Short Course on Polymer Physics Addis Ababa University

Greg Beaucage Prof. of Chemical and Materials Engineering University of Cincinnati, Cincinnati OH

December 17 2 hours (General Descriptions)

Overview

Physical description of an isolated polymer chain Dimensionality and fractals Short-range and long-range interactions Packing length and tube diameter Questions

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December 18 2 hours (Some Theoretical Basis) Questions

Long-range interactions and chain scaling Flory-Krigbaum theory The semi-dilute and concentrated regimes Blob theory (the tensile, concentration, and thermal blobs) Coil collapse/protein folding Ouestions

December 19 2 hours (Analytic Techniques for Polymer Physics)

Questions Measurement of the size of a polymer chain Rg Rh, Reted Small-angle neutron, x-ray scattering and static light scattering Intrinsic viscosity Dynamic light scattering

Polymer melt rheology

Questions

Polymer Physics

Dr. Greg Beaucage Professor of Chemical and Materials Engineering University of Cincinnati, USA 35,085 undergraduate students 10,054 full-time graduate (6,739 part-time undergraduate students 3,366 part-time graduate) 80.9 percent residents of Ohio

\$532.0 million External Grants (2015) 4,500 full time faculty





US 325,600,000 Ethiopia ~110,000,000







Cincinnati 2,100,000 Addis 3,400,000









Most of Africa is near the equator, this distorts the size in a 2d projection.

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Questions

Structure	Name	Where Used
4-CH	"Vinyf" class	
time In a		
	Polosthylene	Plantic
R = - R	Pulyanopylene	Rope
	DARUS of an and an had readed in the second	Philipping com
R=()	Polystyrene	Denirol cole
R =Cl	Poly(vinyl chloride)	"Viepl", water
		bibes
0		
$R = -O - C - CH_0$	Poly(vinyl aortain)	Lates paints
R = -OH	Puty(vinyl alcohol)	Filter
x	X =H. anylics	
$(-CH_2 - \dot{C} -)_4$	X Cit, astheredies	
0-C-0-R	A = - CHI, accast just	
X = - H. R = - C.H.	Poly(ethyl acrylate)	Lates paints
X = - CH, R = - CH	Poly(methol methacrylate)	Plexights*
X = -CH ₁ , R = C ₁ H ₁	Poly(ethyl methacrylate)	Adhesives
H		
1 m car in in	Polyacrolonitrile*	Orlon*
t-cm-c-s	and the second family should be used	
C=N	"Direct" class	
+ CH ¹ - C = CH - CH ¹ - P.	Evene Case	
R		
R = -H	Polybutadiene	Tarm
$R = -CH_1$	Polyisoprene	Natural rubbe
R = -CI	Polychiloroprese	Netroberne
$(-CX_2 - CR_2 -)_2$	Vinylidenes	mint
X = -H, R = -F	Poly(visylidene fluoride)	Plastic
X = -F, R = -F	Polytetrafluoroethylene	Tellon*
$X = -H, R = -CH_0$	Polyisobutane*	Elastomer
	Common Copolymers	
EPDM	Ethylene-propylene-diene-monomer	Elastomer
SBR	Styrene-butadiene-rubber	Tire rubber
0-C-0-C	Puly/styrene-stat-butadiene/	
NBR	Acrylonitrile-butadiene-rubber	Elastomer
	A up (and particular from disease any second	Plastic
ABS	Automatic Strategy solution	

Polymers



0

	Polyamide 6	the following identifying groups:		1.0, 10
	Polyether	and the second se	0	
	and particulations	Polyenies	-c-	0
	Spandes Lycra®	Polyamides	N	C
Silice	Silver other	Polyurethanes	H	i
	Service report		CH,	
		Silicones	5-	0-
	Lexan®		CH ₃ H	H

Epony resiss

Polyethers

Because of the oxygen atom, poly(ethylene oxide) is water soluble.

-C-C

0

-0-

 $\rightarrow -CH_1 - CH_2 - O - R$

To summarize the material in Table 1.6, the major stepwise polymer classes contain

*Polyacrytonitrile is wohalcally a number of the acrytic class because it forms acrytic acid on hydrolpsis. * T_{CPAC} recommends $+ C_{c} = CH - CH_{1} - CH_{2} - h_{2}$

⁶ Also called polytochetylen. The 2% copolymer with isoprese, after vulcaninetion, is called butyl rubber. ⁷The term-stat-means statistical, as explained in Chapter 2.

"ABS is actually a bland or graft of two random copolymers, poly(acrylonizzie-mar-butadene), and poly (acrylonizzie-mar-styrem).

http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PolymerChemicalStructure.html

renewing build are to P/M, 10.

+CH=CHCH,CH,+

polybutadiene"

poly(1-butenylene)

+ C=CHCH3CH3+

polyisoprene*

poly(1-methyl-1-butenylene)

+ (HCH, +,

polystyrene

poly(1-phenylethylene)

+CHCH₂+, ÔN

polyacry/onitrile poly(1-cyanoethylene)

+ CHCH ; +,

OOCCH,

poly(vinyl acetate)

ĊH,

+ CH, CH, +, polyethylene poly(methylene)

+CHCH2+ ĊH.

polypropylene poly(1-methylethylene)

> CH. +CH2-C+ ĊH,

polyisobutylene poly(1,1-dimethylethylene)

+CHCH,+ ÓĦ poly(vinyl alcohol) poly(1-hydroxyethylene)

12

+CHCH,+ poly(vinyl chloride)

poly(1-acetosyethylene) + CCH27. poly(vinylidene .iuoride) poly(1-chloroeths/ene) poly(1,1-diffuoroethylene)

"Polybutadiene is usually written +CH2CH=CHCH2+, that is, with the double bond in the center. The structure-based name is given. CH₃

*Polyisoprene is usually written +CH2C=CHCH2+

Polymers

+CF2CF2+

poly(tetrafluoroethylene) poly(diffuoromethylene)

> +CHCH2+ COOCH,

poly(methyl acrylate) poly[1-(methoxycarbonyl)ethylene]

+OCH2+

polyformaldehyde poly(oxymethylene)

+NH(CH2),NHCO(CH2),CO+

polyamide 66" poly(hexamethylene adipamide) poly(iminohexamethyleneiminoadipoyl)

OCH2CH2OOC

polyamide 6^b poly(e-caprolactam) poly[imino(1-oxohexamethylene)]

mon name. Other ways this is named include nylon 6,6, 66-nylon, 6,6-nylon, and nylon

poly(ethylene terephthalate) poly(oxyethyleneoxyterephthaloyl)

Code	Letter LD.	Polymer Name
0	PETE	Poly(rilplene terephthalate
2	HDPE	High-density polyethylene
0	V SALES	Puty(vinpl abloride)
2	LDPE	Low-density polyethylene
2	77	Polypropylana
2	n	Polystymme
0	Other	Different polymers

Inwer From the Plastic Container Coale Josters, The Plastic Bottle Information Burnes, Washington, DC

The chemicals above cannot form a polyester because they have only one functional

http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PolymerChemicalStructure.html

-CH2+

C.H.

poly(vinyl butyral) poly[(2-propyl-1,3-dioxane-4, 6-diyl)methylene]

CH₃ C-CH27

COOCH, poly(methyl methacrylate) poly[1-(methoxycarbonyl)-[-methylethylene]

poly(phenylene oxide) poly(oxy-1,4-phenylene)

+OCH2CH2+

+NHCO(CH2)3+

poly(ethylene oxide) poly(oxyethylene)

Polymers

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. I"



Newtonian Fluid Bubbles

| 3

Bubbles in Polymer Solution

Polymer Rheology

http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PolymerChemicalStructure.html



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Polymers

Paul Flory [1] states that "... perhaps the most significant structural characteristic of a long polymer chain... (is) its capacity to assume an enormous array of configurations."

Which are Polymers? http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/Pictu resDNA.html

> http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/What Does Searching Configurational Space Mean for Polymers.html

 Principles of Polymer Chemistry, Flory PJ, (1953). ww.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/WhatIsAPolymerPlastic.html http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/MacroMolecularMaterials.html

Random Walk Generator (Manias Penn State)

nttp://zeus.pimsc.psu.edu/~manias/matSE445/Study/7.ntmr



-Polymers do not have a discrete size, shape or conformation.

-Looking at a single simulation of a polymer chain is of no use.

-We need to consider average features.

-Every feature of a polymer is subject to a statistical description.

-Scattering is a useful technique to quantify a polymer since it describes structure from a statistically averaged perspective.

-Rheology is a major property of interest for processing and properties

-Simulation is useful to observe single chain behavior in a crowded environment etc.



Polymers

Fig. 1-1 Dependence of melting temperatures, T_M , and boiling temperatures, T_{bp} , of alkanes and poly(methylene)s, H(CH₂)_NH, on the number N of methylene groups per molecule [1, 2].



Specific Viscosity versus Concentration for Solutions

Polymers

Squite 11.17. Concentration, dependence of the quantum space in the second state of th

17

From J. R. Fried, "Polymer Science and Technology"





Polymers

If polymers are defined by dynamics why should we consider first statics?

Statistical Mechanics: Boltzmann (1896) Statistical Thermodynamics: Maxwell, Gibbs (1902)

We consider the statistical average of a thermally determined structure, an equilibrated structure

Polymers are a material defined by dynamics and described by statistical thermodynamics



Polymers

In a polymer melt, the viscous properties of Newtonian liquids combine with elastic forces. The latter contribute a real part to the dynamic shear compliance, to be identified with J_c^0 :

$$J'(\omega \to 0) = J_c^0$$
. (6.102)

Combining Eqs. (6.99) and (6.102) gives the dynamic shear compliance of polymeric fluids in the limit of low frequencies

$$J(\omega \rightarrow 0) = J_e^0 + i \frac{1}{\eta_0 \omega}$$
. (6.103)

As we can see, η_0 and J_a^0 show up directly and separately, in the limiting behavior of J' and J".

The dynamic shear modulus follows as

$$G(\omega \rightarrow 0) = \frac{1}{J(\omega \rightarrow 0)} = \frac{\eta_0 \omega}{\eta_0 \omega J_c^0 + 1}$$

= $\frac{\eta_0^2 \omega^2 J_c^0 - i \eta_0 \omega}{(\eta_0 \omega J_c^0)^2 + 1}$, (6.104)

-0.2.3

giving

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$$G'(\omega \rightarrow 0) = J_{\pm}^{*} \eta_{0}^{*} \omega^{*}$$

in agreement with Fig. 6.16, and

 $G''(\omega \to 0) = \eta_0 \omega$. (6.106)

(6.105)

We thus find characteristic power laws also for the storage and the loss modulus that again include J_a^0 and η_0 in a well-defined way.





Consider that all linear polymer chains can be reduced to a step length and a free, universal joint This is the Kuhn Model and the step length is called the Kuhn length, I_K

This is extremely easy to simulate I)Begin at the origin, (0,0,0) 2)Take a step in a random direction to (i, j, k) 3)Repeat for N steps

On average for a number of these "random walks" we will find that the final position tends towards (0,0,0) since there is no preference for direction in a "random" walk

The walk does have a breadth (standard deviation), i.e. depending on the number of steps, N, and the step length $I\kappa$, the breadth of the walk will change.

IK just changes proportionally the scale of the walk so $<\!R^2\!>^{1/2}\sim I_K$

The walk does have a breadth, i.e. depending on the number of steps, N, and the step length I_K , the breadth of the walk will change.

IK just changes proportionally the scale of the walk so $<\!R^2\!>^{1/2}\sim I_K$

The chain is composed of a series of steps with no orientational relationship to each other. So $\langle R \rangle = 0$ $\langle R^2 \rangle$ has a value:

$$\langle R^2 \rangle = \sum_i \sum_j r_i \cdot r_j = \sum_i r_i \cdot r_i + \sum_i \sum_{j \neq i} r_i \cdot r_j$$

We assume no long range interactions so that the second term can be 0.

$$\langle R^2 \rangle = Nr^2$$

$$< R^2 > 1/2 \sim N^{1/2} I_K$$

This function has the same origin as the function describing the root mean square distance of a diffusion pathway $(R^2)^{1/2} \sim t^{1/2}(2D)^{1/2}$ So the Kuhn length bears some resemblance to the diffusion coefficient

And the random walk polymer chain bears some resemblance to Brownian Motion

The random chain is sometimes called a "Brownian Chain", a drunken walk, a random walk, a Gaussian Coil or Gaussian Chain among other names.

Random Walk Generator (Manias Penn State)

nttp://zeus.pimsc.psu.edu/~manias/MatSE445/Study/7.ntmr



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The Primary Structure for Synthetic Polymers

Worm-like Chain Freely Jointed Chain Freely Rotating Chain Rotational Isomeric State Model Chain (RISM) Persistent Chain Kuhn Chain

These refer to the local state of the polymer chain.

Generally the chain is composed of chemical bonds that are directional, that is they are rods connected at their ends.

These chemical steps combine to make an effective rod-like base unit, the persistence length, for any synthetic polymer chain (this is larger than the chemical step).

The persistence length can be measured in scattering or can be inferred from rheology through the Kuhn length

Ικ = 2 Ι_Ρ

The Primary Structure for Synthetic Polymers



The synthetic polymer is composed of linear bonds, covalent or ionic bonds have a direction.

Coupling these bonds into a chain involves some amount of memory of this direction for each coupled bond.

Cumulatively this leads to a persistence length that is longer than an individual bond.

Observation of a persistence length requires that the persistence length is much larger than the diameter of the chain. Persistence can be observed for worm-like micelles, synthetic polymers, DNA but not for chain aggregates of nanoparticles, strings or fibers where the diameter is on the order of the persistence length.

> http://www.eng.uc.edu/~gbeaucag/Classes/Introto PolySci/PicturesDNA.html

Boltzman Probability For a Thermally Equilibrated System

$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability For a Chain of End to End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

By Comparison The Energy to stretch a Thermally Equilibrated Chain Can be Written

$$E = kT \frac{3R^2}{2nl_K^2}$$

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By Comparison The Energy to stretch a Thermally Equilibrated Chain Can be Written



$$F = \frac{dE}{dR} = \frac{3kT}{nl_K^2}R = k_{spr}R$$

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Assumptions: -Gaussian Chain -Thermally Equilibrated -Small Perturbation of Structure (so it is still Gaussian after the deformation)

$$E = kT \frac{3R^2}{2nl_K^2}$$

Boltzman Probability For a Thermally Equilibrated System

$$P_{B}(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

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$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

Use of P(R) to Calculate Moments:

$$\left\langle R^{n}\right\rangle = \int_{-\infty}^{\infty} R^{n} P(R) dR$$

Mean is the I'st Moment:

$$\langle R \rangle = \int_{-\infty}^{\infty} RP(R) dR = 0$$

Boltzman Probability For a Thermally Equilibrated System

$$P_{\beta}(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability For a Chain of End to End Distance R

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This is a consequence of symmetry of the Gaussian function about 0.

Boltzman Probability For a Thermally Equilibrated System

$$P_{B}(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

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Gaussian Probability For a Chain of End to End Distance R

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Use of P(R) to Calculate Moments:

$$\left\langle R^{n}\right\rangle = \int_{-\infty}^{\infty} R^{n} P(R) dR$$

Mean Square is the 2'ndMoment:

$$\langle R^2 \rangle = \int_{-\infty}^{\infty} R^2 P(R) dR \equiv \sum_{i=0}^{N} \sum_{j=0}^{N} r_i \cdot r_j = Nr^2$$

Gaussian Probability For a Chain of End to End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{1}{2}} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

Mean Square is the 2'ndMoment:

$$\left\langle R^2 \right\rangle = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} R^2 \exp\left(-\frac{3R^2}{2\sigma^2}\right) dR$$

There is a problem to solve this integral since we can solve an integral of the form $k \exp(kR) dR$ $R \exp(kR^2) dR$ but not $R^2 \exp(kR^2) dR$

There is a trick to solve this integral that is of importance to polymer science and to other random systems that follow the Gaussian distribution.

$$\left\langle R^{2} \right\rangle = \frac{\int_{-\infty}^{\infty} R^{2} P_{G}(R) dR}{\int_{-\infty}^{\infty} P_{G}(R) dR} = \frac{\int_{-\infty}^{\infty} R^{2} \exp\left(\frac{R^{2}}{k^{2}}\right) dR}{\int_{-\infty}^{\infty} \exp\left(\frac{R^{2}}{k^{2}}\right) dR}$$
(3)

These integrals require a trick to solve. First the integral is squared in x and y: $G(\alpha) = \int_{-\infty}^{\infty} \exp(-\alpha x^{2}) dx$ $(G(\alpha))^{2} - \int_{-\infty}^{\infty} \exp(-\alpha x^{2}) dx \int_{-\infty}^{\infty} \exp(-\alpha y^{2}) dy - \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp(-\alpha (y^{2} + x^{2})) dy$ Then Cartesian coordinates are replaced with circular coordinates, r and θ , $(G(\alpha))^{2} = \int_{0}^{\infty} r dr \int_{0}^{2\pi} d\theta \exp(-\alpha r^{2}) = 2\pi \int_{0}^{\infty} r dr \exp(-\alpha r^{2})$ $= \frac{-2\pi}{2\alpha} \int_{0}^{\infty} -2\alpha r dr \exp(-\alpha r^{2}) = \frac{-\pi}{\alpha} \left[\exp(-\alpha r^{2}) \right]_{0}^{\infty} = \frac{\pi}{\alpha}$ The integral in the numerator can be solved by another trick, $H(\alpha) = \int_{-\infty}^{\infty} x^{2} \exp(-\alpha x^{2}) dx = -\frac{dG(\alpha)}{d\alpha}$

and since $G(\alpha) = (\pi/\alpha)^{1/2}$, then $H(\alpha) = \frac{\pi^{1/2}}{2\alpha^{3/2}}$ so, with $\alpha = 1/k^2$ and x = R,

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$$\left\langle R^2 \right\rangle = \frac{\int\limits_{-\infty}^{\infty} R^2 \exp\left(\frac{R^2}{k^2}\right) dR}{\int\limits_{-\infty}^{\infty} \exp\left(\frac{R^2}{k^2}\right) dR} = \frac{H(\alpha)}{G(\alpha)} = \frac{k^3 \pi^{3/2}/2}{k \pi^{3/2}} = \frac{k^2}{2}$$
(4)

http://www.eng.uc.edu/~gbeaucag/Classes/Properties/GaussianProbabilityFunctionforEnd.pdf
Gaussian Probability For a Chain of End to End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

Mean Square is the 2'nd Moment:

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$$\left\langle R^2 \right\rangle = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} R^2 \exp\left(-\frac{3R^2}{2\sigma^2}\right) dR = \sigma^2 \equiv nl_K^2$$

So the Gaussian function for a polymer coil is:

$$\left\langle R^2 \right\rangle = \left(\frac{3}{2\pi n l_K^2}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} R^2 \exp\left(-\frac{3R^2}{2n l_K^2}\right) dR$$

$$\langle R^2 \rangle = n l_K^2$$

Means that the coil size scales with n^{1/2} Or Mass ~ n ~ Size² Generally we say that Mass ~ Size^{df} Where df is the mass fractal dimension A Gaussian Chain is a kind of 2-dimensional object like a disk.

$$\langle R^2 \rangle = n l_K^2$$

A Gaussian Chain is a kind of 2-dimensional object like a disk.

The difference between a Gaussian Chain and a disk lies in other dimensions of the two objects.

Consider an electric current flowing through the chain, it must follow a path of n steps. For a disk the current follows a path of $n^{1/2}$ steps since it can short circuit across the disk. If we call this short circuit path p we have defined a connectivity dimension c such that: $p^c \sim n$ And c has a value of 1 for a linear chain and 2 for a disk

$$\langle R^2 \rangle = n l_K^2$$

A Gaussian Chain is a kind of 2-dimensional object like a disk. A linear Gaussian Chain has a connectivity dimension of I while the disk has a connectivity dimension of 2.

The minimum path p is a fractal object and has a dimension, d_{min} so that, p ~ R^{dmin} For a Gaussian Chain $d_{min} = 2$ since p is the path n For a disk $d_{min} = 1$ since the short circuit is a straight line.

We find that $d_f = c d_{min}$

There are other scaling dimensions but they can all be related to two independent structural scaling dimensions such as c and d_{min} or d_{min} and d_f



Random Coil



Unfolded Gaussian chain





How Complex Mass Fractal Structures Can be Decomposed



isornal of Polymer Science: Part B: Polymer Physics, Vol. 36, 3147-3154 (199



(10)

Figure 1. Micrographs of GMF sample showing micron-scale silica glass fibers in a polymer-like mat. (a) SEM micrograph after gold coating. This size scale corresponds to the persistence regime and the high-q end of the scaling regime. (b) Optical micrograph at 20%. This size scale would correspond to the scaling regime of Figure 2 below. Fibers follow either Gaussian or Self-avoiding structure depending on binding of fibers





region at long to be yet of the source of the second secon

Figure 5. Orientation function and SALS data for GMF in cross-section as a function of q. Perpendicular and parallel are with respect to the plane of the mat.

Orientation partly governs separation

Pore size and fractal structure govern wicking



Figure 6. Cumulative pore volume vs. pore size from SALS and from capillary porosimetry.

Short-Range Interactions

The persistence length is created due to interactions between units of the chain that have similar chain indices

These interactions are termed "short-range interactions" because they involve short distances along the chain minimum path

Short-range interactions lead to changes in the chain persistence. For example, restrictions to bond rotation such as by the addition of short branches can lead to increases in the persistence length in polymers like polyethylene. Short-range interactions can be more subtle. For instance short branches in a polyester can disrupt a natural tendency to form a helix leading to a reduction in the persistence length, that is making the chain more flexible.

All interactions occur over short spatial distances, short-range interactions occur over short-distances but the distinguishing feature is that they occur over short differences in chain index.

Short-range interactions do not have an effect on the chain scaling.

Short-Range Interactions

Consider the simplest form of short range interaction We forbid the chain from the preceding step

Consider a chain as a series of steps ri ri is a vector of length r and there are n such vectors in the chain

The mean value for r_{i+1} is 0

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$$\left\langle r_{i+1}\right\rangle = \sum_{k=1}^{k=z} b_k = 0$$

bk is a unit vector in a coordinate system,6 of these vectors in a cubic system

Short-Range Interactions

$$\langle r_{i+1} \rangle = \sum_{k=1}^{k=z} b_k = 0$$

For exclusion of the previous step this sum does not equal 0

$$\langle r_{i+1} \rangle_{Random} = \sum_{k=1}^{k=z} b_k = 0 = (z-1) \langle r_{i+1} \rangle_{ShortRangeInteraction} - r_i$$

so

$$\langle r_{i+1} \rangle_{ShortRangeInteraction} = \frac{r_i}{(z-1)}$$

Short-Range Interactions

$$\langle r_{i+1} \rangle_{ShortRangeInteraction} = \frac{r_i}{(z-1)}$$

For Gaussian Chain

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 $\langle R^2 \rangle = \sum_i \sum_j r_i \cdot r_j = \sum_i r_i \cdot r_i + \sum_i \sum_{j \neq i} r_i \cdot r_j$ yields $\langle R^2 \rangle = Nr^2$

For SRI Chain the first term is not 0.

$$\langle r_i \cdot r_j \rangle = \frac{b^2}{(z-1)^{|i-j|}}$$
 and $\langle R^2 \rangle = \sum_{i=1}^n \sum_{j=1}^n \langle r_i \cdot r_j \rangle \cong \sum_{i=1}^n \sum_{k=-\infty}^\infty \frac{b^2}{(z-1)^{|k|}} = nb^2 \frac{z}{z-2} = nb_{effective}^2$

The second to the last equality is the result of the Sum of Geometric Progression Rule, lim n-> ∞ of a + ar + ar² +... = a/(1-r) substituting x=1/(z-1) results in 2/(1-x) - 1 = 2(z-1)/(z-2) - 1 = z/(z-2)

For Cartesian simulation z = 6 and beff is 1.22 b so about a 25% increase for one step selfavoidance. http://www.enguc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

Short-Range Interactions

Short-Range Interactions Increase the persistence length

Chain scaling is not effected by short-range interactions.

http://www.eng.uc.edu/~gbeaucag/Gasses/Physics/Chapter1.pdf

Short-Range Interactions

What kinds of short-range interactions can we expect

- -Bond angle restriction
- -Bond rotation restriction
- -Steric interactions
- -Tacticity
- -Charge (poly electrolytes)
- -Hydrogen bonds
- -Helicity

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter I.pdf

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction

-Bond rotation restriction

Characteristic Ratio, C.

Polymer C (M = ∞ Polyethylene 0.7
Polyethylene 0.7
Polyethyleneoxide 4.0
Polystyrene, atactic 10.0

Source: Flory (1989) *See eq. (2.7).

$$\left\langle R^{2} \right\rangle = n_{Kuhn} l_{Kuhn}^{2} = L l_{Kuhn} = C_{\infty} n_{Bond} l_{Bond}^{2} = C_{\infty} L l_{Bond}$$
$$l_{Kuhn} \sim b_{Effective}$$

$$C_{\infty} = \frac{l_{Kuhn}}{l_{Bond}}$$

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http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter I.pdf

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction -Bond rotation restriction



Figure 7. The persistence length plots, (f_{μ}^{\pm}) , obtained via eq 10, versus segment number, k, for various semiflexible, linear polymers, each of length 48. The strength of the intrinsic stiffness is varied between polymers by increasing the strength of the bending penalty, $\lambda_{\mu\nu}$ from 0 (bottom)...5, 10 (top).

Macromoleculos 8865, 16, 5268-5298

'Intrinsic' and 'Topological' Stiffness in Branched Polymers

Bonan Connelly,' Govanni Beliosia,' Edward G. Timodoniko,''' Yuri A. Kumetsev,' Nefano Elk,' and Fahir Ganazooli'

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$$C_{\infty} = \frac{l_{Kuhn}}{l_{Bond}}$$

The Characteristic Ratio varies with N due to chain end effects. There is generally an increase in C with N and it plateaus at high molecular weight.

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction -Bond rotation restriction -Steric interactions -Tacticity -Charge (poly electrolytes) -Hydrogen bonds -Helicity

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction -Bond rotation restriction





1.20 1.80

http://cbp.tnw.utwente.nl/PolymeerDictaat/node4.html

Polyethylene

http://www.eng.uc.edu/~gbeaucag/Gasses/Physics/Chapter1.pdf

-180 -120 -00

c, Accal mol-

Figure 1.2: Dihedral angle energy of n-butane.

0

60

ð

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction -Bond rotation restriction



Figure 3.2 Conformational energy of ethane as a function of torsion angle.





Figure 2.4 Conformational energy of n-butane as a function of tomion angle of the central carbon-carbon bond. The outer carbon-carbon bonds are assumed to be in their minimum energy states (staggered positions).



Butane

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http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter I.pdf

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction

-Bond rotation restriction

Characteristic Ratio, C.

$C (M = \infty)^{*}$
0.7
4.0
10.0

Source: Flory (1989) *See eq. (2.7).

$$\left\langle R^{2} \right\rangle = n_{Kuhn} l_{Kuhn}^{2} = L l_{Kuhn} = C_{\infty} n_{Bond} l_{Bond}^{2} = C_{\infty} L l_{Bond}$$
$$l_{Kuhn} \sim b_{Effective}$$

$$C_{\infty} = \frac{l_{Kuhn}}{l_{Bond}}$$

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http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter I.pdf

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction -Bond rotation restriction

$$C_{\infty} = \frac{l_{Kuhn}}{l_{Bond}}$$

Consider a freely rotating chain that has a bond angle restriction of 109.5 $^\circ$

The scalar product of the arbitrary segment vectors $\tilde{\mathbf{r}}_i$ and $\tilde{\mathbf{r}}_i$ is:

 $\langle \hat{\mathbf{r}}, \hat{\mathbf{r}}, \rangle = l^2 \langle \cos \theta_z \rangle$ (2.14)

where θ_c is the angle between the two bond vectors. The following relationship is obtained by combining eqs (2.13) and (2.14):

$$\begin{split} \langle r^2 \rangle &= \kappa l^2 + 2 l^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \cos \theta_{ij} \rangle \\ &= \begin{bmatrix} l^2 &+ l^2 \langle \cos \theta_{ij} \rangle + \cdots + l^2 \langle \cos \theta_{ij} \rangle + \\ l^2 \langle \cos \theta_{2i} \rangle + &l^2 &+ \cdots + l^2 \langle \cos \theta_{2i} \rangle + \\ \cdots &\cdots &\cdots &\cdots \\ l^2 \langle \cos \theta_{ij} \rangle + l^2 \langle \cos \theta_{ij} \rangle + \cdots + &l^2 \end{bmatrix} \end{split}$$

Equation (2.15) is still a general formulation and is

valid for any continuous polymer chain.

Polymer physics By UIT W. Godde

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter I.pdf

Short-Range Interactions

Consider a freely rotating chain that has a bond angle restriction of 109.5 $^\circ~$ = τ

$$\langle \bar{\mathbf{r}}_{i} \bar{\mathbf{r}}_{i+1} \rangle = l^{2} \cos(180 - \tau)$$

$$\langle \bar{\mathbf{r}}_{i} \bar{\mathbf{r}}_{i+2} \rangle = l^{2} \cos^{2}(1\dot{8}0 - \tau)$$

$$\langle \bar{\mathbf{r}}_{i} \bar{\mathbf{r}}_{j} \rangle = l^{2} [\cos(180 - \tau)]^{l-i}$$

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} [\cos(180 - \tau)]^{j-i}$$

$$= \begin{bmatrix} l^2 + l^2 \cos(180 - \tau) + \dots + l^2 [\cos(180 - \tau)]^{n-1} + \\ l^2 \cos(180 - \tau) + l^2 + \dots + l^2 [\cos(180 - \tau)]^{n-2} + \\ \dots & \dots & \dots & + \\ \dots & \dots & \dots & \dots & + \\ l^2 [\cos(180 - \tau)]^{n-1} + \dots & \dots & l^2 \end{bmatrix}$$
(2.17)

The summation can be performed over a single variable (k) by substituting j = i by k:

$$\langle r^{2} \rangle = n^{2} \left[1 + \frac{2}{n} \sum_{k=1}^{n-1} (n-k) \alpha^{k} \right]$$
 (2.18)

where $\alpha = \cos(180 - \tau)$.

Polymer physics By Ulf W. Gedde Equation (2.18) can be simplified as follows:

$$\begin{split} \langle r^{2} \rangle &= n l^{2} \bigg[1 + \frac{2}{n} \sum_{k=1}^{n-1} (n-k) \alpha^{k} \bigg] \\ &= n l^{2} \bigg[1 + 2 \sum_{k=1}^{n-1} \alpha^{k} - \frac{2}{n} \sum_{k=1}^{n-1} k \alpha^{k} \bigg] \\ &= n l^{2} \bigg[1 + \frac{2(n-\alpha^{n})}{1-\alpha} - \frac{2}{n} \left(\frac{\alpha(1-\alpha)^{n}}{(1-\alpha)^{2}} - \frac{n\alpha^{n}}{1-\alpha} \right) \bigg] \\ &= n l^{2} \bigg[1 + \frac{2\alpha}{1-\alpha} - \frac{2\alpha}{n} \frac{(1-\alpha)^{n}}{(1-\alpha)^{2}} \bigg] \end{split}$$

Short-Range Interactions

Consider a freely rotating chain that has a bond angle restriction of 109.5 $^{\circ}$ = τ





For infinitely long chains
$$(n = \infty)$$
:
 $\langle r^2 \rangle = nl^2 \left[1 + \frac{2\pi}{1-\pi} \right] = nl^4 \left[\frac{1+\pi}{1-\pi} \right]$
 $= nl^2 \left[\frac{1 + \cos(180 - \tau)}{1 - \cos(180 - \tau)} \right]$ (2.19)

$$\langle r^2 \rangle \approx 2nl^2$$

Table 2.1 C values for some polymers under theta conditions

Polymer	$C (M = \infty)$	
Polyethylene Polyethyleneoxide Polyethyleneoxide	6.7 4.0 E	- Kond angles 109.5°: 104.5°
rotystytene, atactic	10.0	

Source: Flory (1989) *See eq. (2.7).

Moderate Flexibility

High Rotational Flexibility Lower Rot. Flexibility

 $C_{\infty} = \frac{l_{Kuhn}}{l_{Bond}} = 1.40$

For a Freely Rotating Polyethylene Chain

http://books.google.com/books?id=Iem3fC7XdnkC&pg=PA23&lpg=PA23&dq=coil+expansion+factor &source=bl&ots=BGRfhZYaU&sig=10OPb2VRuf8Dm&qnrmrhyjXyEC&&hl=en&sa=X&ei=fSV0T-XqMMHVV0QHII-T Ag8ved=0CF0Q6AEwBw#v=onepage&q=coil%20expansion%20factor&f=false

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Short-Range Interactions

Consider a freely rotating chain that has a bond angle restriction of 109.5 $^\circ~$ = τ

Table	2.1	C values	for	some	polymers	under
theta o	cond	itions				

Polymer	$C (M = \infty)^{s}$
Polyethylene	6.7
Polyethyleneoxide	4.0
Polystyrene, atactic	10.0

Source: Flory (1989)

*See eq. (2.7).

 $\langle r^2 \rangle \approx 2nl^2$

$$C_{\infty} = \frac{l_{Kuhn}}{l_{Bond}}$$

If we consider restrictions to bond rotation for first order interactions

$$C_{\infty} = \frac{l_{Kuhn}}{l_{Bond}} \Longrightarrow 3.4$$

which is lower than the experimentally obtained (6.7 \pm 0.1) n^{p} (Table 2.1). Agreement with experimental data is obtained by also considering higher-order interactions. Flory showed that an analysis using second-order interactions brings the predicted data closer to the experimental data.

http://books.google.com/books?id=lem3fC7XdnkC&pg=PA23&lpg=PA23&dq=coil+expansion+factor &scurce=bl&ots=BGjRfnZYaU&sig=10OPb2VRuf8DmBqnmmthyjXyEC&&h1=en&sa=X&ei=fSV0T-XqMMHV0QHi1-T Ag&ved=0CF0Q6AEwBw#A=onepage&q=coil%20expansion%20factor&f=false

Polymer physics By Ulf W. Gedde

Short-Range Interactions

theta conditions		
Polymer	$C (M = \infty)^{\mu}$	
Polyethylene	6.7	
Polyethyleneoxide	4.0	
Polystyrene, atactic	10.0	

Table 2.1 C values for some polymers under

Source: Flory (1989) * See eq. (2.7).

> Polymer physics By Ulf W. Gedde

hilymer physics: from basic concepts to modern developments 55 Solf and flexible chains these the Kuhn segment length I to characterise stiffness. The value of I is in larger than the contour length per monomer unit lp. The ratios 1/lp for some solvmers are shown below. poly(ethylene oxide) 2.5 poly(propylene) poly(methyl methacrylate) 3 4 poly(vinyl chloride) 4 poly(styrene) 5 poly(acrylamide) 6.5 26 cellulose diacetate poly(para-bennamide) 200 DNA (in double belix) 300 poly(benzyl glutamate) (in o-belix) 500 a macroscopic viewpoint, a polymer chain can be always represented locally as linearest which is characterized by two microscopic lengths: the Kubs reparent

We have a subscription in this balance of the fibrare of a characteristic disserter d. (This describes the thickness of the set.) Depending on the ratio between these two lengths, we can now introduce the of stiff and flexible chains. Stiff chains are those for which $1 \gg d$, while for fit sets $\ell \gg d$. Some examples of stiff chains are DNA, belied polypeptides, aromatic institution, i.e., Examples of flexible chains are polyrethylene, polypeptides, aromatic institution, i.e., polymers having a single-chain carbon backbone.

Alexei Khokhlov in Soft and Fragile Matter (2000)

Contour length per monomer is 2 * bond length

 $C_{\infty} = \frac{l_{Kuhn}}{l_{Bond}}$

Short-Range Interactions

Persistence Length, Ip (Arun Yethiraj J. Chem. Phys. 125, 204901 (2006))

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Several Definitions

definitions are in terms of the projection of the end-to-end vector, R, on a bond vector, averaged over all conformations, i.e.,

$$l_{i} = \langle \mathbf{R} \cdot \mathbf{u}_{i} \rangle$$
, (2)

where \mathbf{u}_k is the (normalized) bond vector between sites k and k+1. Flory²¹ defined the persistence length as the average projection of \mathbf{R} on an interior bond vector \mathbf{u}_m far from any chain ends, while Yamakawa²¹ defined the persistence length as l_1 , i.e., the projection of \mathbf{R} on the first bond. One can also define the persistence length in terms of the bond angle correlation function, (cos $\theta(s)$), where θ is the angle between bond vectors separated by s segments along the backbone. For an ideal semiflexible chain (cos $\theta(s)$)~ exp($-st/\lambda_c$), where λ_c is a persistence length.

For the purposes of comparing the stiffness of molecules with different length and spacing of branches, we define the persistence length, l_{μ} , in terms of the wormlike chain. In this model,²⁰ the mean-square end-to-end distance, $\langle R^2 \rangle$, is given by

$$\langle R^2 \rangle = \frac{L}{\lambda} - \frac{1}{2\lambda^2} (1 - e^{-2\lambda L}),$$
 (3)

where L is the contour length and λ is a parameter that characterizes the stiffness. We define the persistence length as twice the value of l_1 for this model, i.e.,

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$$l_p = \frac{1}{\lambda}(1 - e^{-2\lambda l}).$$
 (4)

 ¹⁰ P. J. Flory, Statistical Mechanics of Chain Molecules (Wiley-Interscience, New York, 1969).
 ¹¹ H. Yamakawa, Modern Theory of Polymer Solutions (Harper & Row,

- Tamazwa, stokern Theory of Polymer Solations (traper & Kow New York, 1971).
- ²⁰O. Kratky and G. Porod, Recl. Trav. Chim. Pays-Bas 68, 1106 (1949).

-Appendix of Flory's book, **Iin**. -Yamakawa's book is online, **II**. -Bond Angle Correlation, λC. -Kratky-Porod Worm-like Chain Model, **Ip**.

Scattering Observation of the Persistence Length

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Figure 2. Kratky/Porod graphical analysis in a log-log plot of corrected SANS data from a 5% by volume d-PHB sample in h-PHB. The lower power -2 line is the best visual estimate; the upper line is shifted to match a global unified fit. Key: left, q* corresponds to best visual estimate; right, plot to match global unified fit. The statistical error in the data is shown [3].

A power-law decay of -I slope has only one structural interpretation.

Consider a Brownian path with an index or continuous postion variable "s". For the simulated walks "s" is the time. For a polymer chain "s" is the chain index. Next consider an arbitrary origin of a coordinate system (0,0,0) and vectors to positions of the walk $\mathbf{r}(s)$. The unit tangent vector to the walk, $\mathbf{t}(s)$, is defined by,



Figure 1. Brownian Path.

The end-to-end distance for the Brownian path is given by,

$$\overline{R} = \int_{0}^{L} \overline{t}(s) ds$$
(2)

http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplex/Materials/Persistence/Persistence.html

The auto-correlation function for the tangent vector can be written,

$$\langle t(s) \bullet t(0) \rangle = e^{-s/l_p}$$
⁽³⁾

if a linear decay in correlation can be assumed. That is,

$$d(\langle t(s) \bullet t(0) \rangle) = -\langle t(s) \bullet t(0) \rangle \left(\frac{1}{l_p}\right) ds$$

(4)

The persistence length is then similar to the linear absorption coefficient for radiation.

(2) and (3) can be used to calculate the mean square end-to-end distance \underline{R}^2 ,

$$\begin{split} \left\langle R^2 \right\rangle &= \left\langle \overline{R} \bullet \overline{R} \right\rangle = \left\langle \int_0^L \overline{t}(s) ds \bullet \int_0^L \overline{t}(s') ds' \right\rangle = \int_0^L \left(ds \int_0^L \left\langle \overline{t}(s) \bullet \overline{t}(s') \right\rangle ds' \right) = \int_0^L \left(ds \int_0^L \exp\left(\frac{-|s-s'|}{l_p}\right) ds' \right) \\ &= 2l_p L \left(1 - \frac{l_p}{L} \left(1 - e^{-L/l_p} \right) \right) \cong 2l_p L \end{split}$$

We also can consider that for a freely jointed chain composed of nK Kuhn steps of length lK,

$$\left\langle R^2 \right\rangle = n_{\kappa} l_{\kappa}^2 = l_{\kappa} L = 2 l_{p} L$$

Showing that the freely jointed Kuhn length is just twice the persistence length.

Other measures of Local Structure

Kuhn Length, Persistence Length: Static measure of step size

Tube Diameter: Dynamic measure of chain lateral size

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Packing Length: Combination of static and dynamic measure of local structure

Packing Length and Tube Diameter

Chain dynamics in the melt can be described by a small set of "physically motivated, material-specific paramters"

Tube Diameter dτ Kuhn Length lκ Packing Length p



Strobel Chapter 8

$$u = q^2 a_{\rm R}^2 \left(\frac{t}{\tau(\delta=\pi)} \right)^{1/2} = q^2 \left(\frac{12kT a_{\rm R}^2 t}{\zeta_{\rm R}} \right)^{1/2}$$

u reflects Rouse behavior. In plots versus u,

deviations from ideal Rouse Behavior indicate tube constraints.



Fig. 8.8. Results of a quasichestic neutron scattering experiment on a solit of particular lines corporations) at 190°C (1965 protonated chains disordered in a designand matrix: $M = 8.6 \cdot 10^{9}$): Intermediate matrixing have measured at the indimetric antioning vectors (ine); data representation using the dimensionless vectories is $m_{1}^{-1}(1200 M_{10}^{-1})^{-1}$ (indication). Relative et al. [87]



Quasi-elastic neutron scattering data demonstrating the existence of the tube

Unconstrained motion => S(q) goes to 0 at very long times

Each curve is for a different q = 1/size

At small size there are less constraints (within the tube)

At large sizes there is substantial constraint (the tube)

By extrapolation to high times a size for the tube can be obtained $d\tau$



Iulia Higgins Review Article (2016)



There are two regimes of hierarchy in time dependence Small-scale unconstrained Rouse behavior Large-scale tube behavior

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We say that the tube follows a "primitive path" This path can "relax" in time = Tube relaxation or **Tube Renewal**

A model called **Tube Dilation** also exists to describe deviations between the tube model and experiment

Without tube renewal the Reptation model predicts that viscosity follows N^3 (observed is $N^{3.4})$



Without tube renewal the Reptation model predicts that viscosity follows N³ (observed is N^{3.4})



Reptation predicts that the diffusion coefficient will follow N^2 (Experimentally it follows N^2) Reptation has some experimental verification

Where it is not verified we understand that tube renewal is the main issue.

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(Rouse Model predicts $D \sim I/N$)

Reptation of DNA in a concentrated solution



Fig. 6.13. Series of images of a fluorescently stained DNA chain embedded in a concentrated solution of unstained chains: Initial conformation (*left*); partial stretching by a rapid move of the bead at one end (*second from the left*); chain recoil by a reptative motion in the tube (*subsequent pictures to the right*). Reprinted with permission from T.Perkins, D.E.Smith and S.Chu. *Science*, 264:819, 1994. Copyright (1994) American Association for the Advancement of Science
Simulation of the tube



Fig. 3. Result of the primitive-path analysis of a melt of 200 chains of N + 1 = 350 beads. We show the primitive path of one chain (red) together with all of those it is entangled with (blue). The primitive paths of all other chains in the system are shown as thin lines.



Fig. 3. A representative amorphous polymer sample and the corresponding network of primitive paths.

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Simulation of the tube

Packing Length

Origin of the Packing Length:

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Contemporary Topics in Polym, Sci. Vol. 6 Multiphase Macromolecular Systems, Culbertson BM Ed. Theory of Stress Distribution in Block Copolymer Microdomains, Witten TA, Milner ST, Wang Z-G p. 656

Consider a di-block copolymer domain interface (and blends with homopolymers as a compatibilizer)



http://pubs.rsc.org/en/content/articlehtml/2012/cs/c2cs35115c



Fig. 3 Schematic illustration of the possible polymer chain arrangements in different morphologies of AB diblocks changing from sphere (a) to cylinder (b) and to lamella (c), as the volume fraction (f_A) of the A block (black) increases to ~0.5. The dash curve in each morphology represents a part of the interface between A and B domains. The concept of this figure originates from ref. 24. This reference contributes to BCP self-assembly in solution, and is cited accordingly in Section 3.1.

http://pubs.rsc.org/en/content/articlehtml/2012/cs/c2cs35115c

Free Energy Contributions:

Interfacial Energy Proportional to the Total Surface Area (makes domains large to reduce surface area) $Sur = \chi kTAdt/Vc$

dt is the thickness of the interfacial layer where the A-B junction is located

A is the cross sectional area of a polymer chain

 $V_{\mbox{\scriptsize c}}$ is the occupied volume of a unit segment of a polymer chain

The total occupied volume of a block copolymer chain is Voccupied = NABVc;

This occupied volume is also given by $V_{occupied} = d_{AB} A$ where d_{AB} is the length of the block copolymer chain assuming it forms a cylindrical shaped object and the block copolymer domain spacing.

Energy of Elongation of Polymer Chains, Elastic Energy

(makes domains small)

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Assumes that one end is at the interface and the other end must fill the space.

Chain = $-3kT d_{AB}^2/(2 < R^2 >) = -3kT N_{AB}V_c^2/(I\kappa^2 A^2)$ dAB = NAB V_c/A from above and $< R^2 > = N_{AB}I\kappa^2$

The free energy will be minimized in A to obtain the optimum phase size dAB. So it is the packing of the chains at the interface that governs the phase behavior of BCP's.

$$\begin{split} &\Delta G/kT = \chi kTA dt/V_c - 3kT NABVc^2/(2(l\kappa A)^2) \\ &d(\Delta G/kT)/dA = \chi dt/V_c + 3 NABVc^2/(l\kappa^2 A^3) = 0 \\ &A = \{3 NABVc^3/(l\kappa^2 \chi dt)\}^{1/3} \\ &dAB = NABVc^3/(aR^2 \chi dt)^{1/3} This is verified by experiment (Hashimoto papers) \end{split}$$

Three terms arise from the consideration of microphase separation

A is the cross sectional area of a polymer chain V_c is the occupied volume of a unit segment of a polymer chain V_{occupied} = N_{AB}V_c The total occupied volume of a block copolymer chain

Witten defines a term "a" that he calls the intrinsic elasticity of a polymer chain Elastic Energy/ $(3kT) = a < R^2 > /(2V_{occupied})$ where $a = V_{occupied} / < R_0^2 > = V_{occupied} / (N_K I_K^2)$ (Previously we had the spring constant kspr/kT = $3/<R_0^2 > = 3a/V_{occupied}$; $a = k_{spr} V_{occupied}/3$)

"a" has units of length and is termed by Witten the "*packing length*" since it relates to the packing or occupied volume for a chain unit, V_{occupied}. "a" is a ratio between the packing volume and the molar mass as measured by $\langle R_0^2 \rangle$.

Since V_{occupied} = N_KV_c, and $\langle R_0^2 \rangle = N_K | \kappa^2$, then a = V_c/l κ^2 , so the packing length relates to the lateral occupied size of a Kuhn unit, the lateral distance to the next chain. This is a kind of "*mesh size*" for the polymer melt. The cross sectional area, A, is defined by "a", A = πa^2 , and V_c = a $|\kappa^2$, so the BCP phase size problem can be solved using only the parameter "a".

Contemporary Topics in Polym, Sci. Vol. 6 Multiphase Macromolecular Systems, Culbertson BM Ed. Theory of Stress Distribution in Block Copolymer Microdomains, Witten TA, Milner ST, Wang Z-G p. 656

Other uses for the packing length

The packing length is a fundamental parameter for calculation of dynamics for a polymer melt or concentrated solution.

Plateau modulus of a polymer melt G ~ 0.39 kT/a^3

Structural Control of "a"

 $a = m_0/(\rho \ l\kappa \ l_0)$

Vary mass per chain length, mo/lo

Contemporary Topics in Polym. Sci. Vol. 6 Multiphase Macromolecular Systems. Culbertson BM Ed. Theory of Stress Distribution in Block Copolymer Microdomains, Witten TA, Milner ST, Wang Z-G p. 656

Lin, Y-H Macro. 20 3080 (1987)

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Lohse DT J. Macromol. Sci. Part C Polym. Rev. 45 298 (2005).



Fig. 5.12. General shape of the complete creep curve of PS, as suggested by the appearance of the different parts shown in Fig. 5.11



Fig. 5.15. Storage shear moduli measured for a series of fractions of PS with different molecular weights in the range $M = 8.9 \cdot 10^3$ to $M = 5.81 \cdot 10^5$. The dashed line in the upper right corner indicates the slope corresponding to the power law Eq. (6.81) derived for the Rouse-model of the glass-transition. Data from Onogi et al.[54]

Strobl, Physics of Polymers

$$J^{*}(\omega \rightarrow 0) = J_{\pi}^{0} - i \frac{1}{\eta_{0}\omega}$$
 (5.103)

As we see, η_0 and J_e^0 show up directly and separately, in the limiting behavior of J' and J''.

The dynamic shear modulus follows as

$$G^{*}(\omega \rightarrow 0) = \frac{1}{J^{*}(\omega \rightarrow 0)} - \frac{\eta_{0}\omega}{\eta_{0}\omega J_{q}^{0} - 1}$$

 $= \frac{\eta_{0}^{2}\omega^{2}J_{q}^{0} + i\eta_{0}\omega}{(\eta_{0}\omega J_{q}^{0})^{2} + 1}$ (5.104)

 $G'(\omega \rightarrow 0) = J_{\pi}^{0} \eta_{0}^{2} \omega^{2}$ (5.105)

in agreement with Fig. 5.15, and

giving

$$\tilde{r}''(\omega \to 0) = \eta_0 \omega$$
 (5.106)

We thus find characteristic power laws also for the storage and the loss modulus which again include J_a^{0} and η_0 in a well-defined way.

One may wonder if η_0 and J_n^0 can also be deduced from the time dependent response functions, as for example from G(t). Indeed, direct relationships exist, expressed by the two equations

Low Frequency G' ~ ω^2 From definition of viscoelastic

High Frequency G' ~ $\omega^{1/2}$ From Rouse Theory for Tg

Plateau follows rubber elasticity G' ~ $3kT/(N_{K,e} l\kappa^2)$

Plateau Modulus







Fig. 2. Dimensionless plateau moduli Gl k/kaT as a function of the dimensionless ratio I, Jp of Kuhn length Ir and packing length p. The figure contains (i) experimentally measured plateau moduli for polymer melts (25) (+; colors mark different groups of polymers as indicated) and semidilute solutions (26-28) (×); (ii) plateau moduli inferred from the normal tensions measured in computer simulation of bead-spring melts (35, 36) (0) and a semi-

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atomistic polycarbonate melt (37) (\diamond) under an elongational strain; and (iii) predictions of the tube model Eq. 1 based on the results of our primitive-path analysis for bead-spring melts (**a**), bead-spring semidilute solutions (**b**), and the semi-atomistic polycarbonate melt (**4**). The line indicates the best fit to the experimental data for polymer melts by Fetters *et al.* (24). Errors for all the simulation data are smaller than the symbol size.

this implies that $d\tau \sim p$

Kuhn Length- conformations of chains $\langle R^2 \rangle = I \kappa L$

Packing Length- length were polymers interpenetrate $p = 1/(\rho_{chain} < R^2 >)$ where ρ_{chain} is the number density of monomers

Structure and linear viscoelasticity of flexible polymer solutions: comparison of polyelectrolyte and neutral polymer solutions R. Colby, Rheo, Acta **49** 425-442 (2010)



Fig. 1 Conformations of polymers in dilute solution. Neutral polymers in poor solvent collapse into dense coils with size $\approx bN^{1/3}$ (purple). Neutral polymers in θ -solvent are random walks with ideal end-to-end distance $R_0 = bN^{1/2}$ (black). Neutral polymers in good solvent are self-avoiding walks with Flory end-toend distance $R_F = bN^{0.588}$ (red). Polyelectrolytes with no salt adopt the highly extended directed random walk conformation (blue) with length L proportional to N

Summary

Short Course on Polymer Physics Dire Dawa University

Greg Beaucage Prof. of Chemical and Materials Engineering University of Cincinnati, Cincinnati OH

December 10 2 hours (General Descriptions)

Physical description of an isolated polymer chain

Dimensionality and fractals Short-range and long-range interactions Packing length and tube diameter

December 11 2 hours (Some Theoretical Basis) Questions

Long-range interactions and chain scaling Flory-Krigbaum theory The semi-dilute and concentrated regimes Blob theory (the tensile, concentration, and thermal blobs) Coil collapse/protein folding Questions

Long Range Interactions

The Secondary Structure for Synthetic Polymers

Long-Range Interactions

Boltzman Probability For a Thermally Equilibrated System Gaussian Probability For a Chain of End to End Distance R

$$P_{B}(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

By Comparison The Energy to stretch a Thermally Equilibrated Chain Can be Written

$$E = kT \frac{3R^2}{2nl_K^2}$$

For a Chain with Long-Range Interactions There is and Additional Term

$$P_{\ell_{0}}(R) = \left(1 - V_{c}/R^{3}\right)^{n/2} = \exp\left(\frac{n^{2}\ln(1 - V_{c}/R^{3})}{2}\right) \sim \exp\left(-\frac{n^{2}V_{c}}{2R^{3}}\right)$$
 Number of pairs $\frac{n(n-1)}{2!}$

So,

$$E = kT \left(\frac{3R^2}{2nl_K^2} + \frac{n^2 V_c}{2R^3} \right)$$

$$R^* \sim l_K n^{3/5}$$

 $W_c(R)$ is the Gaussian probability $P(R,N)4\pi R^2 dR$ times the total number of chain conformations possible for chains of N steps, Z^N ,

$$W_0(R)dR = Z^N 4\pi R^2 \left(\frac{2\pi}{3}Nb^2\right)^{-3/2} \exp\left[-\frac{3}{2}\left(\frac{R}{b\sqrt{N}}\right)^2\right] dR$$

of this number the fraction which follow self-avoidance is $p(R) = (1 - V_C/R^3)^{N(N-1)/2}$ where V_C is the volume of one segment of the chain so $(1 - V_C/R^3)$ is the probability of the chain avoiding one segment, and this is raised to the total number of possible combinations of two segment pairs, N(N-1)/2!. This function for p(R) can be expressed as an exponential,

$$p(R) = \exp\left[\frac{1}{2}N(N-1)\ln\left(1-\frac{V_c}{R^3}\right)\right] = \exp\left(-\frac{N^2V_c}{2R^3}\right)$$

where the second equality uses the fact that for small x, ln(1-x) = -x, and that for large N, (N-1)=>N. W(R)dR for the excluded volume chain can be estimated by $W_o(R)p(R)dR$ and since both are expressed as exponentials the powers sum leading to,

$$W(R)dR = W_0(R)p(R)dR = kR^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2V_c}{2R^3}\right)$$

The derivative of $W_0(R)$ will equal 0 at $R^*_0 = (2Nb^2/3)^{1/2}$. This is proportional to $N^{1/2}b$ as expected. Setting the derivative of W(R) to 0 yields,

$$-\frac{3R^{*2}}{2Nb^2} + \frac{3N^2V_c}{4R^{*3}} + 1 = 0$$

Rearranging and substituting R', yields,

$$\left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 = \frac{9\sqrt{6}}{16} \frac{V_c}{b^3} \sqrt{N}$$

For large N the R ratio is large and the cubic term can be ignored with respect to the 5'th power term. This yields,

$$R^{*} = R_{0}^{*} \left(\frac{N^{\frac{1}{2}} V_{C}}{b^{3}} \right)^{\frac{1}{2}} = k N^{\frac{1}{2}}$$

This critical result was first noted by Flory and Krigbaum and its development is termed Flory-Krigbaum theory.



The Secondary Structure for Synthetic Polymers

Linear Polymer Chains have Two Possible Secondary Structure States:

Self-Avoiding Walk Good Solvent Expanded Coil (The Normal Condition in Solution) Gaussian Chain Random Walk Theta-Condition Brownian Chain (The Normal Condition in the Melt/Solid)

$$\mathbf{R}^* \sim \mathbf{l}_{\mathbf{K}} \mathbf{n}^{3/5}$$
 $\langle \mathbf{R}^2 \rangle = N l^2$

$$d_f = \frac{5}{3} \approx 1.67$$

 $d_{f} = 2$

These are statistical features. That is, a single simulation of a SAW and a GC could look identical.

The Secondary Structure for Synthetic Polymers

Linear Polymer Chains have Two Possible Secondary Structure States:

	Gaussian Chain
Self-Avoiding Walk	Random Walk
Good Solvent	Theta-Condition
Expanded Coil	Brownian Chain
(The Normal Condition in Solution)	(The Normal Condition in the Melt/Solid)

Consider going from dilute conditions, $c < c^*$, to the melt by increasing concentration. The transition in chain size is gradual not discrete.

Synthetic polymers at thermal equilibrium accommodate concentration changes through a scaling transition. Primary, Secondary, Tertiary Structures.



Figure 3. Radius of gyration, R_{\otimes} and hydrodyamic radius R_h versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].

We have considered an athermal hard core potential

$$E = kT \left(\frac{3R^2}{2nl_K^2} + \frac{n^2 V_c}{2R^3} \right)$$

But V_c actually has an inverse temperature component associated with enthalpic interactions between monomers and solvent molecules

The interaction energy between a monomer and the polymer/solvent system is on average $\langle E(R) \rangle$ for a given end-to-end distance R (defining a conformational state). This modifies the probability of a chain having an end-to-end distance R by the Boltzmann probability,

$$P_{Boltzman}(R) = \exp\left(\frac{-\langle E(R) \rangle}{kT}\right)$$

 $\langle E(R) \rangle$ is made up of pp, ps, ss interactions with an average change in energy on solvation of a polymer $\Delta \epsilon = (\epsilon_{PP} + \epsilon_{ss} - 2\epsilon_{Ps})/2$

For a monomer with z sites of interaction we can define a unitless energy parameter $\chi = z\Delta\epsilon/kT$ that reflects the average enthalpy of interaction per kT for a monomer

For a monomer with z sites of interaction we can define a unitless energy parameter $\chi = z\Delta\epsilon/kT$ that reflects the average enthalpy of interaction per kT for a monomer

The volume fraction of monomers in the polymer coil is nV_c/R^3

And there are n monomers in the chain with a conformational state of end-to-end distance R so,

$$\frac{\left\langle E(R)\right\rangle}{kT} = \frac{n^2 V_c \chi}{R^3}$$

We can then write the energy of the chain as,

$$E(R) = kT\left(\frac{3R^2}{2nl^2} + \frac{n^2 V_c\left(\frac{1}{2} - \chi\right)}{R^3}\right)$$

This indicates that when $\chi = \frac{1}{2}$ the coil acts as if it were an ideal chain, excluded volume disappears. This condition is called the theta-state and the temperature where $\chi = \frac{1}{2}$ is called the theta-temperature. It is a critical point for the polymer coil in solution.



Figure 3. Radius of gyration, R_p, and hydrodyamic radius R_h versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].

$$R^* = R_0^* \left(\frac{n^{1/2} V_0 \left(\frac{1}{2} - \chi \right)}{b^3} \right)^{1/5}$$



16 Properties of an isolated polymer molecule



Fig. 1.6 The coll-globule transition in a solution of polystyrene in cyclohexane. The radius of gyration R_0 and the hydrodynamic radius R_0 of the polymer show a dramatic change as temperature passes through the Rtemperature. The hydrodynamic radius R_0 is defined by $R_0 = k_0 T/6m D$, where D is the diffusion constant of the polymer and η is the viscosity of the solvent. (Sun, S.T., Nishio, I., Swislow, G., and Tanaka, T. (1990). J. *Chem. Phys.*, 73, 5971, Fig.2.)

Flory Krigbaum prediction (left) and experimental measurement (right)



FIG. 1. Schematic phase diagram of a polymer solution in the space of the temperature T and the volume fraction ϕ . The coexistence curve separates a dilute solution of collapsed chains [at $\phi_{coex}^{(2)}$] from a semidilute solution of overlapping chains [at $\phi_{coex}^{(2)}$]. These two branches of the coexistence curve merge at a critical point $T_c(N)$, $\phi_c(N)$. For $N \rightarrow \infty$ the critical point merges with the Θ point of a dilute polymer solution [$T_c(N \rightarrow \infty) \rightarrow \Theta$, $\phi_c(N \rightarrow \infty) \rightarrow 0$] and the unmixing transition has a tricritical character. At $T=\Theta$, the chain con/Egurations are ideal Gaussian coils, while their structure at $T_c(N)$ is nontrivial.

All three equalities apply At the critical point



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Φ

$\phi^* = \frac{n}{V} = \frac{n}{R^3}$ ~ $n^{-\frac{4}{5}}$ (for good solvents) or ~ $n^{-\frac{1}{2}}$ (for theta solvents)

(1)

(2)



FIG. 1. Schematic phase diagram of a polymer solution in the space of the temperature T and the volume fraction ϕ . The coexistence curve separates a dilute solution of collapsed chains [at $\phi_{\text{text}}^{(2)}$] from a semidilute solution of overlapping chains [at $\phi_{\text{text}}^{(2)}$]. These two branches of the coexistence curve merge at a critical point $T_c(N)$, $\phi_c(N)$. For $N \rightarrow \infty$ the critical point merges with the Θ point of a dilute polymer solution $[T_c(N \rightarrow \infty) \rightarrow \Theta, \phi_c(N \rightarrow \infty) \rightarrow 0]$ and the unmixing transition has a tricritical character. At $T = \Theta$, the chain conÆgurations are ideal Gaussian coils, while their structure at $T_c(N)$ is nontrivial.



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So there is a regime of coil collapse below the binodal at Φ^* in composition and temperature



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So there is a regime of coil collapse below the binodal at Φ^* in composition and temperature

For a polymer in solution there is an inherent concentration to the chain since the chain contains some solvent



The polymer concentration is Mass/Volume, within a chain

$$c^* = \frac{Mass}{Volume} = \frac{Mass}{Size^3} = \frac{Size^{d_f}}{Size^3} \sim Size^{d_f - 3}$$
$$c^* \sim n^{\left(1 - 3/d_f\right)}$$

When the solution concentration matches c* the chains "overlap" Then an individual chain is can not be resolved and the chains entangle This is called a concentrated solution, the regime near c* is called semi-dilute and the regime below c* is called dilute



In concentrated solutions with chain overlap chain entanglements lead to a higher solution viscosity



Figure 11.17. Concentration dependence of the specific viscosity of data and moderately concentrated solutions of cellulose acetate in disactly iniferite.³ The intersection of straight lines that are drawn through the dilute-solution (\odot) and concentration, c^{*} (ca. 3.7 g dL⁺ is this case).

J.R. Fried Introduction to Polymer Science

$$\eta \sim c^P$$

 $P = 1$ for c < c*

Shadowgraph images from the capillary breakup of a 0.2 wt. % polyethylene oxide (PEO, Mw= 4 × 106 g/mol) in a 60/40 wt. % glycerol/water solution. Images are taken at t = -0.05, 0.25, 0.43, and 0.65 s (cf. Fig. 4). The size of the images is 0.55 × 1.1 mm. The horizontal lines in the second image indicate the region shown in Fig. 5. The last image shows the final instability of the viscoelastic thread when many small droplets are formed.


How does a polymer chain respond to external perturbation?

The Gaussian Chain

Boltzman Probability For a Thermally Equilibrated System

$P_{B}(R) = \exp$	E(R)
	$\left[kT \right]$

Gaussian Probability For a Chain of End to End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

By Comparison The Energy to stretch a Thermally Equilibrated Chain Can be Written



$$F = \frac{dE}{dR} = \frac{3kT}{nl_{K}^{2}}R = k_{spr}R$$



Assumptions: -Gaussian Chain -Thermally Equilibrated -Small Perturbation of Structure (so it is still Gaussian after the deformation)

$$E = kT \frac{3R^2}{2nl_K^2}$$

For Larger Perturbations of Structure

Tensile Blob

-At small scales, small lever arm, structure remains Gaussian -At large scales, large lever arm, structure becomes linear Perturbation of Structure leads to a structural transition at a size scale ξ

$$E = kT \frac{3R^2}{2nl_{\kappa}^2} \qquad F = \frac{dE}{dR} = \frac{3kT}{nl_{\kappa}^2}R$$

For weak perturbations of the chain $R = n^{\frac{1}{2}} I_{\kappa} = \xi_{\text{result}}$

$$\xi_{Tensile} = \frac{3kT}{F}$$

Application of an external stress to the ends of a chain create a transition size where the coil goes from Gaussian to Linear called the Tensile Blob. Because the mechanical response of a polymer chain depends on its size or mass, n

$$F = \frac{dE}{dR} = \frac{3kT}{nl_K^2}R = k_{spr}R$$
$$k_{spr} = \frac{3kT}{nl_K^2}$$

Mechanical deformation leads to a transition size scale, $\boldsymbol{\zeta}$

$$\xi_{Tensile} = \frac{3kT}{F}$$

For sizes smaller than ζ the structure is not perturbed.

This can be generalized to say that any response of a polymer chain (or any other mass fractal structure) will depend on its size or mass, n, and will lead to a transition size scale called a 'blob'. There are three classic types of blobs: Thermal blob (de Gennes), Concentration blob (Edwards) and Tensile blob (Pincus)

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Mechanical deformation leads to a transition size scale, ζ

$$\xi_{Tensile} = \frac{3kT}{F}$$

For sizes smaller than ζ the structure is not perturbed.

Overlap concentration depends on size so depending on sub-segment size a chain component can be in dilute (low n, $d_f = 5/3$) or concentrated (high n, $d_f = 2$) regimes

$$c^* \sim \frac{n}{R^3} \sim \frac{n}{n^{\frac{9}{5}}} = n^{-\frac{4}{5}}$$

This can be generalized to say that any response of a polymer chain (or any other mass fractal structure) will depend on its size or mass, n, and will lead to a transition size scale called a 'blob'. There are three classic types of blobs: Thermal blob (de Gennes), Concentration blob (Edwards) and Tensile blob (Pincus)

Mechanical deformation leads to a transition size scale, ζ

$$\xi_{Tensile} = \frac{3kT}{F}$$

For sizes smaller than ζ the structure is not perturbed.

Chain Energy depends on size so depending on sub-segment size a chain component can have large excluded volume component and be in good solvent (high n, $d_f = 5/3$) regime or small excluded volume component and be in theta solvent (low n, $d_f = 2$) regime

 $E(R) = kT \left(\frac{3R^2}{2nl^2} + \frac{n^2 V_c \left(\frac{1}{2} - \chi\right)}{R^3} \right)$

Semi-Dilute Solution Chain Statistics

In dilute solution the coil contains a concentration $c^* \sim 1/[\eta]$

 $c^* = k n/R^3 = k n^{-4/5}$ for good solvent conditions

For semi-dilute solution the coil contains a concentration $c > c^*$

At large sizes the coil acts as if it were in a concentrated solution ($c >> c^*$), $d_f = 2$. At small sizes the coil acts as if it were in a dilute solution, $d_f = 5/3$. There is a size scale, ξ , where this "scaling transition" occurs.

We have a primary structure of rod-like units, a secondary structure of expanded coil and a tertiary structure of Gaussian Chains.

What is the value of ξ ?

 ξ is related to the coil size R since it has a limiting value of R for c < c* and has a scaling relationship with the reduced concentration c/c*

$$\xi \sim R (c/c^*)^P \sim n^{(3+4P)/5}$$

There are no dependencies on n above c^* so (3+4P)/5 = 0 and P = -3/4

$$\xi \sim R (c/c^*)^{-3/4}$$

Coil Size in terms of the concentration

$$\begin{aligned} \xi &= b \left(\frac{N}{n_{\xi}} \right)^{\frac{3}{5}} \sim \left(\frac{c}{c^*} \right)^{-\frac{3}{4}} \\ n_{\xi} &\sim \left(\frac{c}{c^*} \right)^{\binom{3}{4}\binom{5}{3}} = \left(\frac{c}{c^*} \right)^{\binom{5}{4}} \\ R &= \xi n_{\xi}^{\frac{1}{2}} \sim \left(\frac{c}{c^*} \right)^{-\frac{3}{4}} \left(\frac{c}{c^*} \right)^{\binom{5}{8}} = \left(\frac{c}{c^*} \right)^{-\frac{1}{8}} \end{aligned}$$

$$\mathbf{R} = \xi \, \mathbf{n}_{\xi}^{1/2} = \mathbf{R}_{F0} \, (\mathbf{c/c^*})^{-3/4} \, (\mathbf{c/c^*})^{5/8} = \mathbf{R}_{F0} \, (\mathbf{c/c^*})^{-1/8}$$

This is called the "Concentration Blob"

J. Physique 43 (1982)531 - 538

Star shaped polymers :

a model for the conformation and its concentration dependence

M. Daoud and J. P. Cotton



Fig. 1. — A representation of our model : every branch is made of a succession of blobs with a size ξ increasing from the centre of the star to the outside.

Abstract. — We propose a model giving the conformation of a star shaped polymer by taking into account the radial variation of the monomer concentration $\varphi(r)$.

For an isolated star when increasing r (at the centre of the star r = 0), the variation of $\varphi(r)$ is first given by a constant value ($r < f^{1/2} l$) then has a $(r/l)^{-1}$ variation (for $f^{1/2} l < r < f^{1/2} v^{-1} l$) and finally a $(r/l)^{-4/3}$ variation (for $r > f^{1/2} v^{-1} l$); where f is the number of branches, N the number of monomers in a branch and v and l are the excluded volume and the length associated to a monomer. For all these cases, it is shown that the size of a branch is always larger than that of a linear polymer made of N monomers.

Beyond the overlapping concentration the star conformation is obtained from two characteristic lengths essentially : $\chi(c)$ a radius inside which the branches of the other stars do not penetrate, this radius defines a domain where the conformation of a star is similar to that of an isolated one. Beyond $\chi(c)$ the interpenetration of branches is characterized by a screening length $\xi(c)$ very similar to that found for semi-dilute solutions of linear polymers. For all these regimes the variation of the size of a star is predicted as a function of N, f, v and c.



Figure 3. Radius of gyration, R_{p} , and hydrodyamic radius R_{h} versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].

Chain expands from the theta condition to fully expanded gradually. At small scales it is Gaussian, at large scales expanded (opposite of concentration blob).

$$E = kT \left(\frac{3R^2}{2nl_K^2} + \frac{n^2 V_c}{2R^3} \right) \qquad \qquad E = kT \left(\frac{3R^2}{2nl_K^2} + \frac{n^2 V_c (1 - 2\chi)}{2R^3} \right)$$



$$E = kT \left(\frac{3R^2}{2nl_K^2} + \frac{n^2 V_c}{2R^3} \right) \qquad \qquad E = kT \left(\frac{3R^2}{2nl_K^2} + \frac{n^2 V_c (1 - 2\chi)}{2R^3} \right)$$

$$E = kT\left(\frac{3R^2}{2nl_k^2} + \frac{n^2V_c(1-2\chi)}{2R^3}\right)$$

Energy Depends on n, a chain with a mer unit of length 1 and n = 10000 could be re cast (renormalized) as a chain of unit length 100 and n = 100The energy changes with n so depends on the definition of the base unit

Smaller chain segments have less entropy so phase separate first. We expect the chain to become Gaussian on small scales first. This is the opposite of the concentration blob.

Cooling an expanded coil leads to local chain structure collapsing to a Gaussian structure first. As the temperature drops further the Gaussian blob becomes larger until the entire chain is Gaussian at the theta temperature.

$$R = N_T^{\frac{3}{5}} \xi_T = \left(\frac{N_{n_T}}{n_T} \right)^{\frac{3}{5}} \xi_T = \left(\frac{N_{n_T}}{\left(\xi_T \right)^2} \right)^{\frac{3}{5}} \xi_T = N^{\frac{3}{5}} \xi_T^{-\frac{1}{5}} l^{\frac{6}{5}}$$

Flory-Krigbaum Theory yields:
$$R = V_c^{\frac{1}{5}} (1 - 2\chi)^{\frac{1}{5}} N^{\frac{3}{5}} l^{\frac{2}{5}}$$

By equating these:

$$\xi_r = \frac{l}{(1-2\chi)}$$



$$E(R) = kT \left(\frac{3R^2}{2nl^2} + \frac{n^2 V_c \left(\frac{1}{2} - \chi\right)}{R^3} \right)$$

$$\frac{\Delta G}{kTN_{cells}} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \phi_A \phi_B \chi$$

$$\chi = \frac{z\Delta \varepsilon}{kT} = \frac{B}{T}$$

Lower-Critical Solution Temperature (LCST)



Polymers can order or disorder on mixing leading to a noncombinatorial entropy term, A in the interaction parameter.

$$\chi = A + \frac{B}{T}$$

If the polymer orders on mixing then A is positive and the energy is lowered.

If the polymer-solvent shows a specific interaction then B can be negative.

This Positive A and Negative B favors mixing at low temperature and demixing at high temperature, LCST behavior.

$$E(R) = kT\left(\frac{3R^2}{2nl^2} + \frac{n^2 V_c(\frac{1}{2} - \chi)}{R^3}\right) \qquad \qquad \chi = \frac{z\Delta\varepsilon}{kT} = \frac{B}{T}$$

Lower-Critical Solution Temperature (LCST)



$$\chi = A + \frac{B}{T}$$



Poly vinyl methyl ether/Water PVME/PS

Coil Collapse Following A. Y. Grosberg and A. R. Khokhlov "Giant Molecules"

What Happens to the left of the theta temperature?



Figure 3. Radius of gyration, R_p , and hydrodyamic radius R_h versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].

The Flory Krigbaum expression for the free energy of a self-avoiding chain is given by,

$$F(R) = \frac{z^2 V_0 (1 - 2\chi) kT}{2R^3} + \frac{3R^2 kT}{2zl^2} = U(R) - TS(R) \qquad (1)$$

Equation (1) can be rewritten using the coil expansion coefficient, α ,

$$\alpha^2 = \frac{R^2}{R_0^2} = \frac{R^2}{zl^2}$$
(2)

$$F(\alpha) = \frac{z^{1/2}BkT}{2\alpha^2 l^3} + \frac{3\alpha^2 kT}{2} = U(\alpha) - TS(\alpha)$$
(3)

where B is the second virial coefficient,

$$B = V_0 (1 - 2\chi)$$
 (4)

Finding the minimum in the free energy expression, equation (3), yields the most probable value for α ,

$$\alpha \sim \left(\frac{z^{1/2}B}{l^3}\right)^{1/5}$$
(5)

$$R \sim R_0 \alpha = z^{1/2} b \alpha \sim z^{3/5} B^{1/5} b$$

The virial expansion of the enthalpic interactions is given by,

$$U(\alpha) = V_{Coll}kT \left[n^2 B + n^3 C + ... \right] \approx V_{Coll}kT n^2 B - \frac{kT R^3 B z^2}{R^6} = \frac{z^{3/2} B kT}{2\alpha^3 l^3}$$
(6)

where n is the segmental density in the coil and V_{Coil} is the volume of the coil. The second virial coefficient describes binary interactions and the third virial coefficient describes ternary interactions. In dilute conditions we can ignore the higher order interactions and use only the second virial coefficient.

Generally B is negative and C is positive, i.e. favors coil collapse So C is important below the theta temperature to model the coil to globule transition For simplicity we ignore higher order terms because C is enough to give the gross features Of this transition. Generally it is known that this transition can be either first order for Biopolymers such as protein folding, or second order for synthetic polymers. First order means that the first derivative of the free energy is not continuous, i.e. a jump in Free energy at a discrete transition temperature, such as a melting point.



$$T_c(N) = \Theta/(1 + 1/\sqrt{N})^2 \approx \Theta - 2\Theta/\sqrt{N}, \quad N \to \infty,$$
 (1)

$$\phi_c(N) = 1/(1 + \sqrt{N}) \approx 1/\sqrt{N}, \quad N \rightarrow \infty.$$
 (2)

Consider the coil of length n as composed of g* chain subunits each with (n/g^*) Kuhn units of length lk. g^* can be any value between one and n.

Small size g* units have a lower Tccompared to large size g* units.

FIG. 1. Schematic phase diagram of a polymer solution in the space of the temperature T and the volume fraction ϕ . The coexistence curve separates a dilute solution of collapsed chains [at $\phi_{\text{coex}}^{(1)}$] from a semidilute solution of overlapping chains [at $\phi_{\text{coex}}^{(2)}$]. These two branches of the coexistence curve merge at a critical point $T_c(N)$, $\phi_c(N)$. For $N \rightarrow \infty$ the critical point merges with the Θ point of a dilute polymer solution $[T_c(N \rightarrow \infty) \rightarrow \Theta]$, $\phi_c(N \rightarrow \infty) \rightarrow 0$ and the unmixing transition has a tricritical character. At $T=\Theta$, the chain conÆgurations are ideal Gaussian coils, while their structure at $T_{c}(N)$ is nontrivial.

Blob model for coil collapse



Assume Gaussian Collection of

Grosberg and Khokhlov's figure 8.6 shows a model for chain collapse that explains the entropic behavior in terms of blobs of g* chain units associated with a confined chain. We can consider the collapsed chain as composed of z/g* collapsed blobs each with an energy kT.

$$F(\alpha) = \frac{z^{1/2}BkT}{2\alpha^3 l^3} + \frac{3\alpha^2 kT}{2} = U(\alpha) - TS(\alpha)$$

$$R^2 \sim g^*$$
(3)

$$\left[-TS(\alpha)\right]_{Confinement} \sim kT \frac{z}{g^*} = kT \frac{zl^2}{R^2} = \frac{kT}{\alpha^2}$$
(7)

In the absence of confinement (coil collapse) the expression was,

$$\left[-TS(\alpha)\right]_{Expansion} \sim kT\alpha^2 \tag{8}$$

and a sum of these terms (approximation),

$$-TS(\alpha) = \left[-TS(\alpha)\right]_{Confinement} + \left[-TS(\alpha)\right]_{Expansion} \sim kT(\alpha^{2} + \alpha^{-2})$$
(9)

$$F(\alpha) \sim kT\left(\alpha^2 + \alpha^{-2}\right) + \frac{kTBz^{1/2}}{2\alpha^3 l^3} + \frac{kTC}{\alpha^6 l^6}$$
(10).

$$F(\alpha) = \frac{z^{1/2}BkT}{2\alpha^3 l^3} + \frac{3\alpha^2 kT}{2} = U(\alpha) - TS(\alpha)$$

$$R^2 \sim g^*$$
(3)

$$\left[-TS(\alpha)\right]_{Confinement} \sim kT \frac{z}{g^*} = kT \frac{zl^2}{R^2} = \frac{kT}{\alpha^2}$$
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In the absence of confinement (coil collapse) the expression was,

$$\left[-TS(\alpha)\right]_{Equasion} \sim kT\alpha^2$$
(8)

and a sum of these terms (approximation),

$$-TS(\alpha) = \left[-TS(\alpha)\right]_{Confinement} + \left[-TS(\alpha)\right]_{Expansion} \sim kT(\alpha^2 + \alpha^{-2})$$
(9)

α is >1 for expansion <1 for contraction

$$F(\alpha) \sim kT(\alpha^{2} + \alpha^{-2}) + \frac{kTBz^{1/2}}{2\alpha^{3}l^{3}} + \frac{kTC}{\alpha^{6}l^{6}}$$
(10).

Which works for both expansion and collapse. Finding the minimum in this free energy yields the most probable value for α , (equivalent of equation (5)),

$$\alpha^5 - \alpha = x + y\alpha^{-3} \tag{11}$$

where x is related to B and is given by,

$$x = K_1 B z^{1/2} / l^3$$
 (12)

and y is related to C and is given by,

$$y = K_2 C/l^6$$
(13).

If α is small you can neglect the terms on the left hand side of equation (11) and solve for R,

$$R \sim \alpha z^{1/2} l \sim \left(\frac{-C}{B}\right)^{1/3} z^{1/3}$$
(14)

Ratio of C/B determines behavior, the collapsed coil is 3d

$$\alpha^5 - \alpha = x + y\alpha^{-3}$$

Equation (11) can be understood by plotting the coil expansion factor, α , versus the reduced temperature function x for fixed values of y as shown in Figure 8.3 from Grosberg and Khokhlov reproduced below. In this figure, at large y the chain is flexible and the coil only slightly collapses on cooling (smaller x). The theta temperature occurs at x = 0. For rigid chains with a small value for y, the curve shows three values for a given x just below the θ -temperature.





FIGURE 8.4 The dependence $F(\alpha)$ in the case where $\alpha(x)$ is multivalued. As x changes (which can be controlled by, say, temperature change), the shape of the $F(\alpha)$ dependence changes such that one minimum gets deeper at the expense of the other. Deeper minimum corresponds to the more stable state. For this figure, we choose the value y = 0.001.



Generally it is known that this transition can be either first order for Biopolymers such as protein folding, or second order for synthetic polymers. First order means that the first derivative of the free energy is not continuous, i.e. a jump in Free energy at a discrete transition temperature, such as a melting point.



Figure 4. Temperature dependence of average radius of gyration ((R_0)) and hydrodynamic radius ((R_0)) of poly(NN-diethylacrylamide) (PDEAM) chains in water in one heating-and-cooling cycle.



Figure 5. Temperature dependence of ratio of average radius of gyration to average hydrodynamic radius $(\langle R_a \rangle I \langle R_b \rangle)$ of poly(N,N-diethylacrylamide) (PDEAM) chains in water in one heating-and-cooling cycle.

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The Coll-to-Ohlude-to-Coll Transition of Linear Polyneer Chains in Dilate Appensis Solutions: Effect of Istrachain Hydrogen Bonding Role Part 710: Lo¹ Johns Li¹ Lei Rec.¹ Soughts-Bong¹⁰ Humit Tec.¹⁰ and 10 (1977) We have the second sec



FIG. 2. Temperature dependence of the average radius of gynation (R_{c}) and the average hydrodynamic radius (R_{c}) , respectively, in the coil-to-globule (heating) and the globule to-coil (cooling) processes, where each point was obtained at least 2 h after the solution reached the thermal equilibrium to emuse that the polymer chains were thermodynamically stable. The inset shows the temperature dependence of $(R_{c})/(R_{c})$ in the heating and the cooling processes.



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Clobule to Coll Transition of a Single Homopolymer Chain in Solution

Chi Wu^{12 a} and Kaohai Wang¹

Summary
Short Course on Polymer Physics Addis Ababa University

Greg Beaucage Prof. of Chemical and Materials Engineering University of Cincinnati, Cincinnati OH

December 19 2 hours (Analytic Techniques for Polymer Physics)

Questions Measurement of the size of a polymer chain R_g, R_h, R_{eted} Small-angle neutron, x-ray scattering and static light scattering Intrinsic viscosity Dynamic light scattering Osmotic Pressure Polymer melt rheology

Questions

Size of a Chain, "R" (You can not directly measure the End-to-End Distance) What are the measures of Size, "R", for a polymer coil?

Radius of Gyration, R_g

$$R_g^2 = \frac{1}{N} \sum_{s=1}^{N} \langle (R_s - R_g)^2 \rangle$$
 $R_g = \frac{1}{N} \sum_{s=1}^{N} R_s$

$$R_{g}^{2} = \frac{1}{N} \sum_{n=1}^{N} \left\langle \left(R_{n} - \frac{1}{N} \sum_{m=1}^{N} R_{m} \right)^{2} \right\rangle = \frac{1}{N} \sum_{n=1}^{N} \left\langle \frac{1}{2N} \sum_{m=1}^{N} \left(R_{n} - R_{m} \right)^{2} \right\rangle = \frac{1}{2N^{2}} \sum_{m=1}^{N} \sum_{m=1}^{N} \left\langle \left(R_{n} - R_{m} \right)^{2} \right\rangle$$

$$\sum_{n=1}^{N} \sum_{m=1}^{N} \left\langle \left(R_{m} - R_{m}\right)^{2} \right\rangle = \sum_{n=1}^{N} \sum_{m=1}^{N} |n - m| b^{2} = 2 \sum_{n=m}^{N} \sum_{m=1}^{N} (n - m) b^{2} = 2 b^{2} \left[Z + 2(Z - 1) + 3(Z - 2)...(Z - 1)2 + Z\right]$$

$$Z = N - 1$$

$$\sum_{p=1}^{Z} (Z+1-p)p = (Z+1)\sum_{p=1}^{Z} p - \sum_{p=1}^{Z} p^{2} = \frac{Z(Z+1)(Z+2)}{6} \cong \frac{N^{3}}{6}$$
$$\sum_{u=1}^{n} u^{p} = \frac{n^{p+1}}{p+1} + \frac{n^{p}}{2} + \frac{pn^{p-1}}{12} \qquad \text{for } p<3 \text{ (other terms needed for higher p's)}$$

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

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What are the measures of Size, "R", for a polymer coil?

Radius of Gyration, Rg

$$R_g^2 = \frac{1}{N} \sum_{n=1}^{N} \langle (R_n - R_g)^2 \rangle$$
 $R_G = \frac{1}{N} \sum_{n=1}^{N} R_n$

$$R_g^2 = \frac{Nb^2}{6} = \frac{R_{RMSeted}^2}{6}$$

 R_g is 1/V6 of the RMS end-to-end distance.

2.45
$$R_g = R_{eted}$$

$R_{g}\xspace$ is a direct measure of the end-to-end distance for a Gaussian Chain

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

Static Light Scattering for Rg

 $I(q) = I_e N n_e^2 \exp\left(\frac{-R_g^2 q^2}{3}\right)$

Guinier's Law

Guinier Plot linearizes this function

$$\ln\left(\frac{I(q)}{G}\right) = -\frac{R_g^2}{3}q^2 \qquad G = I_e N n_e^2$$

The exponential can be expanded at lowq and linearized to make a Zimm Plot

$$\frac{G}{I(q)} = \left(1 + \frac{R_g^2}{3}q^2\right)$$









$$I(q) = \frac{G}{\exp\left(\frac{q^2 R_g^2}{3}\right)}$$
$$\frac{G}{I(q)} = \exp\left(\frac{q^2 R_g^2}{3}\right) \approx 1 + \frac{q^2 R_g^2}{3} + \dots$$
Plot is linearized by $G/I(q)$ versus q^2

$$q = \frac{4\pi}{\lambda} \sin\!\left(\frac{\theta}{2}\right)$$

Concentration part will be described later

$$\frac{\phi}{S(qR_z \ll 1)} = \left(\frac{1}{N} + (1 - 2\chi)\phi\right)\left(1 + \frac{q^2R_z^2}{3}\right) \quad (6).$$

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 $I(q) \sim N n_e^2$

n_e Reflects the density of a Point generating waves

N is total number of points

The Scattering Event



 2) Rather than consider specific structures, we can consider general scattering laws by which all scatters are governed under the premises that 1) "Particles" have a size and
 2) "Particles" have a surface.





-Consider that an in-phase wave scattered at angle θ was in phase with the incident wave at the source of scattering.

-This can occur for points separated by *r* such that

$$|\mathbf{r}| = 2\theta/|\mathbf{q}|$$
$$= \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$



-For high θ , r is small



-For small θ, *r* is large













The particle becomes a probability density function from the center of mass.



That follows a Gaussian Distribution.

$$p(r) = \exp\!\left(\frac{-3r^2}{4R_g^2}\right)$$

The particle becomes a probability density function from the center of mass.



Whose Fourier Transform is Guinier's Law.

$$p(r) = \exp\left(\frac{-3r^2}{4R_g^2}\right) \implies I(q) = G \exp\left(-\frac{q^2R_g^2}{3}\right)$$

G = Nn_e²

Static Light Scattering for Radius of Gyration

Consider binary interference at a distance "r" for a particle with arbitrary orientation Rotate and translate a particle so that two points separated by r lie in the particle for all rotations and average the structures at these different orientations



 $\gamma_0(r) = 1 - \frac{1}{4V}r + \dots$ $\exp\left(\frac{1}{4R}\right) = 1 - \frac{1}{4R} + \dots$ $r \Rightarrow 0$ then $\frac{d(\gamma_{Gaussian}(r))}{dr} \Rightarrow 0$

A particle with no surface

Beaucage G J. Appl. Cryst. 28 717-728 (1995).

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Guinier's Law Pertains to a Particle with no Surface.

$$p(r) = \exp\left(\frac{-3r^2}{4R_g^2}\right) \implies I(q) = G \exp\left(-\frac{q^2R_g^2}{3}\right)$$

G = Nn_e²

Any "Particle" can be Approximated as a Gaussian probability distribution in this context.



Guinier's Law can be thought of as the *First Premise of Scattering:*

All "Particles" have a size reflected by the radius of gyration.

Sphere of radius R	$R_{\rm g}^2 = \frac{3}{5} {\rm R}^2$	
Spherical shell with radii $R_1 > R_2$	$R_{\rm g}^2 = \frac{3}{5} \frac{R_1^5 - R_2^5}{R_1^3 - R_2^3}$	
Ellipse with semiaxes a and b	$R_a^2 = \frac{a^2 + b^2}{4}$	
Ellipsoid with semiaxes a, b , and c	$R_g^2 = \frac{a^2 + b^2 + c^2}{5}$	
Prism with edges A , B , and C	$R_{\rm s}^2 = \frac{A^2 + B^2 + C^2}{12}$	_
Elliptical cylinder with semiaxes a and b and height h	$R_{\rm g}^2 = \frac{a^2 + b^2}{4} + \frac{h^2}{12}$	ad
Hollow circular cylinder with radii $R_1 > R_2$ and height k	$R_{\rm g}^2 = \frac{R_{\rm f}^2 + R_{\rm f}^2}{2} + \frac{h^2}{12}$	



Two possibilities for an arrow with both ends in a particle

(A) Different Particles => Guinier's Law

(B) Same Particle => Surface Scattering

(Only near the surface is there constructive interference with no intermediate

destructive vector at ½ the distance r)

There is a transition between (A) and (B) near r = Rg

Debye Scattering Function for Gaussian Polymer Coil

Consider a chain of length N whose average end to end distance is $N^{1/2}$ b, where b is the effective step length for the chain which has no long-range interactions. For the n'th chain step, $g_n(r)$ is the average density of segments at a radial position r from step n. R_n is here the position vector for the segments of the chain. It is important to keep clear that r_n is a radial position relative to segment "n" while R_n is the segmental position relative to a coordinate system based at the first segment where n = 1. n can have values from 1 to N. Then,

$$g_n(r_n) = \frac{\sum_{m=1}^{N} \left\langle \delta(r_n - (R_m - R_n)) \right\rangle}{N}$$

where the del operator has a value of 1 when the position vector difference (R's) is equal to r. $g_n(r)$ will have values between 0 for r's larger than the chain to 1 for r = 0.

Since $g_{e}(r)$ only considers a single segment, "n", it must be averaged over all segments in order to obtain a statistical description of the spatial distribution of chain segments for the entire coil. This averaging results in the pair correlation function, g(r) for the coil,

$$g(r) = \frac{1}{2N^2} \sum_{n=1}^{N} g_n(r_n) = \frac{1}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} \left\langle \delta \left(r - (R_m - R_n) \right) \right\rangle$$

The pair correlation function, g(r), is directly related to the intensity scattered by light, neutrons or x-rays from a polymer coil. The scattered intensity is measured as a function of scattering angle, θ , and is usually plotted against the reduced parameter, $q = |q| = 4\pi/\lambda \sin(\theta/2)$, which is called the scattering vector. "q" is the inverse space vector and is related to the Bragg spacing, d, by $d = 2\pi/q$.

Scattered Intensity = K g(q) where K is a constant for a given system which includes the contrast and instrumental parameters. g(q) is the Fourier Transform of g(r),

$$g(q) = \int drg(r) \exp(iq \cdot r) = \frac{1}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} \left\langle \exp(iq \cdot (R_m - R_n)) \right\rangle$$

For a Gaussian polymer coil the solution to this double summation is the Debye Equation for Polymer Coils which was first solved in 1946 by P. Debye.

$$g(q)_{Gaussian} = \frac{2}{Q^2} \left[Q - 1 + \exp(-Q) \right]$$

where $Q = q^2 N b^2 / 6 = q^2 R_g^2$

The Debye function for polymer coils describes a decay of scattered intensity following a powerlaw of -2 at high-q and a constant value for intensity at low-q (below Rg).

Debye Paper Deriving this Equation

Low-q and High-q Limits of Debye Function

$$g(q)_{Gaussian} = \frac{2}{Q^2} [Q - 1 + \exp(-Q)]$$

where Q = q²Nb²/6 = q²R_g²

At high q the last term => 0
Q-I => Q
$$g(q) => 2/Q \sim q^{-2}$$

Which is a mass-fractal scaling law with df = 2

At low q, $exp(-Q) => 1-Q+Q^2/2-Q^3/6+...$ Bracketed term => $Q^2/2-Q^3/6+...$

 $g(q) => 1-Q/3+... \sim exp(-Q/3) = exp(-q^2R_g^2/3)$

Which is Guinier's Law

Measurement of the Hydrodynamic Radius, Rh



Figure 3. Radius of gyration, R_{p} and hydrodyamic radius R_{h} versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].

$$[\eta] = \frac{4/3\pi R_H^3}{N} \qquad R_H = \frac{kT}{6\pi\eta D} \qquad \frac{1}{R_H} = \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N \left\langle \frac{1}{|r_i - r_j|} \right\rangle \qquad \frac{\text{Kirkwood, L. Polym. Sci. 12.1(1953)}}{\text{http://theor.jint.ru/~kuzemsky/kirkoto.num}}$$

http://www.eng.uc.edu/~gbeaucag/Classes/Properties/HydrodyamicRadiu s.pdf

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Viscosity





Native state has the smallest volume

Intrinsic, specific & reduced "viscosity"

 $\tau_{xy} = \eta \dot{\gamma}_{xy}$ Shear Flow (may or may not exist in a capillary/Couette geometry)

$$\eta = \eta_0 \left(1 + \phi [\eta] + k_1 \phi^2 [\eta]^2 + k_2 \phi^3 [\eta]^3 + \dots + k_{n-1} \phi^n [\eta]^n \right)$$
(1)

n = order of interaction (2 = binary, 3 = ternary etc.)

$$\frac{1}{\phi} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{\phi} (\eta_r - 1) = \frac{\eta_{sp}}{\phi} \xrightarrow{\text{Limit } \phi \Rightarrow 0} [\eta] = \frac{V_H}{M}$$

We can approximate (1) as:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + \phi[\eta] \exp(K_M \phi[\eta])$$
 Martin Equation

Utracki and Jamieson "Polymer Physics From Suspensions to Nanocomposites and Beyond" 2010 Chapter 1

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Intrinsic, specific & reduced "viscosity"

$$\eta = \eta_0 \left(1 + c [\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right)$$
(1)

n = order of interaction (2 = binary, 3 = ternary etc.)

$$\frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{c} (\eta_r - 1) = \frac{\eta_{sp}}{c} \xrightarrow{\text{Limit } c \Rightarrow 0} [\eta] = \frac{V_H}{M}$$

We can approximate (1) as:

$$\eta_{r} = \frac{\eta}{\eta_{0}} = 1 + c[\eta] \exp(K_{M}c[\eta]) \qquad \text{Martin Equation}$$

$$\frac{\eta_{sp}}{c} = [\eta] + k_{1}[\eta]^{2}c \qquad \qquad \text{Huggins Equation}$$

$$\frac{\ln(\eta_{r})}{c} = [\eta] + k_{1}[\eta]^{2}c \qquad \qquad \text{Kraemer Equation}$$

$$(\text{exponential expansion})$$

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Intrinsic, specific & reduced "viscosity" $\eta = \eta_0 \left(1 + c [\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right)$ (1)n = order of interaction (2 = binary, 3 = ternary etc.) $\frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{c} (\eta_r - 1) = \frac{\eta_{sp}}{c} \xrightarrow{\text{Limit } c \to 0} [\eta] = \frac{V_H}{M}$ **Concentration Effect** 40 $\eta_{ m red}$ / (ml g⁻¹) acetyl starch 36 in H_oO $rac{\eta_{_{sp}}}{\phi}$ 32 28 24 20 Fig. 4.5. Reduced viscosity $\eta_{\rm red}$ as a func-16 tion of the concentration c for acetyl starch of different molar masses in aque-12

Kulicke & Clasen "Viscosimetry of Polymers and Polyelectrolytes (2004)

0.06

 $c / (g ml^{-1})$

0.02

----- M = 709.000 g/mol, DS =0,91

---=-- M_= 517.000 g/mol, DS =0,86

--▲-- M = 263.000 g/mol, DS =0,82 --★-- M = 152.000 g/mol, DS =0,94

0.00

0.04

ous solution at T=25 °C. The degree of

substitution (DS) with acetyl groups is

nearly constant at DS≈0.9. Due to the

tive viscosity range of η_r =1.2–2.5

compact structure of the polymer coil the concentrations of the dilution series are

relatively high to reach the required rela-

Intrinsic, specific & reduced "viscosity"

$$\eta = \eta_0 \left(1 + c [\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right)$$
(1)

n = order of interaction (2 = binary, 3 = ternary etc.)

$$\frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{c} (\eta_r - 1) = \frac{\eta_{sp}}{c} \xrightarrow{\text{Limit } c \Rightarrow 0} [\eta] = \frac{V_H}{M}$$



Concentration Effect, c*

Fig. 4.2. Reduced viscosity η_{red} as a function of the concentration *c* for different molar masses of the polycation poly(acrylamide-*co*-(*N*,*N*,*N*-trimethyl-*N*-[2-methacryloethyl]-ammoniumchloride) (PTMAC) in 0.1 mol/l NaNO₃ solution. Data from [87]. All data points are measured at concentrations below the critical concentration $c^*_{[\eta]}$. The copolymer consists of 8 mol% TMAC and 92 mol% AAm

Kulicke & Clasen "Viscosimetry of Polymers and Polyelectrolytes (2004)

Intrinsic, specific & reduced "viscosity"

$$\eta = \eta_0 \left(1 + c [\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right)$$
(1)

n = order of interaction (2 = binary, 3 = ternary etc.)

$$\frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{c} (\eta_r - 1) = \frac{\eta_{sp}}{c} \xrightarrow{\text{Limit } c \Rightarrow 0} [\eta] = \frac{V_H}{M}$$



Kulicke & Clasen "Viscosimetry of Polymers and Polyelectrolytes (2004)
Intrinsic, specific & reduced "viscosity"

$$\eta = \eta_0 \left(1 + c [\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right)$$
(1)

n = order of interaction (2 = binary, 3 = ternary etc.)

$$\frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{c} (\eta_r - 1) = \frac{\eta_{sp}}{c} \xrightarrow{\text{Limit } c \Rightarrow 0} [\eta] = \frac{V_H}{M}$$



Molecular Weight Effect

Fig. 5.4. Reduced viscosity η_{red} as a function of the concentration *c* for sodium poly(styrene sulfonate) (PSSNa) of different molar masses in aqueous solution. The second virial coefficient of the viscosimetry, $K_{\rm H'}[\eta]^2$, is equivalent to the slope of the curves and is given for each molar mass. The Huggins constant $K_{\rm H}$ is constant and independent of the molar mass. Data from [35,91]

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c$$

Huggins Equation

Kulicke & Clasen "Viscosimetry of Polymers and Polyelectrolytes (2004)



Viscosity

$$\eta_s = \eta_0 \left(1 + [\eta] \phi \right)$$

$$[\eta] \approx rac{V_{Molecule}}{M_{Moledule}}$$

For the Native State Mass ~ ρV_{Molecule} Einstein Equation (for Suspension of 3d Objects) $\eta_s = \eta_0 (1 + 2.5\phi)$

For "Gaussian" Chain Mass ~ Size² ~ $V^{2/3}$ V ~ Mass^{3/2}

For "Expanded Coil" Mass ~ Size^{5/3} ~ $V^{5/9}$ V ~ Mass^{9/5}

For "Fractal" Mass ~ Size^{df} ~ V^{df/3} V ~ Mass^{3/df}

$$[\eta] \sim M_{Molecule}^{rac{3}{d_f}-1}$$



Viscosity

$$\eta_s = \eta_0 \left(1 + [\eta] \phi \right)$$

$$\eta] \approx rac{V_{Molecule}}{M_{Moledule}}$$

For the Native State Mass ~ ρV_{Molecule} Einstein Equation (for Suspension of 3d Objects) $\eta_s = \eta_0 (1 + 2.5\phi)$

For "Gaussian" Chain Mass ~ Size² ~ V^{2/3} V ~ Mass^{3/2} **"Size" is the "Hydrodynamic Size"** For "Expanded Coil" Mass ~ Size^{5/3} ~ V^{5/9} V ~ Mass^{9/5}

> For "Fractal" Mass ~ Size^{df} ~ V^{df/3} V ~ Mass^{3/df}

$$[\eta] \sim M_{Molecule}^{rac{3}{d_f}-1}$$

Intrinsic, specific & reduced "viscosity"

$$\eta = \eta_0 \left(1 + c [\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right)$$
(1)

n = order of interaction (2 = binary, 3 = ternary etc.)

$$\frac{1}{c} \left(\frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{c} (\eta_r - 1) = \frac{\eta_{sp}}{c} \xrightarrow{\text{Limit } c \Rightarrow 0} [\eta] = \frac{V_H}{M}$$

Viscosity itself has a strong temperature dependence. But intrinsic viscosity depends on temperature as far as coil expansion changes with temperature (RH^3) .



Temperature Effect

Fig. 5.5. Zero-shear viscosity η_0 as a function of the temperature *T* for poly (acrylamide) (PAAm) and poly(*N*-iso-propyl-acrylamide) (PipAAm) in aqueous solution (*c*=0.1 wt%). The viscosity for the solvent water as a function of the temperature is plotted as well. Data from [77]

Weaker and Opposite Dependency



Intrinsic "viscosity" for colloids (Simha, Case Western)

$$\eta = \eta_0 (1 + v\phi) \qquad \eta = \eta_0 (1 + [\eta]c)$$
$$[\eta] = \frac{vN_A V_H}{M}$$

For a solid object with a surface v is a constant in molecular weight, depending only on shape

For a symmetric object (sphere) v = 2.5 (Einstein) $[\eta] = \frac{2.5}{\rho} ml/g$

For ellipsoids v is larger than for a sphere,



Intrinsic "viscosity" for colloids (Simha, Case Western)

$$\eta = \eta_0 (1 + v\phi) \qquad \eta = \eta_0 (1 + [\eta]c)$$
$$[\eta] = \frac{vN_A V_H}{M}$$

Hydrodynamic volume for "bound" solvent

$$V_H = \frac{M}{N_A} \left(\overline{v}_2 + \delta_S v_1^0 \right)$$

Partial Specific Volume \overline{v}_2 Bound Solvent (g solvent/g polymer) δ_s Molar Volume of Solvent v_1^0

Intrinsic "viscosity" for colloids (Simha, Case Western)

$$\eta = \eta_0 (1 + v\phi) \qquad \eta = \eta_0 (1 + [\eta]c)$$
$$[\eta] = \frac{vN_A V_H}{M}$$

$$[\eta] = \frac{2}{45} \frac{\pi N_A L^3}{M(\ln J + C_\eta)} \qquad \qquad J = L/d$$

$$C_{\eta}$$
 End Effect term ~ 2 ln 2 – 25/12 Yamakawa 1975

Hydrodynamic Radius from Dynamic Light Scattering

http://www.eng.uc.edu/~gbeaucag/Classes/Properties/HiemenzRaiagopala nDLS.pdf http://www.eng.uc.edu/~gbeaucag/Classes/Physics/DLS.pdf http://www.eng.uc.edu/~gbeaucag/Classes/Properties/HydrodyamicRadiu

s.pdf

Consider motion of molecules or nanoparticles in solution

Particles move by Brownian Motion/Diffusion The probability of finding a particle at a distance x from the starting point at t = 0 is a Gaussian Function that defines the diffusion Coefficient, D

$$\rho(x,t) = \frac{1}{(4\pi Dt)^{1/2}} e^{-x^2/(2Dt)}$$
$$\langle x^2 \rangle = \sigma^2 = 2Dt$$

The Stokes-Einstein relationship states that D is related to RH,

$$D = \frac{kT}{6\pi\eta R_H}$$

A laser beam hitting the solution will display a fluctuating scattered intensity at "q" that varies with q since the particles or molecules move in and out of the beam I(q,t)

This fluctuation is related to the diffusion of the particles

Video of Speckle Pattern (http://www.youtube.com/watch?v=ow6F5HJhZo0)

For static scattering p(r) is the binary spatial auto-correlation function

We can also consider correlations in time, binary temporal correlation function $g1(q,\tau)$

For dynamics we consider a single value of q or r and watch how the intensity changes with time I(q,t)

We consider correlation between intensities separated by t We need to subtract the constant intensity due to scattering at different size scales and consider only the fluctuations at a given size scale, r or $2\pi/r = q$

Dynamic Light Scattering (http://www.eng.uc.edu/~gbeaucag/Classes/Physics/DLS.pdf)

 $\mathbf{I}(\mathbf{R}, t) = \mathbf{Q}_{e} \mathbf{E}_{s}^{*}(\mathbf{R}, t')^{T} \cdot \mathbf{E}_{s}(\mathbf{R}, t')$ $\mathbf{Q}_{e} = quantum efficiency$ $\mathbf{R} = 2\pi/q$ $\mathbf{E}_{s} = amplitude of scattered wave$

$$\langle I(\mathbf{R}) \rangle = Q_c \langle E_s^*(\mathbf{R}, t')^T \cdot E_s(\mathbf{R}, t') \rangle$$

$\langle I(0)I(t) \rangle = \langle I(0)^2 \rangle + Q_e^2 \langle E^*(0)^T \cdot E(t) | E^*(t)^T \cdot E(0) \rangle$

If the intensity correlation function is normalized by <I(0)2> the autocorrelation function results,

 $C(t) = \langle I(0)I(t) \rangle \langle I(0)^2 \rangle = 1 + K g^{(2)}(t)$

where $g^{(2)}(t)$ is the square of the normalized autocorrelation function for electric field, $g^{(2)}(t) = |g^{(1)}(t)|^2$.

$$G_1(\mathbf{K}, t) = \langle \Delta C(\mathbf{K}, 0) \rangle^2 > \exp(-D_m K^2 t) \qquad g^{(1)}(t) = g^{(1)}(\mathbf{K}, t) = \exp(-D_m K^2 t)$$

q or K squared since size scales with the square root of time $\langle x^2
angle = \sigma^2 = 2Dt$

Dynamic Light Scattering



a = RH= Hydrodynamic Radius

The radius of an equivalent sphere following Stokes' Law

Dynamic Light Scattering

my DLS web page

Wiki

Wiki Einstein Stokes

Diffusing Wave Spectroscopy (DWS)

Will need to come back to this after introducing dynamics And linear response theory

http://www.formulaction.com/technology-dws.html

Rg reflects spatial distribution of structure

RHreflects dynamic response, drag coefficient in terms of an equivalent sphere

While both depend on "size" they have different dependencies on the details of structure

If the structure remains the same and only the amount or mass changes the ratio between these parameters remains constant. So the ratio describes, in someway, the structural connectivity, that is, how the structure is put together.



This can also be considered in the context of the "universal constant"

$$[\eta] = \Phi \frac{R_g^3}{M}$$

Lederer A et al. Angewandte Chemi 52 4659 (2013).

(http://www.eng.uc.edu/~gbeaucag/Classes/Properties/DresdenRgbyRh4 659_ftp.pdf)





Scheme s. Variation of the branching degree from linear to hyperbranched structures for polyesters with different functional groups.



Figure 1. Dependence of the branching parameter ρ on the degree of branching for SY- and OH-terminated samples. The lines correspond to tentative fits to the measurement points.

Lederer A et al. Angewandte Chemi 52 4659 (2013).

(http://www.eng.uc.edu/~gbeaucag/Classes/Properties/DresdenRgbyR

$$DB = \frac{D + T}{D + L + T}$$
(1)

where D, T and L are the fractions of dendritic, terminal or linearly incorporated monomers in the resulting hyperbeanched polymers obtained from integration of the respective signals in NMR-spectra. The values commonly reported for DB are in the range of 0.4 to 0.8. Equation (1) has been used

Acta Polymer., 48, 30-35 (1997)

model	P	P_w/P_n
linear chains	0/0_1/1	
polydisperse (m = 1)	31/2	2
polydisperse (m coupled chains)	$\frac{(m+2)^{1/3}}{m+1} 2\Sigma \left(1 + \frac{k-1}{m}\right) c(k)$	1 + (1/m)
star molecules		
regular stars	$\left(\frac{3f-2}{f\pi}\right)^{1/2} \frac{8}{3} \frac{(2-f)+2^{1/2}(f-1)}{f}$	1
polydisperse stars	$\left(\frac{6f}{f+1}\right)^{1/2} \frac{f+3}{2(f+1)}$	1 + (1/f)
polycondensates	(1.1) 201.1)	
Aftype	31/3	$P_w\left(1-\frac{f}{2(f-1)}\right)$
ABC type	$\left(\frac{3}{4}\frac{1+2B}{1+B}\right)^{1/3}\left(\frac{2+B}{1+B}\right)$	2(1 + B)
randomly cross-linked chains (polydisperse ($m = 1$) primary chains) monodisperse spheres	3 ^{1/2} (³ / ₈) ^{1/2}	$_{1}^{2\left(P_{w}/P_{w}p\right) }$
$\rho = (1/R)_2 (S^2)_2^{1/2}$; all other notation is as in Tables I and II.		

Table III $_{\rho}$ Factor and Molecular Polydispersity $P_{\rm w}/P_{\rm n}$ for Some Selected Models^e

Burchard, Schmidt, Stockmaver, Macro, 13 1265 (1980)

(http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhRatioBurchard ma60077a045.pdf)





Figure 3. Dimensionless parameter $\rho = \langle R_h^{-1} \rangle_z R_g$ for three branching models and for compact spheres.

Burchard. Schmidt. Stockmaver. Macro. 13 1265 (1980)

(http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhRatioBurchard ma60077a045.pdf)



Figure 2. Temperature dependence of the average radius of gyration ($\langle R_g \rangle$) of the PNIPAM chains in the coil-to-globule (heating) and the globule-to-coil (cooling) transitions, respectively.



Figure 3. Temperature dependence of the average hydrodynamic radius ($\langle R_h \rangle$) of the PNIPAM chains in the coil-to-globule (heating) and the globule-to-coil (cooling) transitions, respectively.



Figure 4. Temperature dependence of the ratio of radius of gyration to hydrodynamic radius ($\langle R_g \rangle / \langle R_b \rangle$) of the PNIPAM chains in the coil-to-globule (heating) and the globule-to-coil (cooling) transitions, respectively.

1.5 = Random Coil ~0.56 = Globule Globule to Coil => Smooth Transition Coil to Globule => Intermediate State Less than (3/5)^{1/2} = 0.77 (sphere)

Wang X., Oiu X., Wu C. Macro, 31 2972 (1998).

(http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhPNIPA AMma971873p.pdf)



Figure 7. Schematic of four thermodynamically stable states and their corresponding chain density distributions (W(r))along the radius in the coil-to-globule and the globule-to-coil transitions.



Figure 4. Temperature dependence of the ratio of radius of gyration to hydrodynamic radius ($\langle R_g \rangle \langle R_b \rangle$) of the PNIPAM chains in the coil-to-globule (heating) and the globule-to-coil (cooling) transitions, respectively.

1.5 = Random Coil ~0.56 = Globule Globule to Coil => Smooth Transition Coil to Globule => Intermediate State Less than (3/5)^{1/2} = 0.77 (sphere)

Wang X., Oiu X., Wu C. Macro, 31 2972 (1998).

(http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhPNIPA AMma971873p.pdf)



The objectives of the current study are to find whether the intrachain hydrogen boding plays a role in stabilizing individual collapsed single-chain globules, in the formation of the molten globular state during the coil-to-globule transition, and in the hysteresis of the globule-to-coil transition.



Figure 4. Temperature dependence of average radius of gynation ((R_0)) and hydrodynamic radius ((R_0)) of poly(NN-diethylacrylamide) (PDEAM) chains in water in one heating-and-cooling cycle.



Figure 5. Temperature dependence of ratio of average radius of gyration to average hydrodynamic radius ($\langle R_0 \rangle \langle R_1 \rangle$) of poly(NN-diethylacrylamide) (PDEAM) chains in water in one heating-and-cooling cycle.

Zhou K., Lu Y., Li J., Shen L., Zhang F., Xie Z., Wu C. Macro, 41

8927 (2008).

http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhCoilto Globulema8019128.pdf

1.5 to 0.92 (> 0.77 for sphere)

It is important to note that for PDEAM $\langle R_g \rangle / \langle R_h \rangle$ finally reaches ~1.0, higher than 0.774 predicted for a uniform nondraining sphere. This means that individual PDEAM singlechain globules are not hard sphere, but still partially draining, less compact than those PNIPAM single-chain globules because its $\langle R_g \rangle / \langle R_h \rangle$ reaches ~0.78 at high temperatures.²¹ We can attribute such a difference to the lacking of intrachain hydrogen bonding in PDEAM. It has been known that the hydrogen

This ratio has also been related to the shape of a colloidal particle





Solute molecules move with kT and exert a pressure like a gas on the walls of the vessel. This is the osmotic pressure.

We can use this to count the number of solute molecules, n (π is a colligative property). For a known mass used to make the solution we can obtain the number average molecular weight.

Osmotic Pressure





Osmotic Pressure

For non-Ideal conditions we consider a power-series in number concentration, ρ , called a virial expansion.

$$\frac{\pi}{kT} = B_1 \rho + B_2 \rho^2 + B_3 \rho^3 + B_4 \rho^4 + \dots \qquad \rho = \frac{n}{V} = \frac{Mass}{V} \frac{1}{(MW)_n} = \frac{\phi}{N}$$

The first virial coefficient is trivial. The second virial coefficient pertains to binary interactions (if we are considering enthalpic effects).

$$\frac{\pi}{kT} = \frac{\phi}{N} + A_2 \phi^2 + A_3 \phi^3 + A_4 \phi^4 + \dots \qquad A_2 = \left(\frac{1}{2} - \chi\right)$$

For a monomer with z sites of interaction we can define a unitless energy parameter $\chi = z\Delta\varepsilon/kT$ that reflects the average enthalpy of interaction per kT for a monomer



Osmotic Pressure

For non-Ideal conditions we consider a power-series in number concentration, ρ , called a virial expansion.

 $\rho + B_4 \rho^4 + \dots \qquad \rho = \frac{n}{V} = \frac{Mass}{V} \frac{1}{(MW)_n} = \frac{\phi}{N}$ $\frac{\pi}{kT} = B_1 \rho + B_2 \rho^2 + B_3 \rho^3 + B_4 \rho^4 + \dots$ at Second Virial Coefficient for Uncharged Particles umE42 Values of the nonideality correction factor B' and the second virial wherent B for three different models of nonideal colloidal solutions and a had General Noninteracting Noninteracting Interacting Heimez description of model spheres rods random coils "Colloidal 301 RTV Chemistry" AG: Free energy of L: Length; al: Diameter solute-solvent interaction $\frac{L\vec{V}_2}{dM_2^{-1}} = \frac{L}{\rho_2 M_2 d}$ $\frac{\Delta G}{V_s RT} \left(\frac{\hat{V}_s}{M_s} \right)$ $\rho_2 M_2$ 6 Expressed in $\rho_2^2 4 \pi R^2 N_A$ Pit d'NA forms of \$(1-0/T) V R: Radius of d: Diameter sphere of rod Managere gs units! A. y. O: Parameters of interest for the solution



For a monomer with z sites of interaction we can define a unitless energy parameter $\chi = z\Delta\varepsilon/kT$ that reflects the average enthalpy of interaction per kT for a monomer

is tMelexcess interaction per kT for a molecule

and
$$N\rho = \phi$$

So the second term is $\frac{A_2\rho^2}{N}$

Flory's consideration of polymer mixing

Consider the ideal mixing of gas atoms. Then entropy gained in mixing is given by Boltzman interms of the volume fraction Φ as:

$$\Delta S_{mixing} = \phi \ln \phi + (1 - \phi) \ln (1 - \phi)$$

For a polymer each chain acts as a unit so this function is modified as:

$$\Delta S_{mixing} = \frac{\phi}{N} \ln \phi + (1 - \phi) \ln (1 - \phi)$$

To account for enthalpy of mixing Flory introduce a simple binary interaction parameter:

$$\Delta f_{mixing} = \frac{\phi}{N} \ln \phi + (1 - \phi) \ln (1 - \phi) + \chi \phi (1 - \phi)$$

Where Δf is the volumetric (Helmholtz) free energy change on mixing per monomer per kT. To obtain the free energy of mixing for a chain we multiply by kT and by Ω , the number of monomer + solvent sites in the system.



At equilibrium the **<u>chemical potentials</u>** of the solvent (and the polymer) in the two solutions are identical.

Chemical potential is the change in free energy with respect to concentration for a given component in a given phase (you need to specify the component and the phase when you say chemical potential) The chemical potential, here μ_p or μ_s , for one component of a mixture is the derivative of the Gibbs free energy for the system with respect to the number of moles of that component. The Gibbs free energy is related to the Helmholtz free energy by, G = F + PV. For the Flory lattice system the volume equals the number of lattice sites time the volume of one site, $V = \Omega V_c$, where $\Omega = n_s + n_p N$ and N is the degree of polymerization. Changing the number of moles of one component in the Flory lattice model, while retaining the number of moles of the other component will result in a change in the lattice size, Ω and the volume fraction ϕ , and system volume, V. This means,

$$\mu_{x: \text{sp}, T, P \text{ constant}} (\phi, P, T) - \mu^{\alpha}_{x}(T) = (\delta F / \delta \Omega)_{\phi,T} (\delta \Omega / \delta n_{x})_{\text{sp}} + (\delta F / \delta \phi)_{\Omega,T} (\delta \phi / \delta n_{x})_{\text{sp}} + PV_{c}$$

Where µ0,(T) is the chemical potential of the pure solvent.

From the definition of Ω , $(\delta\Omega/\delta n_s)_{sp} = 1$; and given that $\phi = n_p N/(n_p N + n_s) = n_p N/\Omega$, so $(\delta\phi/\delta\Omega)_{sp} = -n_p N/\Omega^2$. $(\delta\phi/\delta n_s)_{sp} = (\delta\phi/\delta\Omega)_{sp} (\delta\Omega/\delta n_s)_{sp} = -n_p N/\Omega^2 = -\phi/\Omega$. $(\delta F/\delta\Omega)_{0,T} = kT f_{ss}(\phi)$, and $(\delta F/\delta\phi)_{0,T} = \Omega kT (\delta f_s/\delta\phi)_{0,T}$, so,

 $\mu_{u \text{ sets } T, P \text{ constant}} (\phi, P, T) = \mu_{u}^{0}(T) + kT (f_{u}(\phi) - \phi (\delta f_{u}/\delta \phi)_{\Omega,T}) + PV_{u}$

and through a similar approach,

 $\mu_{\mu \text{c ns. T. P constant}} (\phi, P, T) = \mu_{\mu}^{\circ}(T) + kT (f_{m}(\phi) - (1-\phi) (\delta f_{m} / \delta \phi)_{GLT}) + PV_{c}$

Osmotic Pressure:

The osmotic pressure is the excess pressure needed to make a solution with a polymer have the same chemical potential as a pure solvent phase at the same temperature,

$$\mu_{c} (\phi, P+\Pi, T) = \mu_{i}(\phi=0, P, T)$$

At $\phi = 0$ f_m = 0 so $\mu_i(\phi=0, P, T) = \mu_{i,i}^0(T) + PV_{i,i}$ and using the above expression,

 $\mu_{a}(\phi, P+\Pi, T) = \mu_{a}^{0}(T) + kT (f_{m}(\phi) - \phi (\delta f_{m}/\delta \phi)_{\Omega,T}) + (P+\Pi)V_{c^{*}}$

so,

 $PV_c = kT (f_m(\phi) - \phi (\delta f_m/\delta \phi)_{GT}) + PV_c + \Pi V_c$

and

 $\Pi = (kT/V_{c}) (\phi (\delta f_{c}/\delta \phi)_{QT} - f_{m}(\phi))$

 $f_{-}(\phi) = \phi \ln \phi / N + (1-\phi) \ln(1-\phi) + \chi \phi (1-\phi)$

 $(\delta f_{u}/\delta \phi)_{QT} = \ln \phi/N + 1/N - (1+\phi)/(1-\phi) - \ln (1-\phi) + \chi(1-2\phi)$

50,

$$\begin{split} \varphi \left(\delta f_{m} / \delta \varphi \right)_{\Omega, T} - f_{m} (\varphi) &= \varphi / N - \ln(1 - \varphi) - \varphi (1 - \varphi) / (1 - \varphi) + \chi \left\{ \varphi (1 - 2\varphi) - \varphi (1 - \varphi) \right\} \\ &= \varphi / N - \ln(1 - \varphi) - \varphi - \chi \varphi^{2} \end{split}$$

for $\phi < 1$, $\ln(1-\phi) = -\{\phi + \phi^2/2 + \phi^3/3 + \phi^4/4 + ...\}$ and,

 $\Pi = (kT/V_{o}) [\phi/N + (1/2 - \chi) \phi^{2} + \phi^{3}/3 + \phi^{4}/4 + ...]$

2 | 3

The Flory Expression indicates a linear dependence of osmotic pressure in concentration at low concentration and a dependence on concentration to the power 2 at high concentration.

$$\Pi = \frac{kT}{V_c} \left(\frac{\phi}{N} + \left(\frac{1}{2} - \chi \right) \phi^2 + \dots \right)$$



From Gert Strobl, Polymer Physics

2 | 4





Right graph shows that:

- 1) c/c* is the natural measure of concentration
- 2) Flory prediction is sufficient at low c/c^* but fails at large c/c^*
- 3) The prediction of the concentration blob model is correct at large c/c^*

Osmotic Pressure for Excluded Volume Coils and Concentration Blobs.

Using the Flory-Huggins equation an expression for the osmotic pressure can be obtained.

$$\Pi = (kT/V_{,}) [\phi/N + (1/2 - \chi) \phi^2 + \phi^2/3 + \phi^2/4 + ...]$$

The Flory-Huggine equation assumes in its derivation that the spatial distribution of monomers is random. This means that the Flory-Huggins equation is restricted to Gaussian Coils and is not strictly appropriate for the normal condition of polymers in a good solvent, i.e. F-H is not appropriate for self-avoiding walks. The F-H expression for osmotic pressure is also not appropriate for concentrations above the overlap concentration in good-solvent systems. F-H is only appropriate for the-L-emperature solutions.

Resolution of good-solvent behavior for osmotic pressure resulted form the work of des Cloizeaux and is one of the major contributions of modern polymer physics.

The approach is based on renormalization of a good-solvent coil using the blob concept. First, a generic expression of osmotic pressure can be written, based on the F-H result,

$\Pi = (kT \phi) f(\phi b^i, N)$

Assuming that the low concentration limit depends linearly on concentration, ϕ_i and that the viral expansion will be dependent on molecular weight, N, and the volume physically occupied by the polymer chains, $\phi_i = b^* n_\mu N((n_\mu N + n_i))$. This expression can be renormalized to account for concentration blobs by defining λ as the number of units of persistence length b in a blob, so that the number of blob units in a chain is N λ (replacing N), the step length is the size of a blob, $b_{\rm inte} = b \lambda^*$, where v is 1/d₀ and the concentration of blobs (rather than statistical segments, ϕ_i is $\phi_{\rm inte} = \phi \lambda$.

$\Pi = (kT \phi \lambda) f(\phi \lambda^{3r-1} b^3, N \lambda)$

and the osmotic pressure is unchanged by renormalization so the two expressions for Π are equivalent. λ can vary from 1 to N. For the limit of $\lambda = N$ the osmotic pressure is proportional to ϕ /N, so the generic expression must be proportional to ϕ /N. The N/ λ dependence already exists in the ϕ term so the two components are redundant. At the limit of λ =N the ϕ expression becomes (N'b)², and the generic expression becomes

$\Pi = (kT \oplus N) f(\oplus N (N'b)^2)$

We can recognize 1/c* = (N'b)7/N and rewrite the expression in terms of c*.

$$\Pi = (kT \phi N) f(\phi \phi')$$

For $\phi > \phi^*$, II is independent of N. Then $f(\phi|\phi')$ must have a linear molecular weight dependence and since $\phi|\phi' = (N'b)^2/N \phi$ or $N^{1-1} b^2 \phi$, we have,

$\Pi = (kT \phi/N) (\phi/\phi^{-})^{1/(2\gamma-1)}$

For theta solvent scaling and concentrations above the overlap concentration this results in $\Pi_n = K c^{2n}$, as predicted from the viral expansion of the F-H equation. For good solvents $\Pi_{max} = K c^{2n}$. This result has been experimentally verified. The F-H result is retained at low concentrations even for good solvent coils, while above the overlap concentration a stronger dependence on concentration of the osmotic pressure is predicted by scaling arguments and renormalization.

Concentration Blob Prediction



Fig. 3.3. Data of Fig. 3.2, presented in a plot of the reduced comotic pressure versus the overlap ratio. The continuous lines correspond to the theoretical results. Eqs. (3.26), (3.41)

$$\pi \approx kT \frac{\phi}{N} \left(\frac{c}{c^*}\right)^p$$

$$c^* \approx N^{-\frac{4}{5}}$$

$$\frac{4}{5}P - 1 = 0$$

$$P = \frac{5}{4}$$

$$\pi \approx c^{\frac{9}{4}}$$
