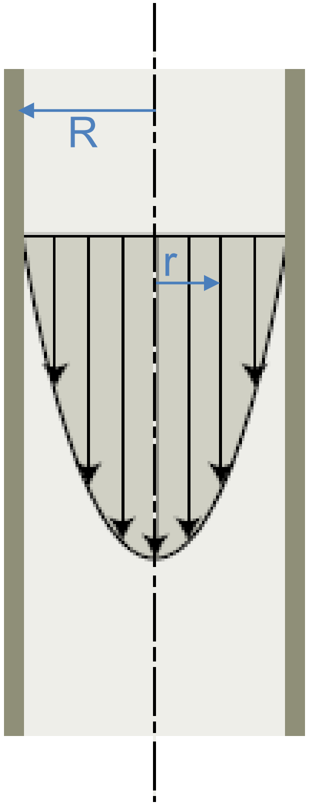
$$v = \frac{\rho g + \frac{\Delta p}{L}}{2\eta}\left(R^2 - r^2\right)$$

This velocity times the cross-sectional area of the shell gives the incremental volume of liquid dV, which is delivered from the capillary in an interval of time Δt. Integration over all r gives the Poiseuille Equation:

$$\boxed{\frac{\Delta V}{\Delta t} = \frac{(\rho g L + \Delta p)\pi R^4}{8\eta L}}$$

ΔV volume of liquid in an intervall of time Δt

ρ	density of the fluid
g	acceleration due to gravity
L	length of capillary
R	radius of capillary
p	mechanical pressure



Cross section of the flow in the capillary. The flow velocity is parallel to the center line of the capillary. Velocity field is parabolic.

Measuring Viscosities of Polymer Solutions

The weight of the liquid is the driving force for the flow, so the Δp term in the Poiseuille equation is zero and the observed flow time equals:

$$\Delta t = \frac{8\Delta V}{\pi g R^4}\,\frac{\eta}{\rho}$$

or

$$\eta = A\rho\,\Delta t$$

For a solute (1) in a solvent (2) with known viscosity:

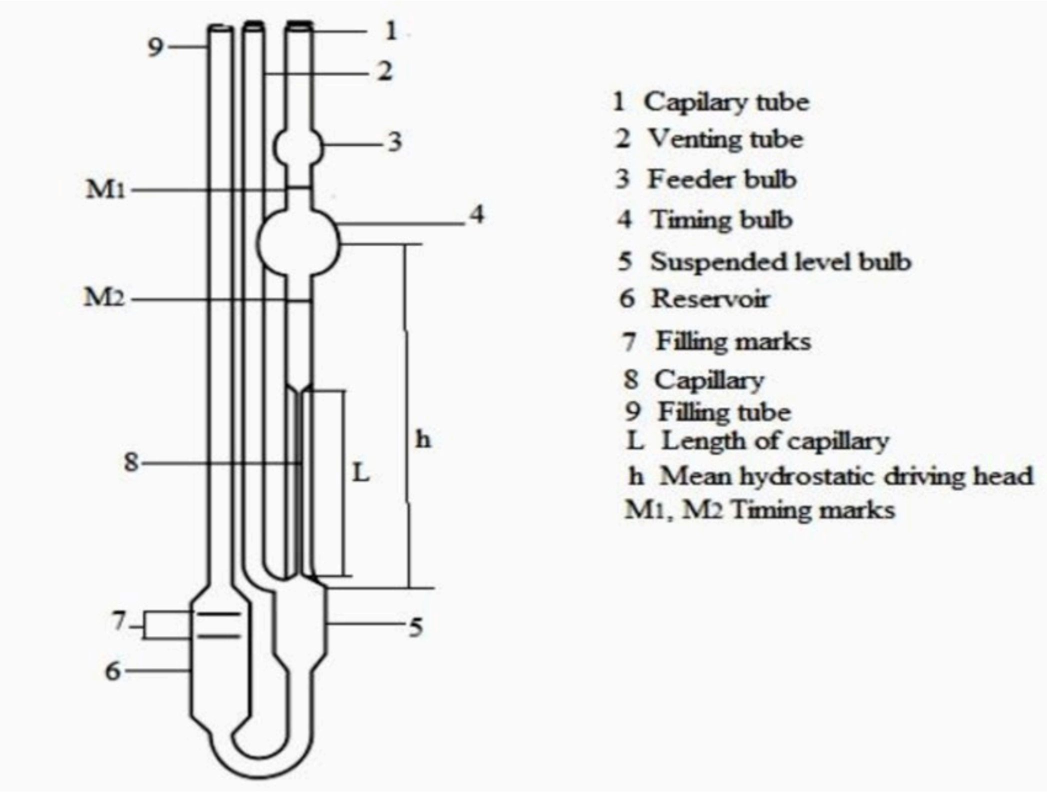
$$\boxed{\eta_1 = \frac{\rho_1}{\rho_2}\,\frac{\Delta t_1}{\Delta t_2}\,\eta_2}$$

1: solute (here **p**olymer)
2: known liquid (**s**olvent)

$$\boxed{\eta_{rel} = \frac{\eta}{\eta_s} \approx \frac{t_p}{t_s}}$$

Ubbelohde viscometer

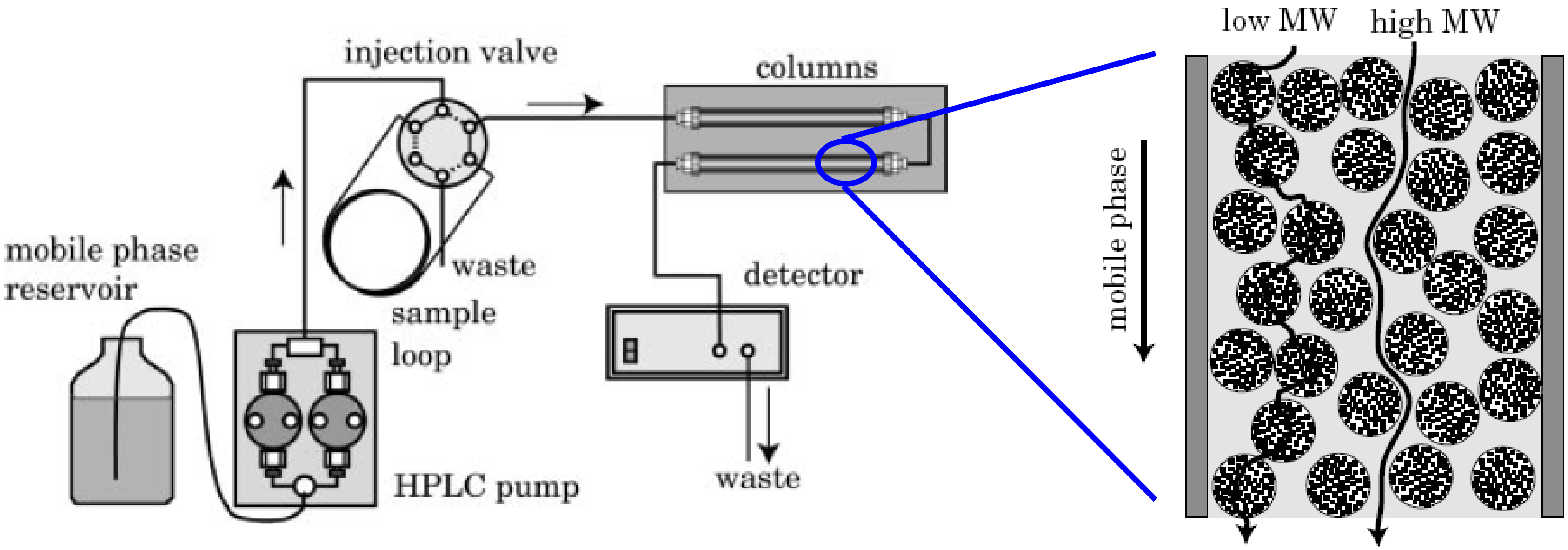
The efflux time between the time when the liquid level crosses the upper marker and the time when it crosses the lower marker is measured



Size Exclusion Chromatography SEC

or

Gel Permeation Chromatography GPC



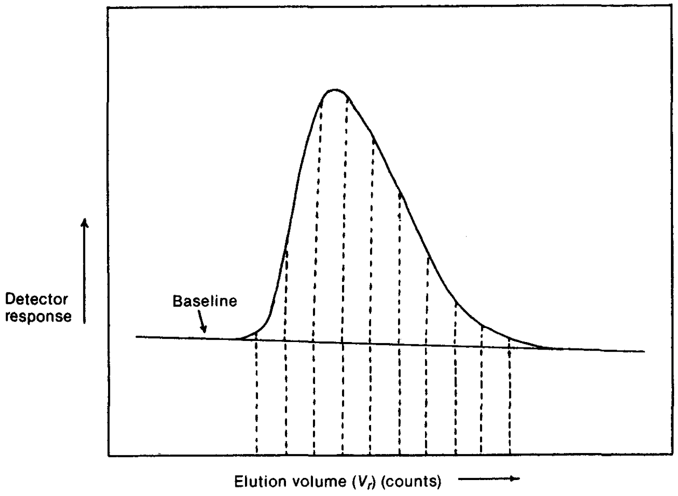
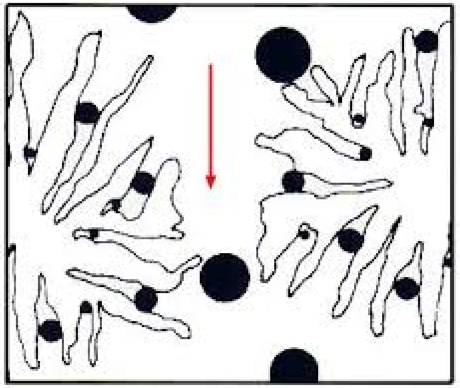


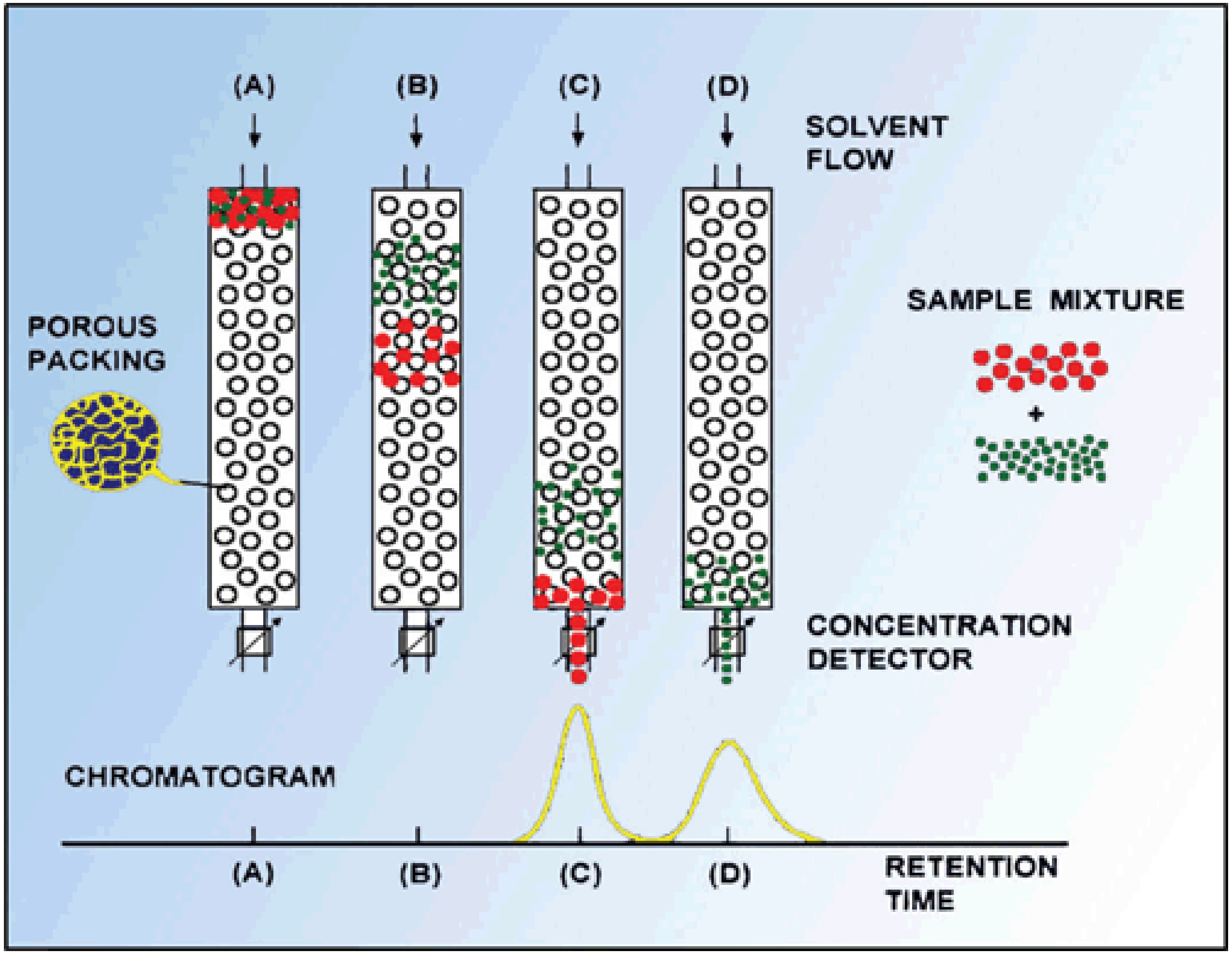
FIGURE 2.10. Typical gel permeation chromatogram. Dotted lines represent volume "counts."

Measuring Molecular Weight Distributions

Gel Permeation Chromatography: schematic representation

GPC/SEC is based on differences in hydrodynamic volume





Determining Molecular Weights by GPC

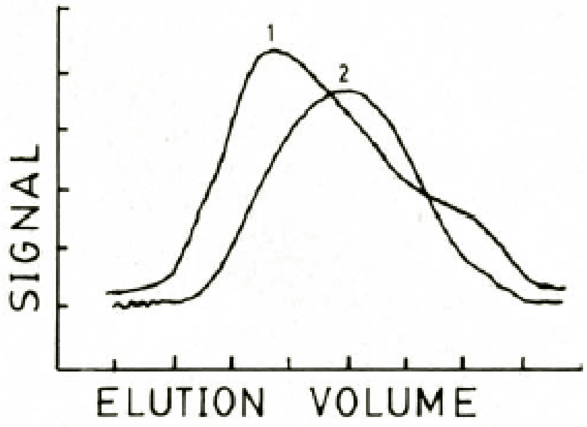


Figure 15. Chromatograms from size exclusion chromatography experiment. The signal is typically a response to polymer concentration in the flow cell. In this example, sample 1 has the higher molecular weight averages.

„Conventional“ calibration with e.g. narrow polydispersity polystyrene standards

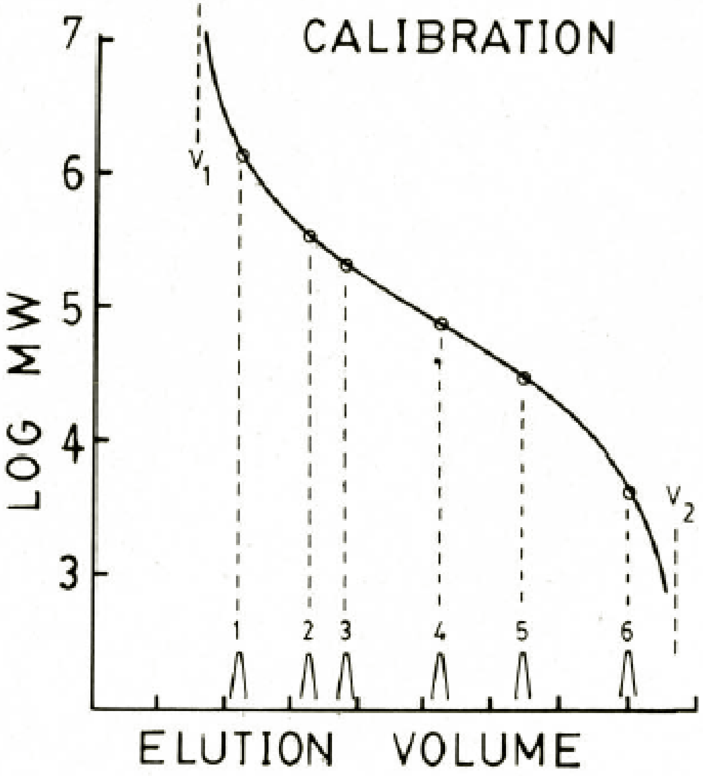


Figure 16. Calibration curve for size exclusion chromatography. Six fractions of narrow MWD were injected. Solvent and temperature must be identical with those used for unknown.

Disadvantage: the reported molecular weights are actually those of the equivalent polystyrene radius of gyration and not necessarily the „real“ molecular weights (this is due to the fact that the relationships between R_G and molecular weight varies from polymer to polymer and solvent to solvent)

Universal Calibration by Benoit*

Retention Volume V_R depends only on the hydrodynamic volume V_h, which itself will be proportional to R_g^3

$$[\eta] \sim \frac{V_h}{M} \approx \frac{R_g^3}{M}$$

Assumption: proportionality factor between V_h and $[\eta]M$ is independent of structure

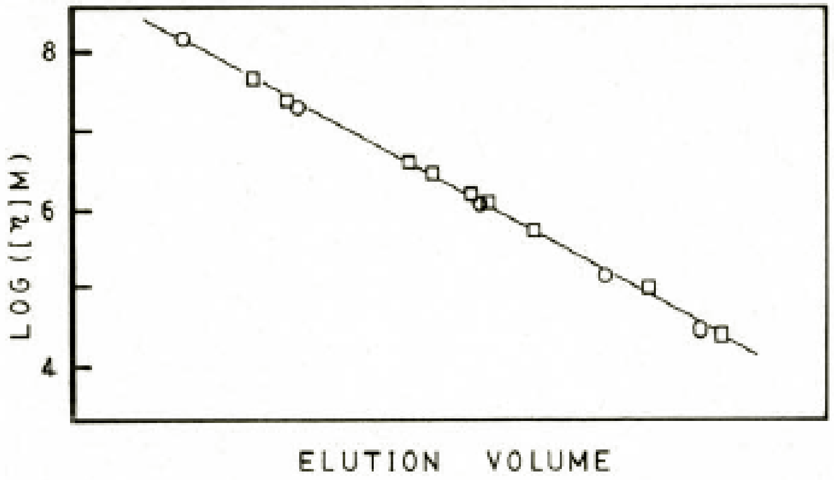


Figure 18. Evaluation of universal calibration procedure in size exclusion chromatography. □ = poly(vinyl acetate) fractions, ○ = polystyrene fractions.

- Corrects for the different hydrodynamic relationships of different polymers
- Analyzed polymer and calibration polymer do not need to be the same
- Convenient for new polymers since [η] is usually easily measured
- NOT applicable for highly branched polymers or polyelectrolytes, which have different hydrodynamic relationships

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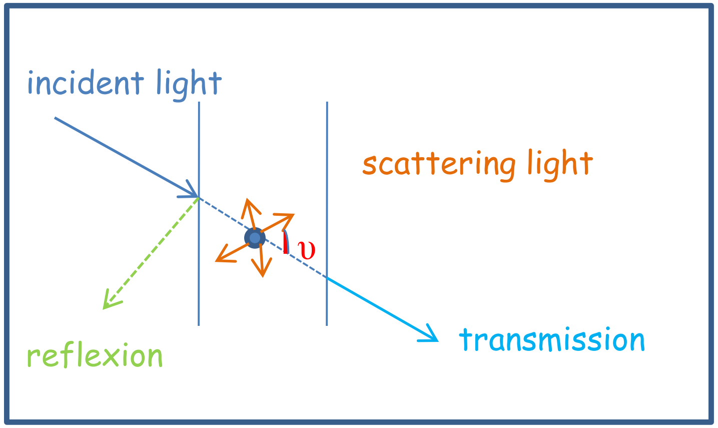
* Grubisic, Z.; Rempp, P.; Benoit, H. A universal calibration for gel permeation chromatography. *J. Polym. Sci., part B: Polym. Lett.* **1967**, *5*, 753-759.

Light Scattering

light scattering occurs in inhomogenous solution:

fluctuations in the refractive index in the solution



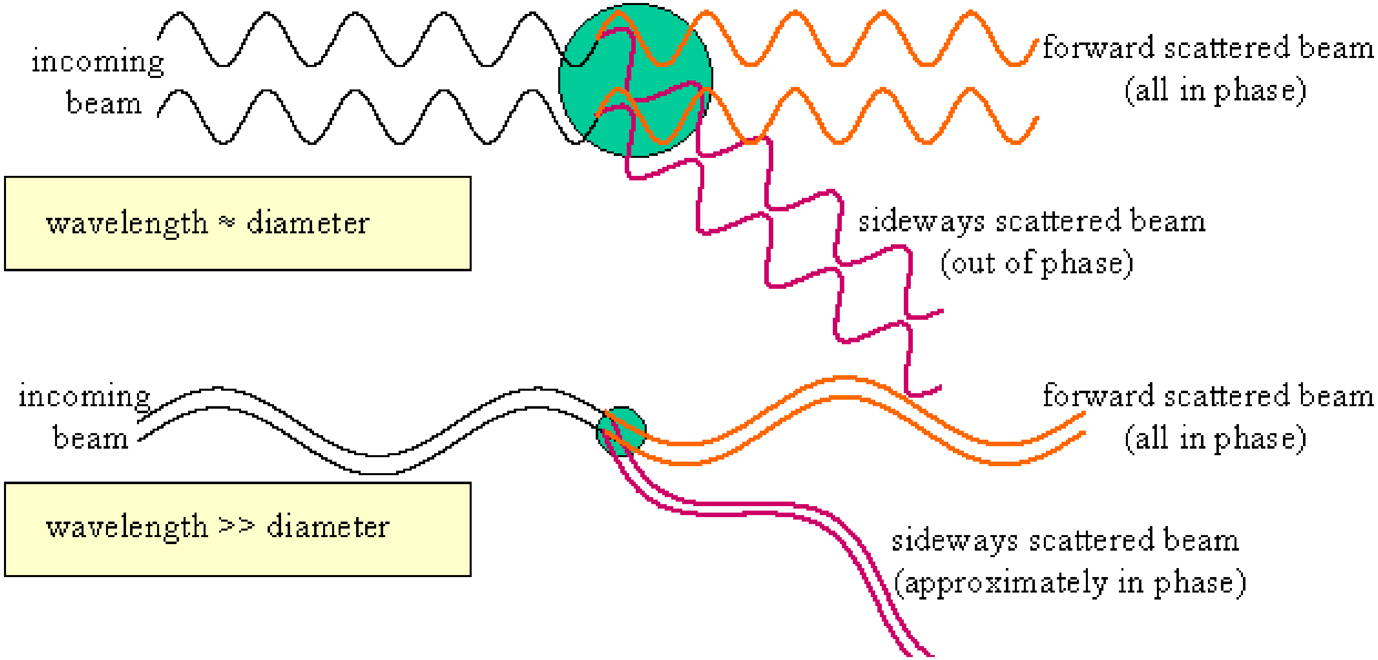
light scattering experiments can be used to measure three parameters:

1. weight average molecular weight $\overline{M_w}$
2. mean-squared radius of gyration R_g^2
3. second virial coefficient A_2.

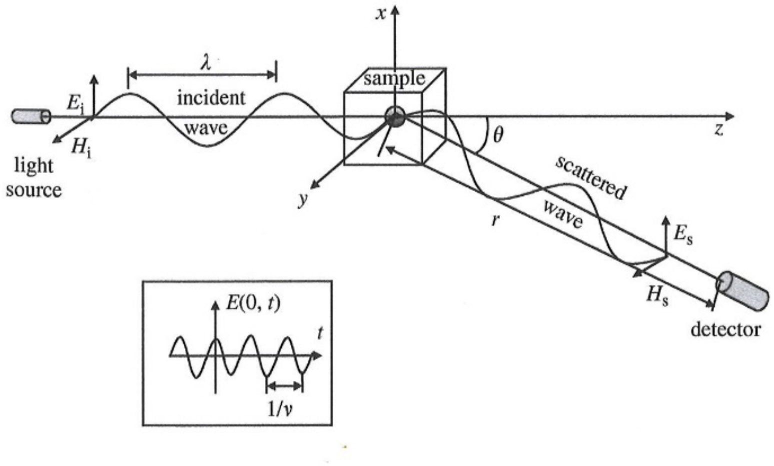
Scattering dependance on diameter of objects

Scattering from objects of different size

with respect to the wavelength of the radiation



Scattering by small molecule: $<R_g^2>^{1/2} < \lambda/20$



λ = wavelength of the primary, vertically polarized light
(using Hg λ= 4000 – 5000Å)
I_0 = intensity of the incident light
I_θ = scattered intensity per unit volume depending on scattering angle θ
n = refractive index of solution
n_0 = refractive index of solvent
N_A = Avogadro number
r = distance to the scattered light detector
A_2 (or B) = 2. virial coefficient

light recognized particle as sphere
only one observing angle

Rayleigh Ratio: $R_\theta \equiv \frac{I_\theta r^2}{I_0}$ [cm^{-1}]

for an ideal polymer solution:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w}$$

Optical constant K = $\frac{4\pi^2 n_0^2}{N_A \lambda^4}\left(\frac{\partial n}{\partial c}\right)^2$

↑
refractive index increment

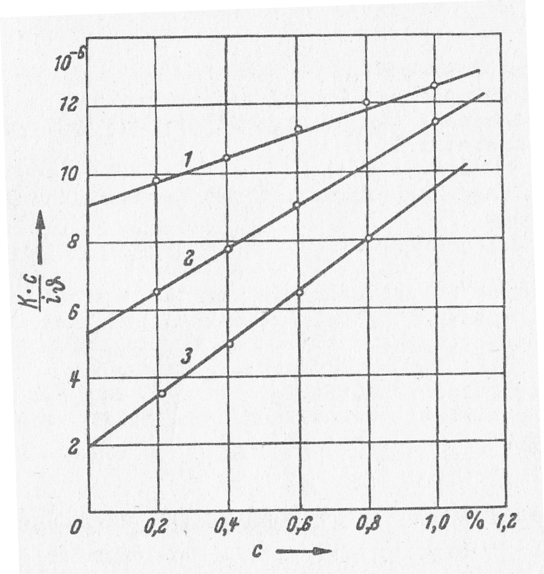
Scattering by small molecule: $\langle R_g^2\rangle^{1/2} < \lambda/20$

for an non-ideal polymer solution:

Debye:

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M_w}} + 2A_2c + 3A_3c^2 + \ldots\ldots$$

$\overline{M}_w$ by extrapolation to c = 0

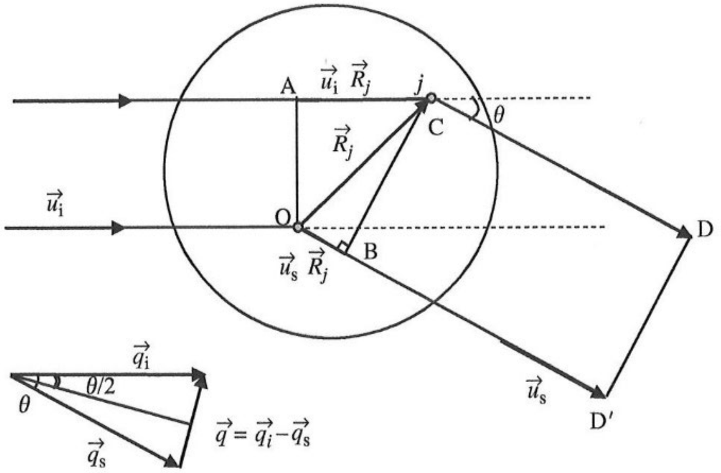


Determination of M and 2. virial coefficient for particels with a diameter < $\lambda/20$ polystyrene in methylethylketon

(1) M_w = 108 000;
(2) M_w = 182 000;
(3) M_w= 500 000

Doty, *Zimm* and *Mark*, J. Chem. Physics, 1944. 12, 144; 1945, 13, 159

Scattering from a sphere with $\langle R_g^2 \rangle^{1/2} > \lambda/20$:



$\overrightarrow{u_i}$: *unit vector*

$\overrightarrow{q_i}$: incident wavevector

$\overrightarrow{q_s}$: scattered wavevector

n: refractive index of solution

$$\overrightarrow{q_{i/s}} \equiv \frac{2\pi n}{\lambda}\,\overrightarrow{u_{i/s}}$$

Scattering wavevector

$$\vec{q} \equiv \overrightarrow{q_i} - \overrightarrow{q_s}$$
$$q \equiv |\vec{q}| = \frac{4\pi n}{\lambda}\, sin\left(\frac{\theta}{2}\right)$$

Scattering intensity depends on the angle θ:

$I_\theta = I_0\, P(\theta)$ with P(θ) scattering form factor

Zimm Equation and Zimm plot

for the scattering of linear polarized light in a dilute polymer solution Zimm suggested following equation based on Debye equation:

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M_w}\, P(\theta)} + 2A_2 c + \ \ldots..$$

with $1/P(\theta) = 1 + \frac{1}{3}\,\frac{16\pi^2 n^2}{\lambda_0^2}\, R_g^2 \sin^2(\theta/2)$

Zimm – Equation

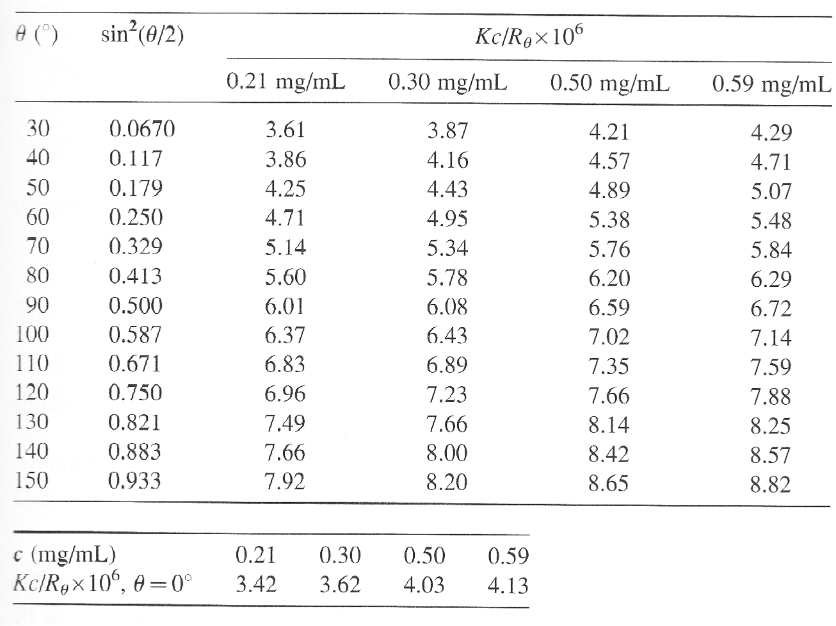
$$\boxed{\frac{Kc}{R_\theta} = \frac{1}{\overline{M_w}} + S\, sin^2\left(\frac{\theta}{2}\right) + 2A_2 c}$$

$$S = \frac{1}{M_w}\left[\frac{1}{3}\,\frac{16\,\pi^2 n^2}{\lambda_0^2}\, R_g^2\right]$$

$\frac{Kc}{R_\theta} = f\left(sin^2\left(\frac{\theta}{2}\right)\right)$: for c=0 slope of the line = R_g^2 → information about particle size and form

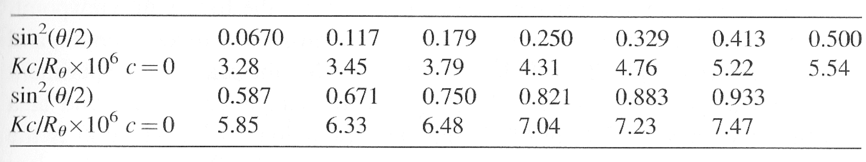
$\frac{Kc}{R_\theta} = f(c)$: for $sin^2\left(\frac{\theta}{2}\right)$ = 0 slope of the line = 2. virial coefficient A_2 (or B) → information of solvation

Example: data set of methylcellulose



θ (°)	$\sin^2(\theta/2)$	$Kc/R_\theta \times 10^6$			
		0.21 mg/mL	0.30 mg/mL	0.50 mg/mL	0.59 mg/mL
30	0.0670	3.61	3.87	4.21	4.29
40	0.117	3.86	4.16	4.57	4.71
50	0.179	4.25	4.43	4.89	5.07
60	0.250	4.71	4.95	5.38	5.48
70	0.329	5.14	5.34	5.76	5.84
80	0.413	5.60	5.78	6.20	6.29
90	0.500	6.01	6.08	6.59	6.72
100	0.587	6.37	6.43	7.02	7.14
110	0.671	6.83	6.89	7.35	7.59
120	0.750	6.96	7.23	7.66	7.88
130	0.821	7.49	7.66	8.14	8.25
140	0.883	7.66	8.00	8.42	8.57
150	0.933	7.92	8.20	8.65	8.82

c (mg/mL)	0.21	0.30	0.50	0.59
$Kc/R_\theta \times 10^6$, $\theta = 0°$	3.42	3.62	4.03	4.13

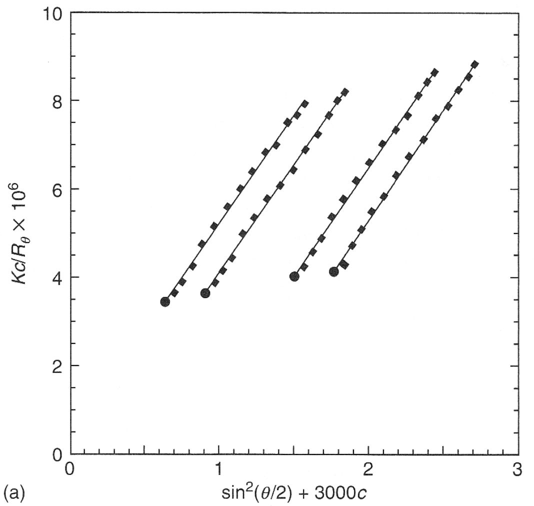


$\sin^2(\theta/2)$	0.0670	0.117	0.179	0.250	0.329	0.413	0.500
$Kc/R_\theta \times 10^6$ $c = 0$	3.28	3.45	3.79	4.31	4.76	5.22	5.54
$\sin^2(\theta/2)$	0.587	0.671	0.750	0.821	0.883	0.933	
$Kc/R_\theta \times 10^6$ $c = 0$	5.85	6.33	6.48	7.04	7.23	7.47	

Data for methylcellulose in water were taken at 20°C with an argon ion laser operating at 488nm. Here n for water is 1.33, and $\delta n/\delta c$ was determined to be 0.137 ml/g.

$M_w = 3.3\text{x}10^5$ g/mol
$A_2 = 9.6\text{x}10^{-4}$ mol cm^3/g^2
$R_g = 64$ nm

Construction of a Zimm- Plot



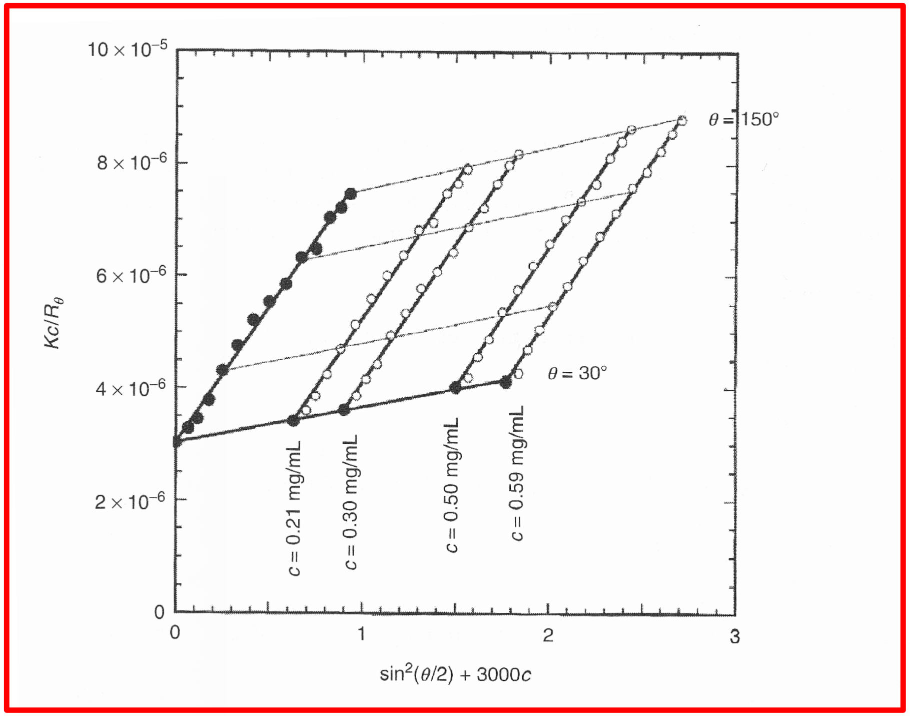
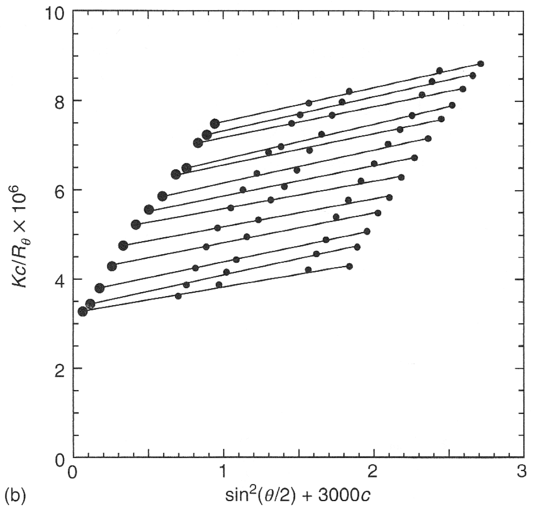


Figure 8.8 Zimm plot for a sample of methylcellulose in water. (Reproduced from Kobayashi, K., Huan C.-I., and Lodge, T.P., *Macromolecules*, 32, 7070, 1999. With permission.)



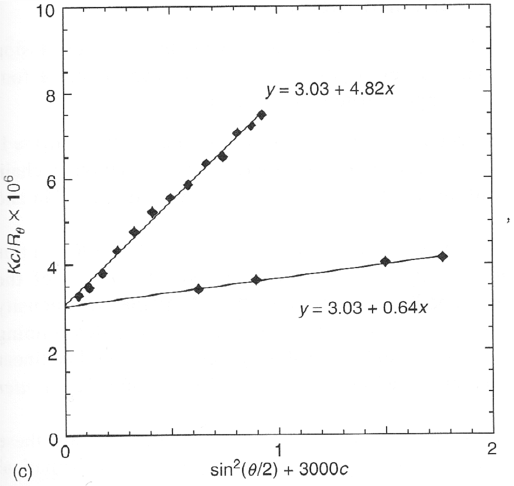
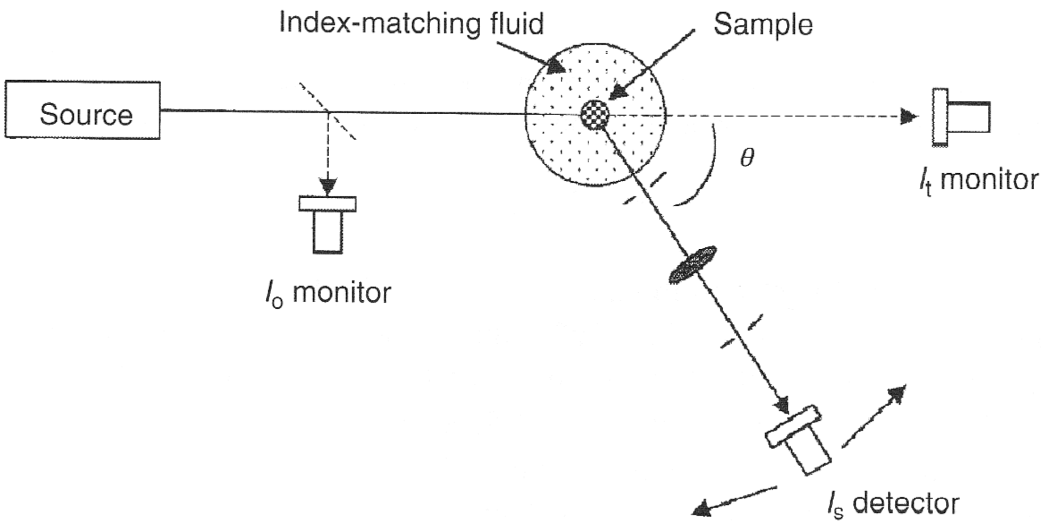
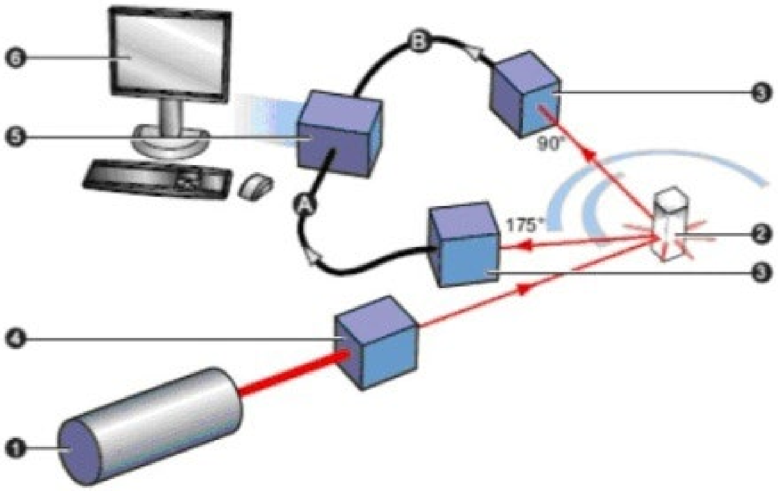


Figure 8.9 (continued) (c) The extrapolations of the $\theta = 0$ data to $c = 0$, and the $c = 0$ data to $\theta = 0$.

Figure 8.9 Construction of the Zimm plot of Figure 8.8 as developed in Example 8.3. (a) The extrapolation to $\theta = 0$ for each concentration. (b) The extrapolation to $c = 0$ for each angle.

Basic Components of a Light Scattering Instrument





1: laser
2: measurement cell
3: detector
4: attenuator
5: correlator
6: data handling PC

Summary of Molecular Weight Methods and Results

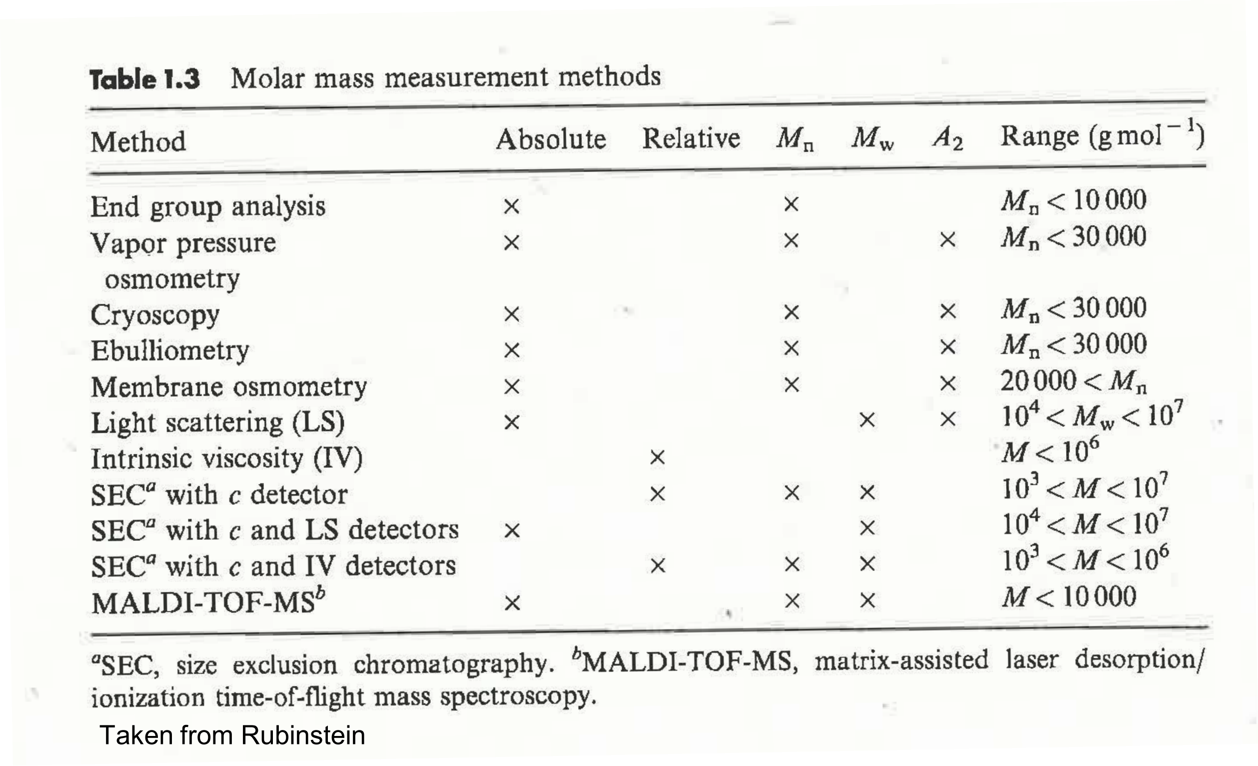


Table 1.3 Molar mass measurement methods

Method	Absolute	Relative	M_n	M_w	A_2	Range ($g\,mol^{-1}$)
End group analysis	×		×			$M_n < 10\,000$
Vapor pressure osmometry	×		×		×	$M_n < 30\,000$
Cryoscopy	×		×		×	$M_n < 30\,000$
Ebulliometry	×		×		×	$M_n < 30\,000$
Membrane osmometry	×		×		×	$20\,000 < M_n$
Light scattering (LS)	×			×	×	$10^4 < M_w < 10^7$
Intrinsic viscosity (IV)		×				$M < 10^6$
SEC[a] with c detector		×	×	×		$10^3 < M < 10^7$
SEC[a] with c and LS detectors	×			×		$10^4 < M < 10^7$
SEC[a] with c and IV detectors		×	×	×		$10^3 < M < 10^6$
MALDI-TOF-MS[b]	×		×	×		$M < 10\,000$

[a] SEC, size exclusion chromatography. [b] MALDI-TOF-MS, matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy.

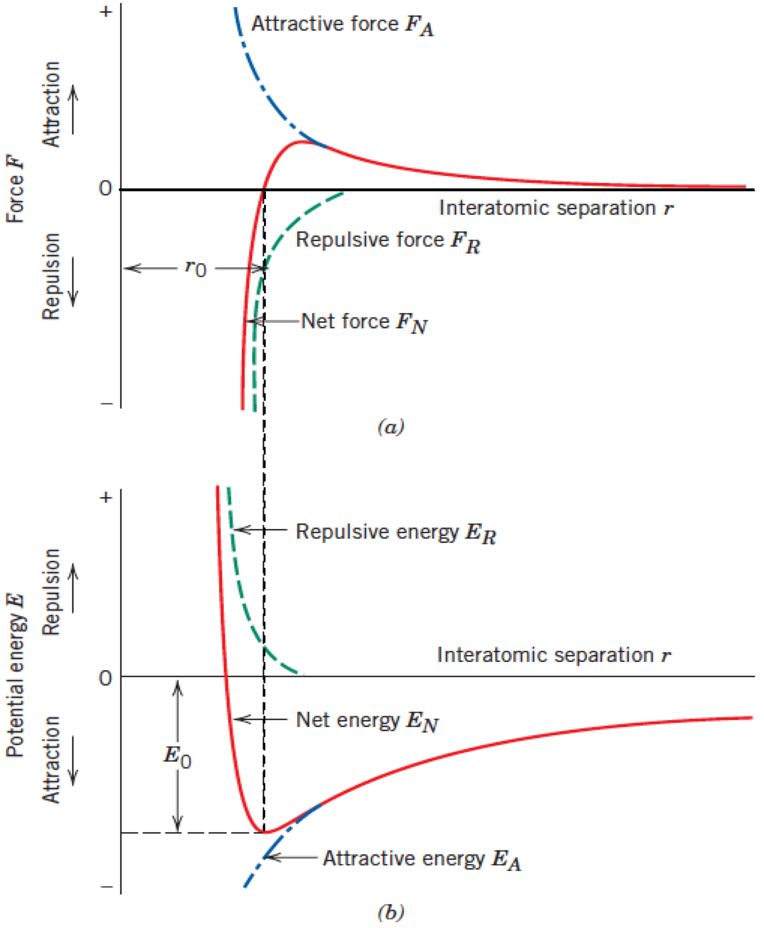
Taken from Rubinstein

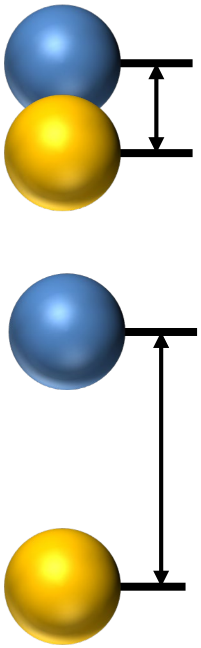
Scanning Probe Microscopy

1986, Binning, Quate, Gerber from IBM first invented AFM.

Basic principle:

Using Van Der Waals force between atoms to characterize the surface properties



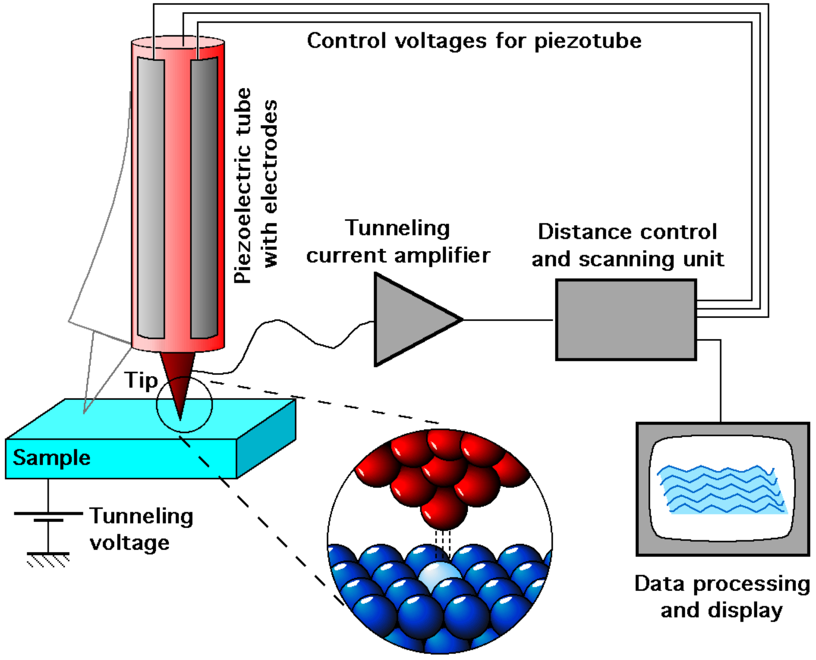


Repulsive force

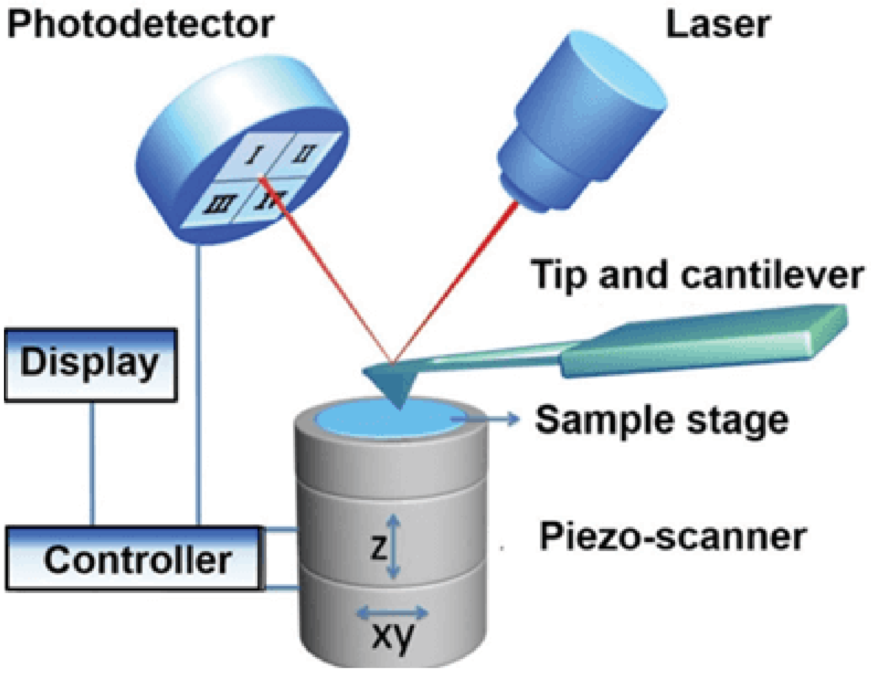
Attractive force

Scanning Probe Microscopies

Scanning Tunneling Microscopy (STM)



Atomic Force Microscopy (AFM)



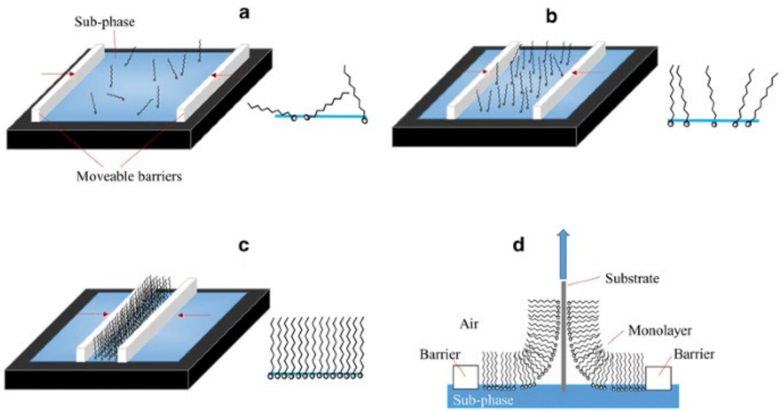
AFM versus STM

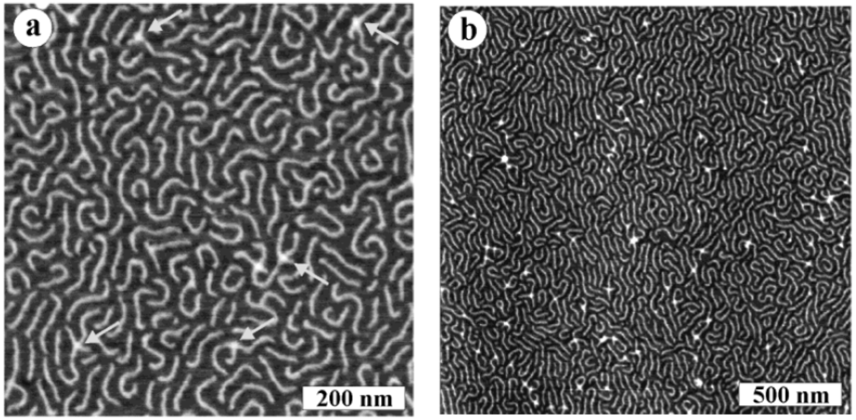
Atomic Force Microscopy	Scanning Tunneling Microscopy
Mechanical probe interacts with sample surfaces through interatomic forces	**Conductive probe** interacts with surface electron states via quantum tunneling
Can image insulators and conductors	Limited to conductive or semiconductive surfaces
Force sensitivity allows high resolution of surface structure and properties	Current sensitivity provides electronic structure and properties
The tip is maintained nanometers from sample surface	The force applied can temporarily deform soft samples
The tip is maintained nanometers from the sample surface	Ambient and liquid imaging are possible
The non-contact technique does not modify the sample	Requires high vacuum conditions
Slower scan rates	Faster scan rates

MW Determination by AFM

Langmuir Blodgett Method

as sample preparation





Individual molecules of polymer B (PBA brushes) were clearly resolved by tapping mode AFM. The higher resolution image (a) demonstrates details of the molecular conformation including crossing molecules indicated by arrows. The larger scale image (b) demonstrates the uniform coverage of the substrate.

Counting number of molecules N of area S_{AFM} giving number of molecules per unit area n_{AFM}: $n_{AFM} = \frac{N}{S_{AFM}}$

From LB the mass per unit area of the polymer is given by $m_{LB} = \frac{c \cdot V}{S_{LB}}$

c: initial conc., S_{LB} area of monolayer

V: volume of polymer solution

Combining (1) + (2):

$$M_n = \frac{m_{LB} \cdot T}{n_{AFM} \cdot m_{am}}$$

T: transfer ratio from LB monolayer to thin film

m_{am}: atomic mass unit 1.6605 x 10^{-24} g

Sergei S. Sheiko, et. al.; J. Am. Chem. Soc. 2003, 125, 6725-6728

Summary

1. The osmotic pressure, Π, of a dilute, uncharged polymer solution is considered. Osmotic pressure measaurements can be used to determine M_n and the second virial coefficient A_2. the latter gives diret information about the solvent quality: $A_2 > 0$ corresponds to a good solvent, and $A_2 < 0$ to a poor solvent.

2.The relation between intrinsic viscosity and molecular weight can be expressed by the Mark-Houwink-Sakurada equation $[\eta] = KM^a$, where the parameters K and a have been tabulated for many polymer and solvent combinations. As $[\eta]$ is relatively easy to measure, this offers a simple route to molecular weight characterization.

3.The technique of SEC is the most commonly applied technique for polymer characterization, as it can determine both average molecular weights and molecular weight distribution. The separation is based on V_h and is of relatively low resolution.

4. Light scattering is a powerful experimental tool, providing both thermodynamic and structural information.
Completely uniform materials do not scatter. Scattering in polymer solutions arises from random fluctuations in concentration. For polymers that are large enough, a significant phase difference can arise between protions of the incident wave that are scattered from different monomers on the same chain. This leads to angle-dependent, or coherent, scattering. The underlying process is very similar to Bragg diffraction from crystals, with the key difference being that in polymer solutions there are onnly average correlations in positions of the various monomers, rather than a permanent lattice.

5. The description of coherent scattering is built around the scattering vector $\vec{q}$. The magnitude of this vector depends on wavelength and scattering angle, and has units of inverse length. Depending on the magnitude of the dimensionless product qR_g, the coherent scattering can give information about the internal structure or the overall size of the polymer. It is often possible to use light scattering to measure R_g in a completely model-independent way.

6. Scanning Probe Microscopies offers the possibility to visualize molecules and determine properties on molecular level depending on the used mode. AFM is a useful method to measure the molecular weight of polymers with complex structure.

7. The concept of a theta solvent emerges as a central feature of polymer solutions. It has 4 equivalent operational definitions:

(a) **the temperature where $A_2 = 0$**
(b) the temperature where the interaction parameter $\chi = ½$
(c) the temperature at which an infinite molecular weight fraction would just precipitate (the limit of the critical temperature T_c as $M \rightarrow \infty$)
(d) a solvent in which $R_g \sim M^{1/2}$