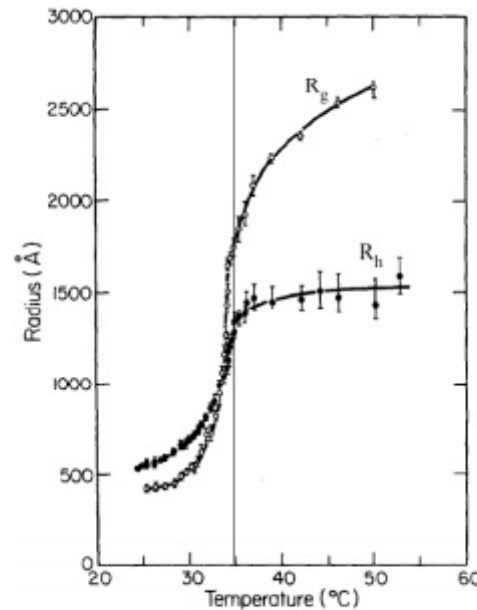


# Measurement of the Hydrodynamic Radius, $R_h$



$R_g/R_h$   
 1.5 Theta  
 1.6 Expanded  
 0.774 Sphere  
 0.92 Draining Sphere

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

$$[\eta] = \frac{4/3\pi R_H^3}{N} \quad R_H = \frac{kT}{6\pi\eta D} \quad \frac{1}{R_H} = \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N \left\langle \frac{1}{|r_i - r_j|} \right\rangle$$

[Kirkwood, J. Polym. Sci. \*\*12\*\* 1 \(1953\).](#)

<http://theor.jinr.ru/~kuzemsky/kirkbio.html>

## A Harmonic Mean

(based on an average of transport rates,  $D = kT/(6\pi\eta R_h)$ )

<http://www.eng.uc.edu/~gbeaucag/Classes/Properties/HydrodynamicRadius.pdf>

## An Arithmetic Mean

1

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

# Measurement of the Hydrodynamic Radius, $R_h$



$$[\eta] = \frac{4}{3}$$

# R<sub>g</sub>/R<sub>H</sub> Ratio

Table III  
 $\rho$  Factor and Molecular Polydispersity  $P_w/P_n$  for Some Selected Models<sup>a</sup>

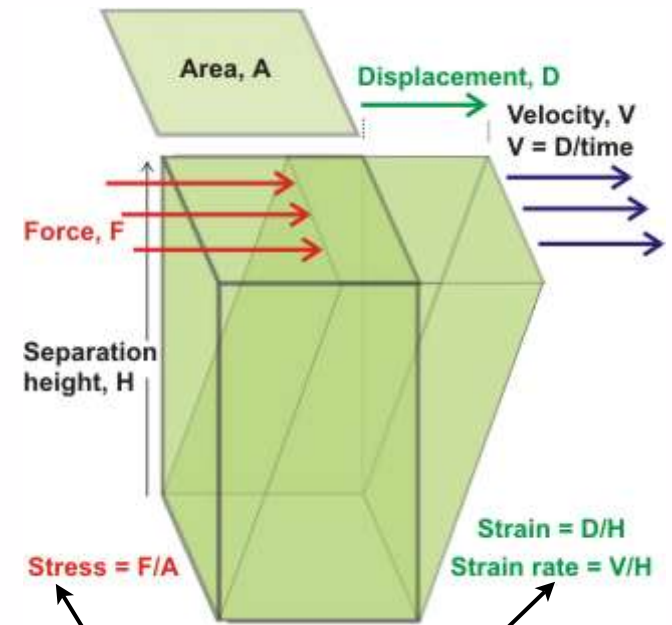
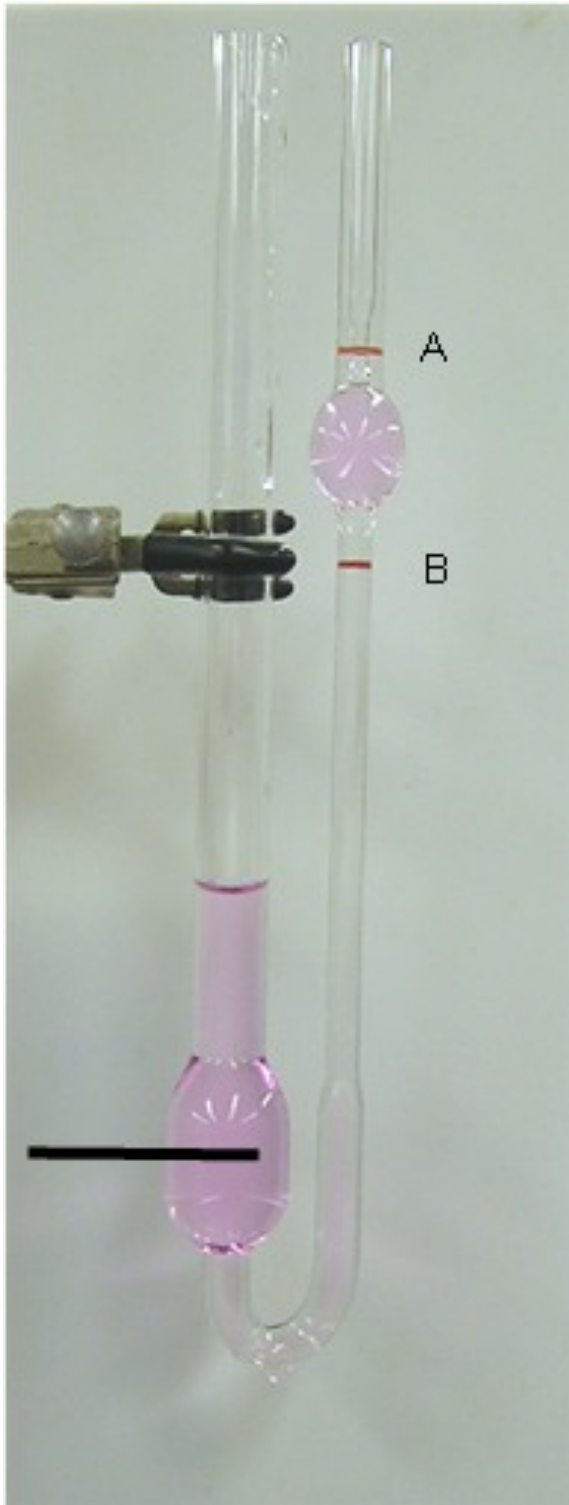
model	$\rho$	$P_w/P_n$
linear chains		
monodisperse	1.5	$8/3\pi^{1/2}$
polydisperse ( $m = 1$ )		$3^{1/2}$
polydisperse ( $m$ coupled chains)		$\frac{(m+2)^{1/2}}{m+1} 2\Sigma \left(1 + \frac{k-1}{m}\right) c(k)$
star molecules		
regular stars		$\left(\frac{3f-2}{f\pi}\right)^{1/2} \frac{8}{3} \frac{(2-f) + 2^{1/2}(f-1)}{f}$
polydisperse stars		$\left(\frac{6f}{f+1}\right)^{1/2} \frac{f+3}{2(f+1)}$
polycondensates		
A <sub>f</sub> type	1.73	$3^{1/2}$
ABC type		$\left(\frac{3}{4} \frac{1+2B}{1+B}\right)^{1/2} \left(\frac{2+B}{1+B}\right)$
randomly cross-linked chains (polydisperse ( $m = 1$ ) primary chains)	1.73	$2(P_w/P_n p)$
monodisperse spheres	0.77	$(3/5)^{1/2}$

<sup>a</sup>  $\rho = \langle 1/R \rangle_z \langle S^2 \rangle_z^{1/2}$ ; all other notation is as in Tables I and II.

[Burchard, Schmidt, Stockmayer, Macro. 13 1265 \(1980\)](http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhRatioBurchardma60077a045.pdf)

(<http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhRatioBurchardma60077a045.pdf>)

# Viscosity



$$\tau = \eta \dot{\gamma}$$

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

$$[\eta] \approx \frac{V_{\text{Molecule}}}{M_{\text{Molecule}}}$$

Native state has the smallest volume

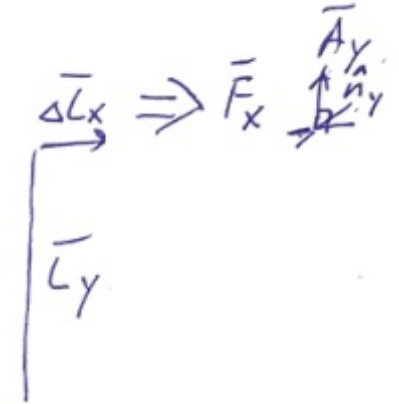
$$\Delta p = \frac{8\mu LQ}{\pi R^4} = \frac{8\pi\mu LQ}{A^2} \quad \text{Poiseuille's Law } (Q = V/\text{time})$$



# Intrinsic “viscosity” as a linear displacement law

$$\tau_{xy} = \eta \dot{\gamma}_{xy}$$

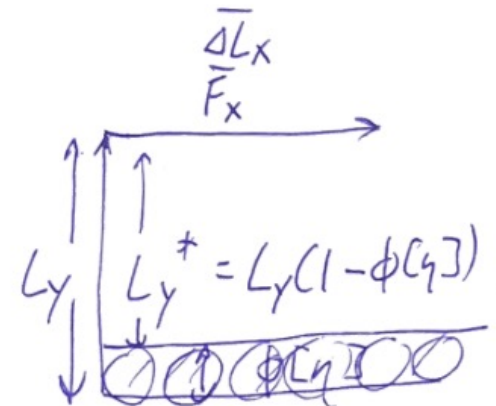
$$\tau_{xy} = \frac{dF_x}{dA_y} = \eta \dot{\gamma}_{xy} = \eta \frac{d\left(\frac{\Delta L_x}{L_y}\right)}{dt}$$



$$\eta = \eta_s (1 + \phi[\eta]) \sim \eta_s \exp(\phi[\eta])$$

At very  
small  $\phi$

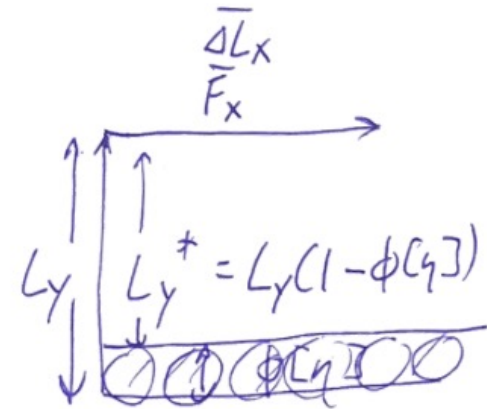
$$\begin{aligned} L_y^* &= L_y \exp(-\phi[\eta]) \\ &\sim L_y (1 - \phi[\eta]) \end{aligned}$$



# Intrinsic “viscosity” as a linear displacement law

$$L_y^* = L_y \exp(-\phi[\eta])$$

$$\sim L_y (1 - \phi[\eta])$$



$$\tau_{xy} = \eta_s (1 + \phi[\eta]) \frac{d \left( \frac{\Delta L_x}{L_y} \right)}{dt}$$

$$= \eta_s \frac{d \left( \frac{\Delta L_x}{L_y^*} \right)}{dt}$$

# Intrinsic, specific & reduced “viscosity”

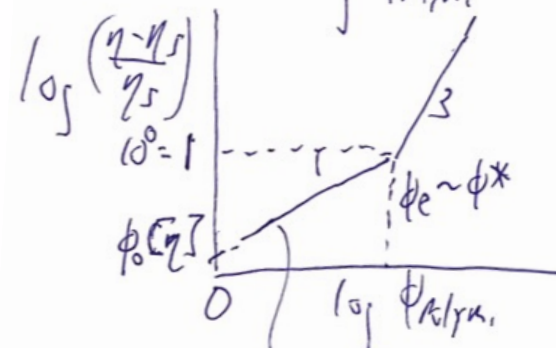
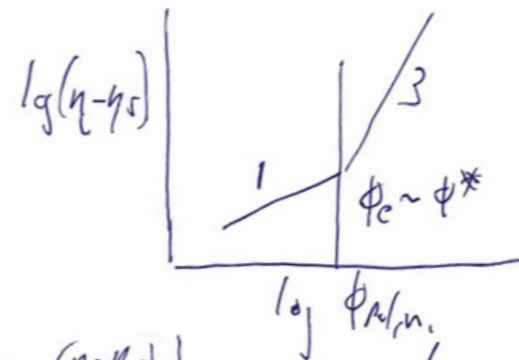
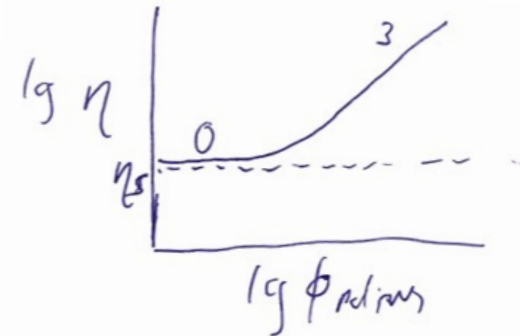
$\tau_{xy} = \eta \dot{\gamma}_{xy}$  Shear Flow (may or may not exist in a capillary/Couette geometry)

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

$$\eta_{rel} = \eta / \eta_s$$

$$\eta_{sp} = (\eta - \eta_s) / \eta_s = \eta_{rel} - 1$$

$$\eta_{red} = \eta_{sp} / c = (\eta_{rel} - 1) / c$$



$$\lim_{\phi \rightarrow 0} \frac{1}{\phi} \frac{\eta - \eta_s}{\eta_s} = [\eta] \quad \text{units inv. concentration}$$

$$\sim \frac{1}{c^*} = \frac{V_H}{M_{chain}}$$

# Intrinsic, specific & reduced “viscosity”

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

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

Reminiscent  
of a virial expansion.

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

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

We can approximate (1) as:

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

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



# Intrinsic, specific & reduced “viscosity”

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

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

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

We can approximate (1) as:

**Relative Viscosity**  $\eta_r = \frac{\eta}{\eta_0} = 1 + c[\eta] \exp(K_M c[\eta])$  **Martin Equation**

**Reduced Viscosity**  $\frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c$  **Huggins Equation**

$\frac{\ln(\eta_r)}{c} = [\eta] + k_1' [\eta]^2 c$  **Kraemer Equation**  
(exponential expansion)

# Intrinsic, specific & reduced “viscosity”

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

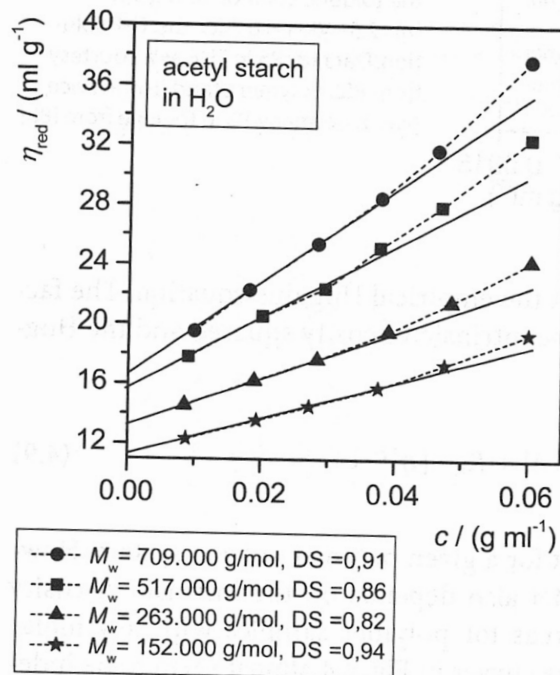
n = order of interaction (2 = binary, 3 = ternary etc.)

**Reduced  
Viscosity**

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

**Reduced  
Viscosity**

$$\frac{\eta_{sp}}{\phi}$$



**Concentration Effect**

**Fig. 4.5.** Reduced viscosity  $\eta_{red}$  as a function of the concentration  $c$  for acetyl starch of different molar masses in aqueous solution at  $T=25^\circ\text{C}$ . The degree of substitution (DS) with acetyl groups is nearly constant at  $DS \approx 0.9$ . Due to the compact structure of the polymer coil the concentrations of the dilution series are relatively high to reach the required relative viscosity range of  $\eta_r = 1.2$ – $2.5$

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

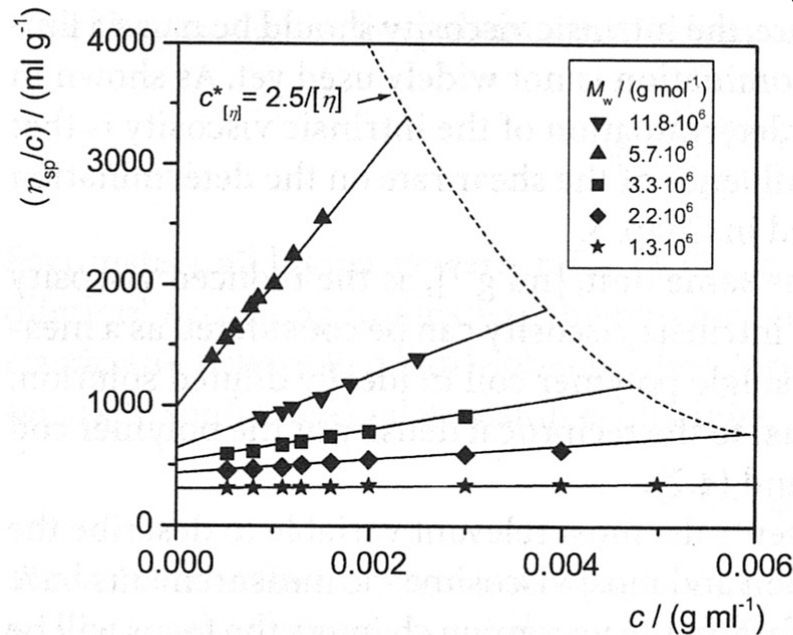
# Intrinsic, specific & reduced “viscosity”

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

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

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

Reduced  
Viscosity



## Concentration Effect, $c^*$

**Fig. 4.2.** Reduced viscosity  $\eta_{red}$  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  $\text{NaNO}_3$  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

# Intrinsic, specific & reduced “viscosity”

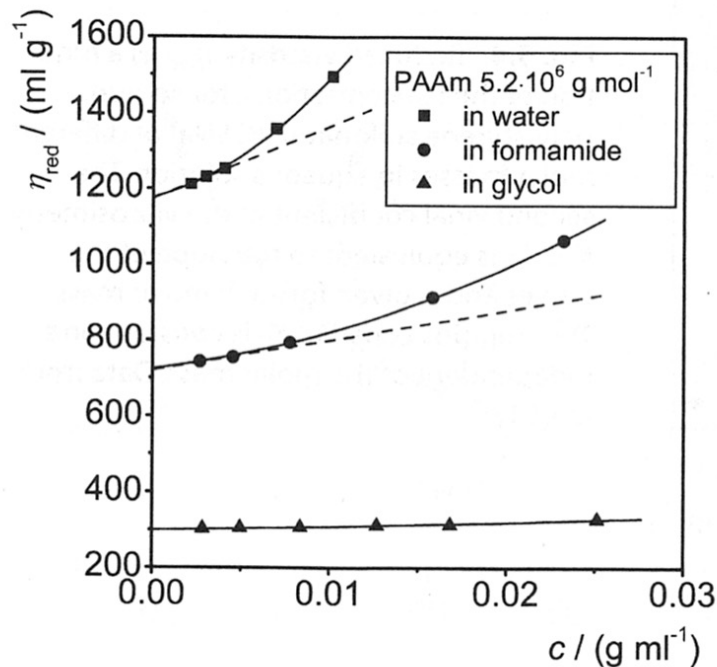
$$\eta = \eta_0 \left( 1 + c[\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right) \quad (1)$$

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

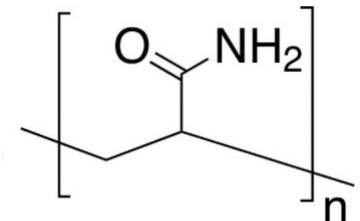
$$\frac{1}{c} \left( \frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{c} (\eta_r - 1) = \frac{\eta_{sp}}{c} \xrightarrow{\text{Limit } c \rightarrow 0} [\eta] = \frac{V_H}{M}$$

Reduced  
Viscosity

$$\frac{\eta_{sp}}{\phi}$$



## Solvent Quality



**Fig. 5.3.** Reduced viscosity  $\eta_{red}$  as a function of the concentration  $c$  for a poly(acrylamide) (PAAm) in the solvents H<sub>2</sub>O, formamide and ethylene glycol at  $T=25$  °C. Data from [89, 90]. The intrinsic viscosity (intersection with the Y-axis) rises with the solvent quality

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



# Intrinsic, specific & reduced “viscosity”

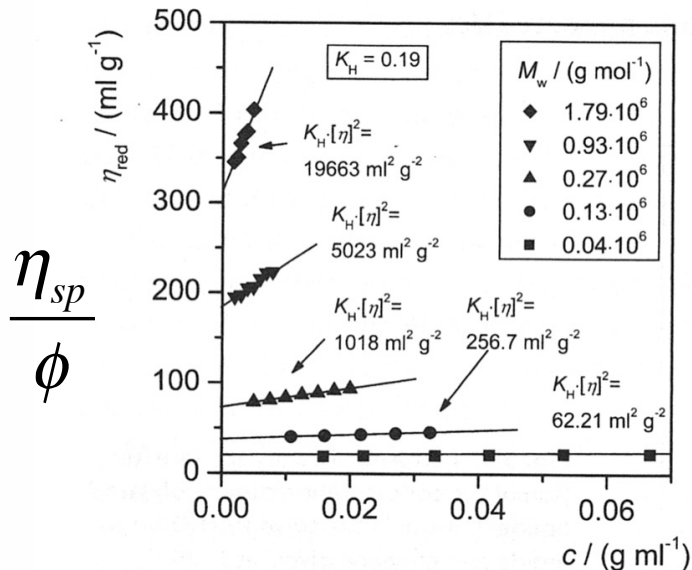
$$\eta = \eta_0 \left( 1 + c[\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right) \quad (1)$$

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

**Reduced  
Viscosity**

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

## Molecular Weight Effect

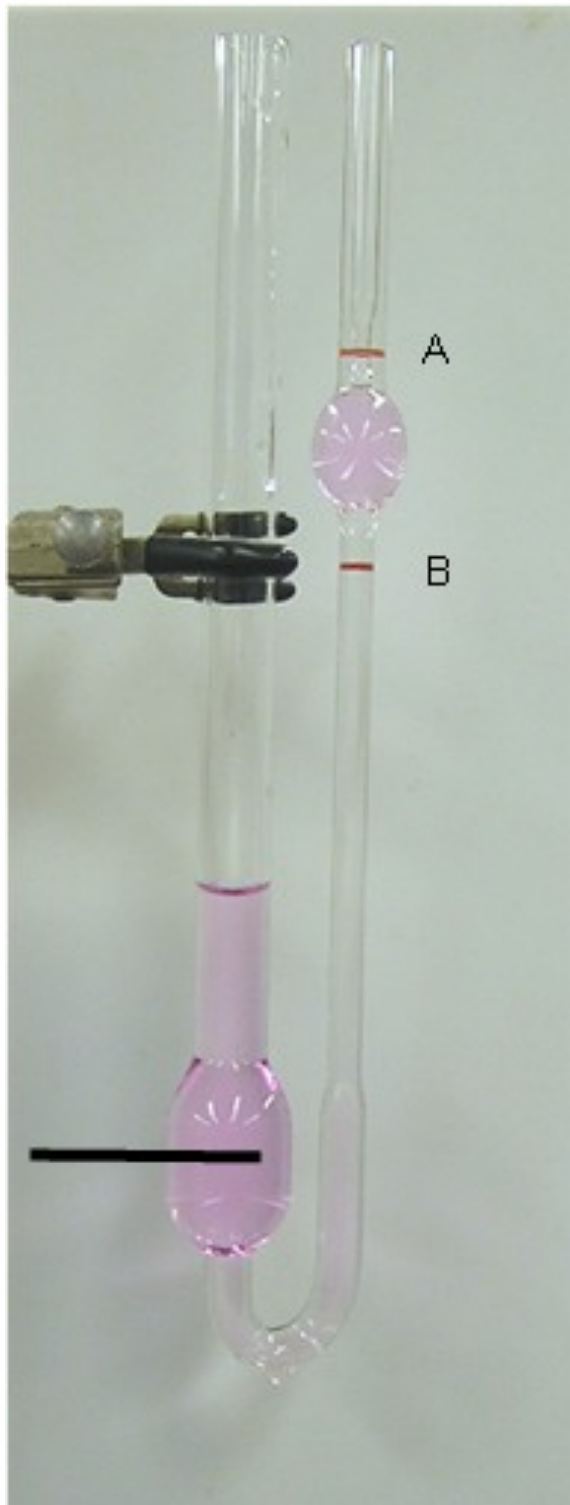


**Fig. 5.4.** Reduced viscosity  $\eta_{red}$  as a function of the concentration  $c$  for sodium poly(styrene sulfonate) (PSSNa) of different molar masses in aqueous solution. The second virial coefficient of the viscosimetry,  $K_H[\eta]^2$ , is equivalent to the slope of the curves and is given for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

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

$$[\eta] \approx \frac{V_{\text{Molecule}}}{M_{\text{Molecule}}}$$

For the Native State  $\text{Mass} \sim \rho V_{\text{Molecule}}$

Einstein Equation (for Suspension of 3d Objects)

$$\eta_s = \eta_0 (1 + 2.5\phi_v)$$

$$[\eta] = \frac{2.5}{\rho} \text{ ml/g}$$

For “Gaussian” Chain  $\text{Mass} \sim \text{Size}^2 \sim V^{2/3}$

$$V \sim \text{Mass}^{3/2}$$

For “Expanded Coil”  $\text{Mass} \sim \text{Size}^{5/3} \sim V^{5/9}$

$$V \sim \text{Mass}^{9/5}$$

For “Fractal”  $\text{Mass} \sim \text{Size}^{d_f} \sim V^{d_f/3}$

$$V \sim \text{Mass}^{3/d_f}$$

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

## Viscosity

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

$$[\eta] \approx \frac{V_{\text{Molecule}}}{M_{\text{Molecule}}}$$

For the Native State Mass  $\sim \rho V_{\text{Molecule}}$

Einstein Equation (for Suspension of 3d Objects)

$$\eta_s = \eta_0 (1 + 2.5\phi)$$

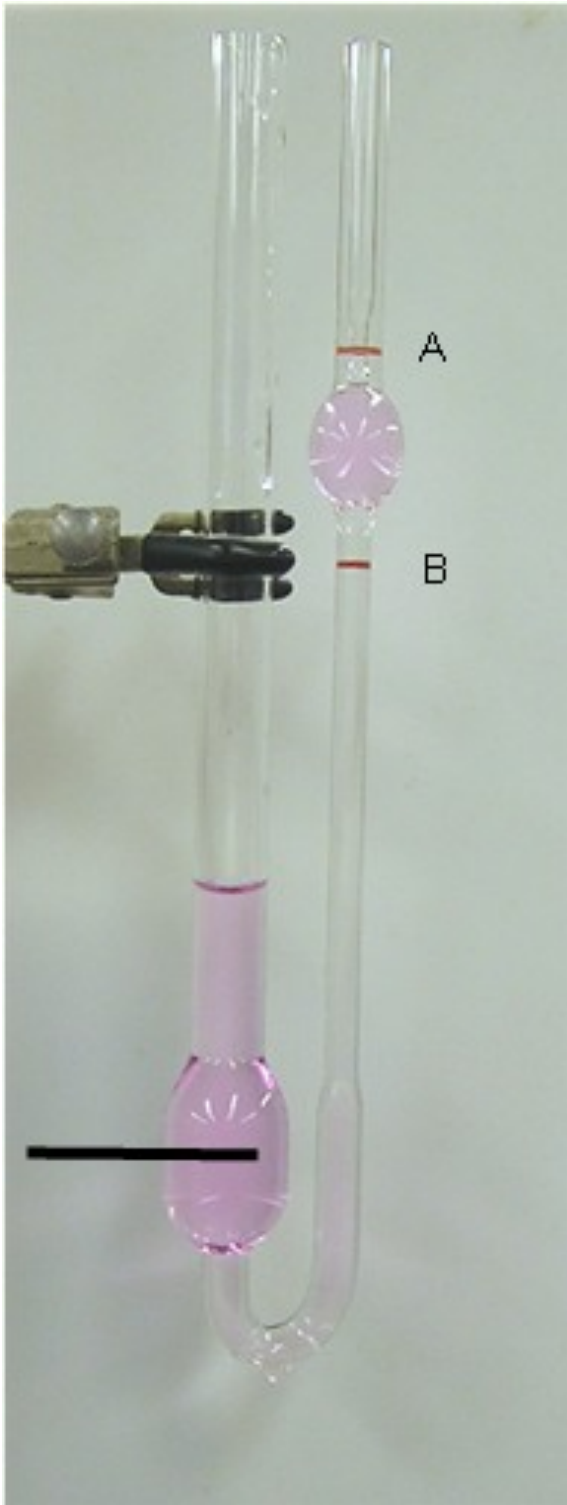
For “Gaussian” Chain Mass  $\sim \text{Size}^2 \sim V^{2/3}$   
 $V \sim \text{Mass}^{3/2}$

**“Size” is the**  
**“Hydrodynamic Size”** For “Expanded Coil” Mass  $\sim \text{Size}^{5/3} \sim V^{5/9}$   
 $V \sim \text{Mass}^{9/5}$

This is the “Zimm Model”  
 Or  
 Non-draining model

For “Fractal” Mass  $\sim \text{Size}^{df} \sim V^{df/3}$   
 $V \sim \text{Mass}^{3/df}$

$$[\eta] \sim M_{\text{Molecule}}^{\frac{3}{df}-1}$$



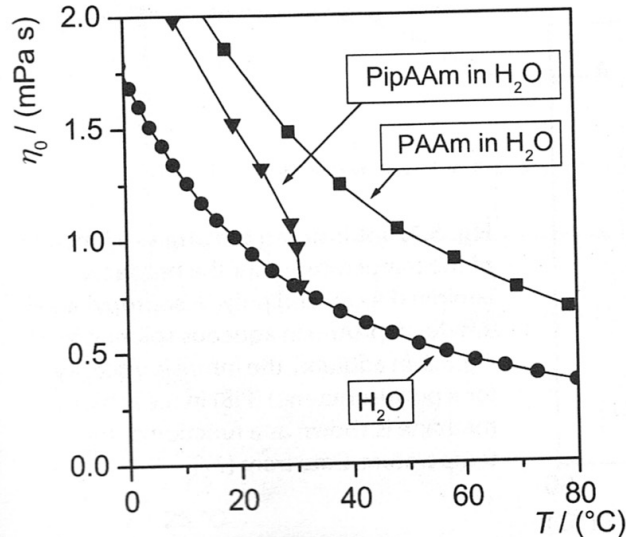
## Intrinsic, specific & reduced “viscosity”

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

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

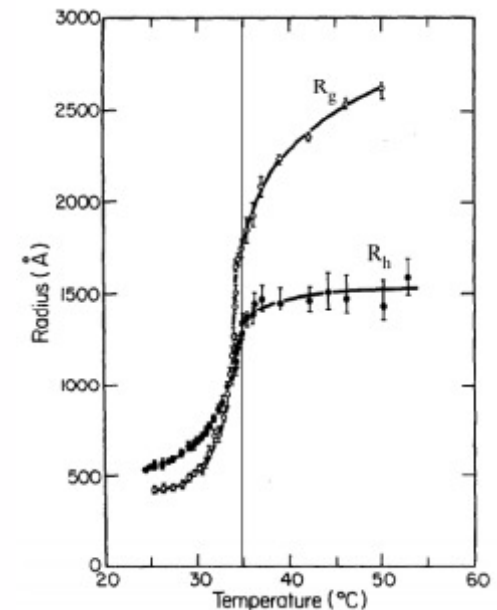
$$\frac{1}{c} \left( \frac{\eta - \eta_0}{\eta_0} \right) = \frac{1}{c} (\eta_r - 1) = \frac{\eta_{sp}}{c} \xrightarrow{\text{Limit } c \rightarrow 0} [\eta] = \frac{V_H}{M}$$

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



### Temperature Effect

**Fig. 5.5.** Zero-shear viscosity  $\eta_0$  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]



$$\eta_0 = A \exp \left( \frac{E}{k_B T} \right)$$

### Weaker and Opposite Dependency



Arrhenius Behavior

$$\eta_0 = A \exp\left(\frac{E}{k_B T}\right)$$

Williams-Landel-Ferry (WLF) Equation

$$\log(a_T) = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)}$$

$$\mu(T) = \mu_0 10^{\left(\frac{-C_1(T-T_r)}{C_2+T-T_r}\right)}$$

$$\frac{\eta}{\eta_0} = \exp\left(\frac{H_a}{kT}\right) \Rightarrow \exp\left(\frac{H_a}{k(T-T_V)}\right) \Rightarrow \exp\left(\frac{E_a}{k(T-T_V)}\right) \Rightarrow \exp\left(\frac{H_a - TS_a}{k(T-T_V)}\right)$$

3 constants  $T_r, H_a, S_a$ ; WLF has 3 constants  $T_V, C_1, C_2$

If  $\exp(x) = 10y$  then  $y = x/(\ln(10)) = x/2.30$

$T_V = (C_2 - T_r)$ ;  $S_a = 2.30 C_1$ ;  $H_a = 2.30 C_1 T_r$

If you choose  $T_r = T_g$  then  $C_1 \sim 17.44$  and  $C_2 \sim 51.6$

If you choose  $T_r = T_g + 43\text{K}$  then  $C_1 \sim 8.86$  and  $C_2 \sim 101.6$

*It might be best to measure H and S and find the Vogel temperature experimentally*

# Intrinsic “viscosity” for colloids (Simha, Case Western)

<https://physicstoday.scitation.org/doi/10.1063/pt.4.2224/full/>

$$\eta = \eta_0 (1 + v\phi) \qquad \eta = \eta_0 (1 + [\eta]c)$$

$$[\eta] = \frac{vN_A V_H}{M}$$

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)  $[\eta] = \frac{2.5}{\rho} \text{ ml/g}$

For ellipsoids  $v$  is larger than for a sphere,

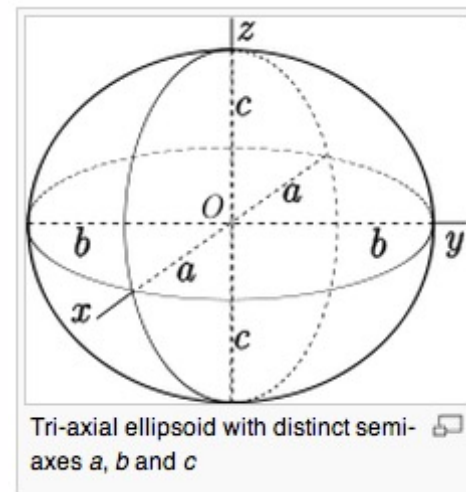
$$v = \frac{J^2}{15(\ln(2J) - 3/2)}$$

prolate  
a, b, b :: a > b

$$J = a/b$$

$$v = \frac{16J}{15 \tan^{-1}(J)}$$

oblate  
a, a, b :: a < b



# 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

$$V_H = \frac{M}{N_A} (\bar{v}_2 + \delta_s v_1^0)$$

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

# Intrinsic “viscosity” for colloids (Simha, Case Western)

$$\eta = \eta_0 (1 + v\phi) \qquad \eta = \eta_0 (1 + [\eta]c)$$

$$[\eta] = \frac{vN_A V_H}{M}$$

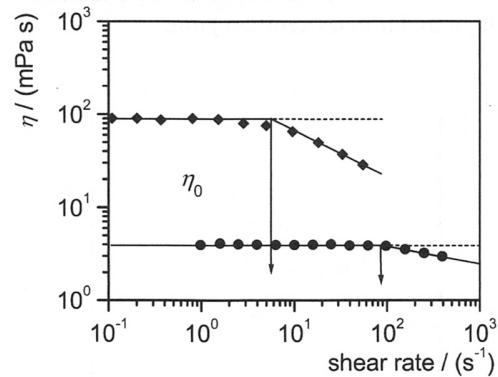
Long cylinders (TMV, DNA, Nanotubes)

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

$C_\eta$  End Effect term  $\sim 2 \ln 2 - 25/12$  Yamakawa 1975

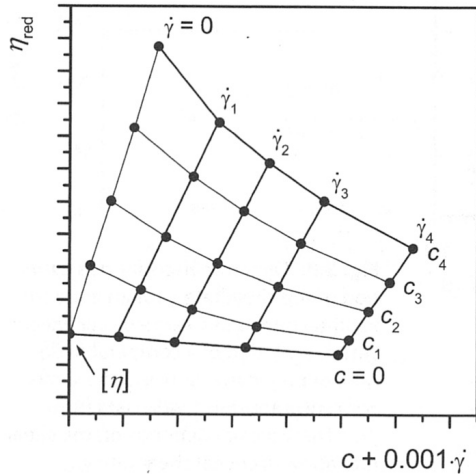


# Shear Rate Dependence for Polymers

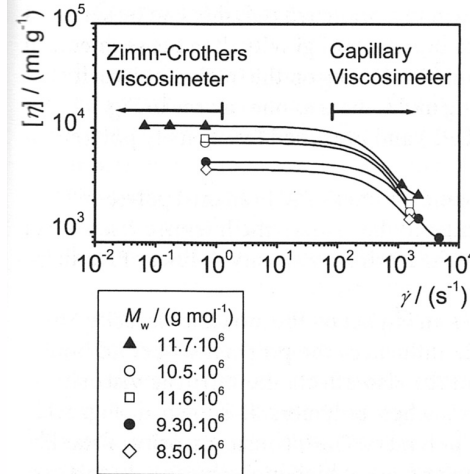


◆ xanthan gum  
 $M_w = 1.8 \cdot 10^6$  g/mol,  $c = 0.1$  %  
 ● poly(acrylamide)  
 $M_w = 7.9 \cdot 10^6$  g/mol,  $c = 0.1$  %  
 $T = 25$  °C

**Fig. 5.8.** Dynamic viscosity  $\eta$  as a function of the shear rate  $\dot{\gamma}$  for an aqueous xanthan gum and an aqueous poly(acrylamide) solution of a comparable degree of polymerization and the same concentration  $c=0.1$  wt% data from [92]. The viscosity depends on the shear rate above a critical shear rate  $\dot{\gamma}_{crit}$



**Fig. 5.9.** Net diagram for the determination of the intrinsic viscosity  $[\eta]$  from measurements of the reduced viscosity at shear rates  $\neq 0$



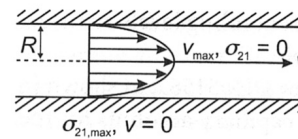
**Fig. 5.10.** Intrinsic viscosity  $[\eta]$  determined at high shear rates  $\dot{\gamma}$  with a capillary viscosimeter and at lower shear rates with a Zimm-Crothers viscosimeter for different xanthan gums in 0.1 mol/l sodium chloride (NaCl) solution at 25 °C. Data from [93]. For strongly shear thinning polymer solutions, only low shear viscosimeters reach the shear rate independent viscosity region

## Capillary Viscometer

$$\frac{\text{Volume}}{\text{time}} = \frac{\pi R^4 \Delta p}{8 \eta l}$$

$$\Delta p = \rho g h$$

$$\dot{\gamma}_{Max} = \frac{4 \text{Volume}}{\pi R^3 \text{time}}$$

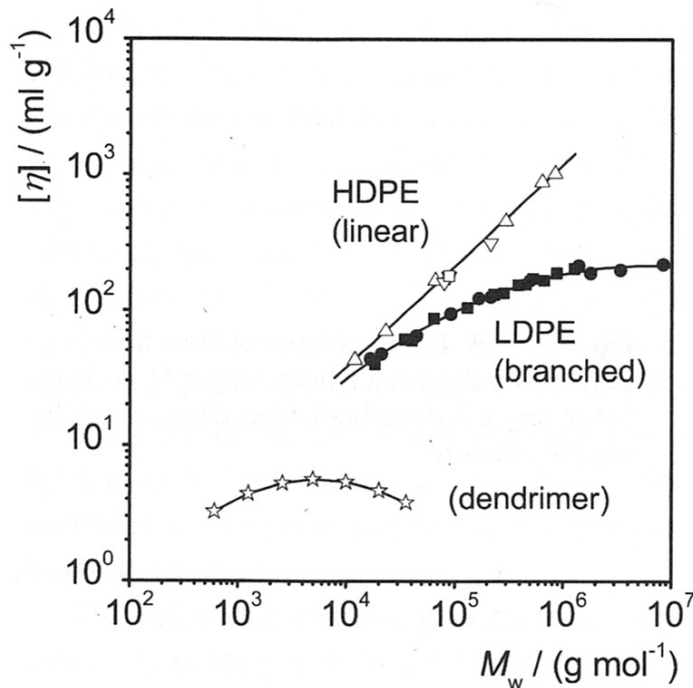


**Fig. 3.2.** Velocity profile in a capillary viscosimeter. The fluid velocity  $v$  has a parabolic profile with a maximum in the middle of the capillary; the shear rate  $\dot{\gamma}$  and the shear stress  $\tau$  have a maximum at the capillary wall and are zero in the middle of the capillary

# Branching and Intrinsic Viscosity

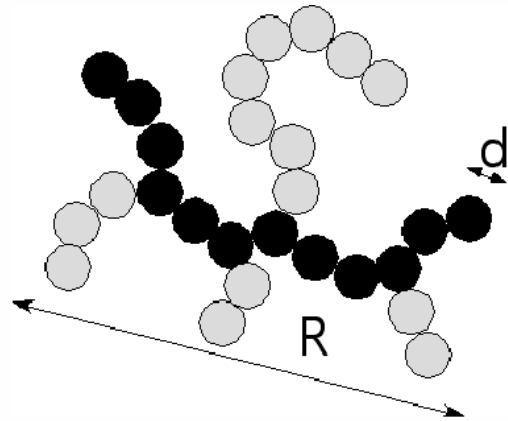
## 5.5 Branching

Branching in a polymer coil leads for polymers of the same molar mass to changes of the intrinsic viscosity. Although the chemical composition is the same, branched polymers have a higher density  $\rho_{\text{equ}}$  in solution than linear polymers and therefore



**Fig. 5.11.** Intrinsic viscosity  $[\eta]$  as a function of the molar mass  $M$  for linear poly(ethylene) (high density poly(ethylene), HDPE) and longchain branched poly(ethylene) (low density poly(ethylene), LDPE) in tetraline at  $T=120^\circ\text{C}$  (data from [47, 94]) as well as for a dendrimer with 3,5-dioxybenzylidene units in tetrahydrofuran at  $T=30^\circ\text{C}$  (data from [47, 95])

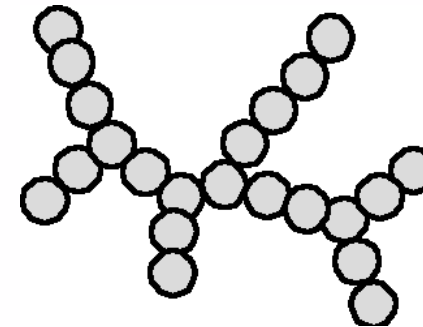
# How Complex Mass Fractal Structures Can be Decomposed



Tortuosity



Connectivity



$$z \sim \left(\frac{R}{d}\right)^{d_f} \sim p^c \sim s^{d_{\min}}$$

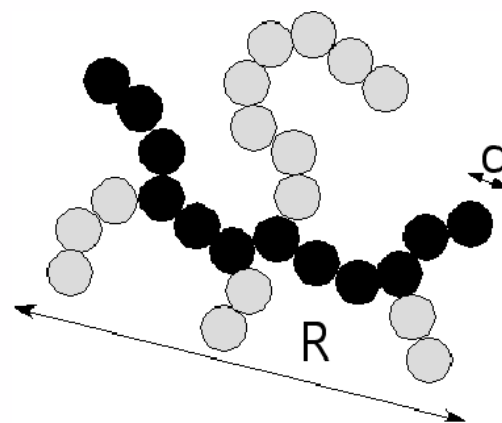
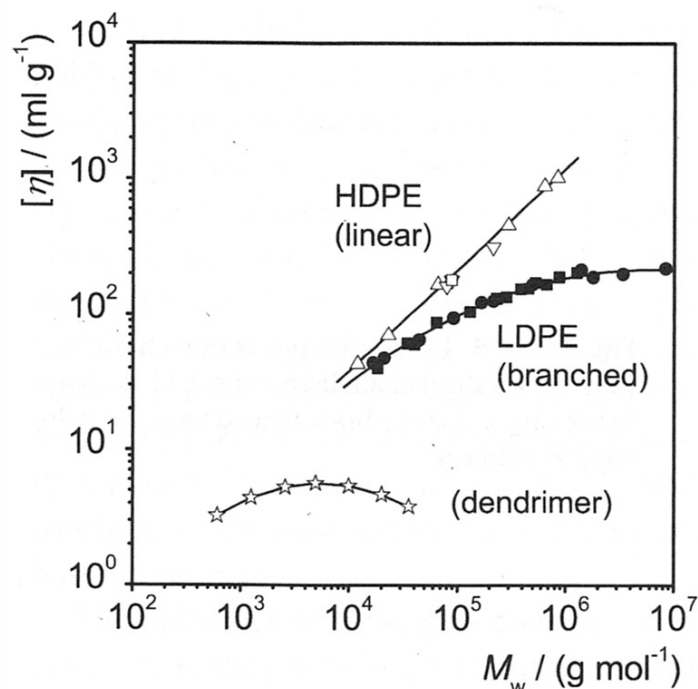
$$p \sim \left(\frac{R}{d}\right)^{d_{\min}}$$

$$s \sim \left(\frac{R}{d}\right)^c$$

$$d_f = d_{\min} c$$

z	d <sub>f</sub>	p	d <sub>min</sub>	s	c	R/d
27	1.36	12	1.03	22	1.28	11.2

# Branching and Intrinsic Viscosity



$$R_H \sim p^{1/d_{\min}}$$

$$z \sim p^c$$

$$R_H \sim z^{cd_{\min}} = z^{df}$$

At low  $z$ ;  $d_{\min} = 2$ ,  $c = 1$ ;  $d_f = d_{\min}c = 2$  (linear chain)

At high  $z$ ;  $d_{\min} \Rightarrow 1$ ,  $c \Rightarrow 2$  or  $3$ ;  $d_f = d_{\min}c \Rightarrow 2$  or  $3$   
(highly branched chain or colloid)

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

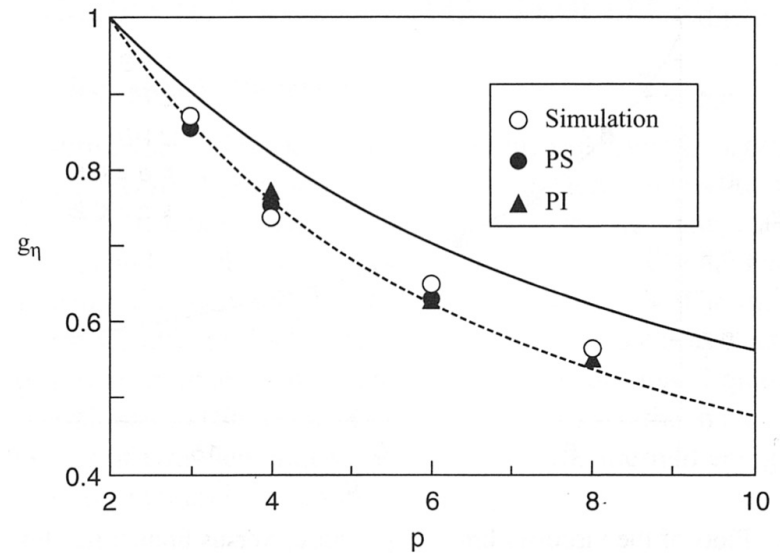
# Branching and Intrinsic Viscosity

$$R_{g,b,M}^2 \leq R_{g,l,M}^2$$

$$g = \frac{R_{g,b,M}^2}{R_{g,l,M}^2}$$

$$g = \frac{3f - 2}{f^2}$$

$$g_\eta = \frac{[\eta]_{b,M}}{[\eta]_{l,M}} = g^{0.58} = \left( \frac{3f - 2}{f^2} \right)^{0.58}$$

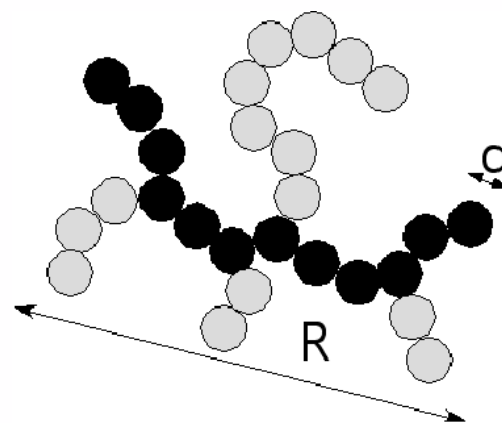
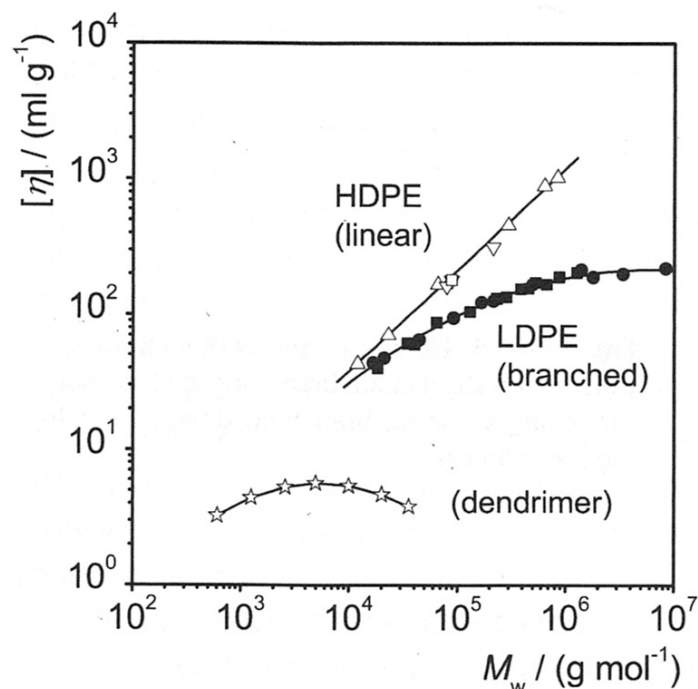


**FIGURE 1.7** Plots of viscometric branching parameter,  $g_\eta$ , versus branch functionality,  $p$ , for star chains on a simple cubic lattice (unfilled circles), together with experimental data for star polymers in theta solvents: ●, polystyrene in cyclohexane; ▲, polyisoprene in dioxane. Solid and dashed lines represent calculated values via Eqs. (1.70) and (1.71), respectively. (Adapted from Shida et al. [2004].)

**Keep in mind stars are a special case!**

Utracki and Jamieson “Polymer Physics From Suspensions to Nanocomposites and Beyond” 2010 Chapter I

# Branching and Intrinsic Viscosity



$$(\mathbf{R}_{H,B} / \mathbf{R}_{H,L})^2 \sim \mathbf{Z}^2(df,B - df,L)$$

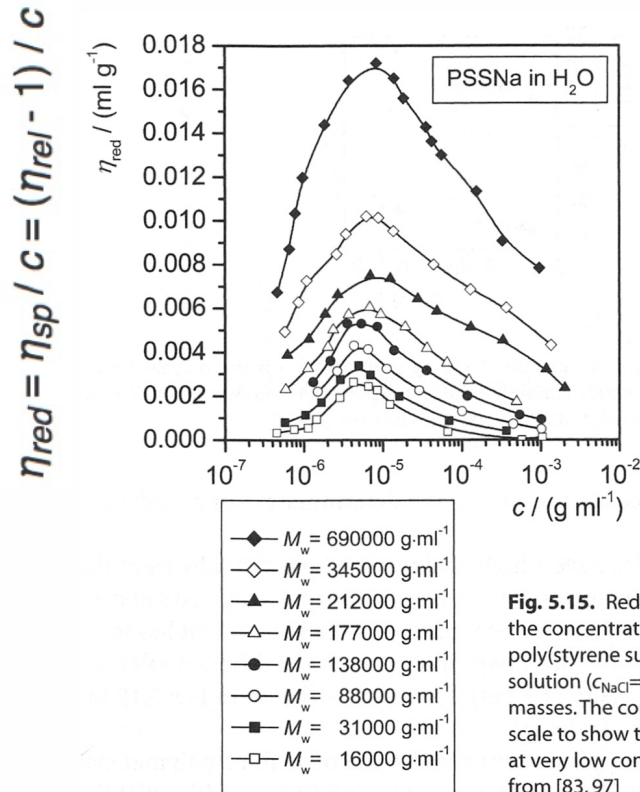
*This is still just looking at density! There is not topological information here which is critical to describe branching*

At low  $z$ ;  $d_{\min} = 2$ ,  $c = 1$ ;  $d_f = d_{\min}c = 2$  (linear chain)

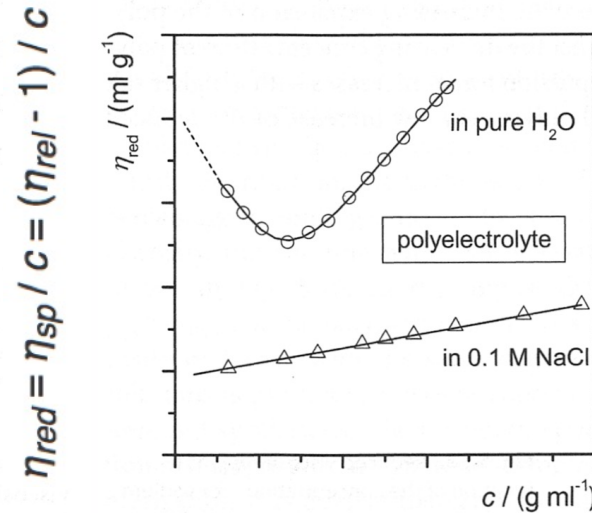
At high  $z$ ;  $d_{\min} \Rightarrow 1$ ,  $c \Rightarrow 2$  or  $3$ ;  $d_f = d_{\min}c \Rightarrow 2$  or  $3$   
(highly branched chain or colloid)

# Polyelectrolytes and Intrinsic Viscosity

## Low Concentration



## Very High Concentration



**Fig. 5.16.** Different behavior of a polyelectrolyte in aqueous solution and a salt solution. At high concentrations of the polyelectrolyte in aqueous solution is the concentration of counter ions inside the polymer coil higher than outside, leading to an expansion of the coil due to osmotic pressure. At low concentrations of the polyelectrolyte in aqueous solution, the polyelectrolyte is highly dissociated, leading to an expansion of the coil due to coulomb repulsion forces. Both expansion effects are compensated in the salt solution

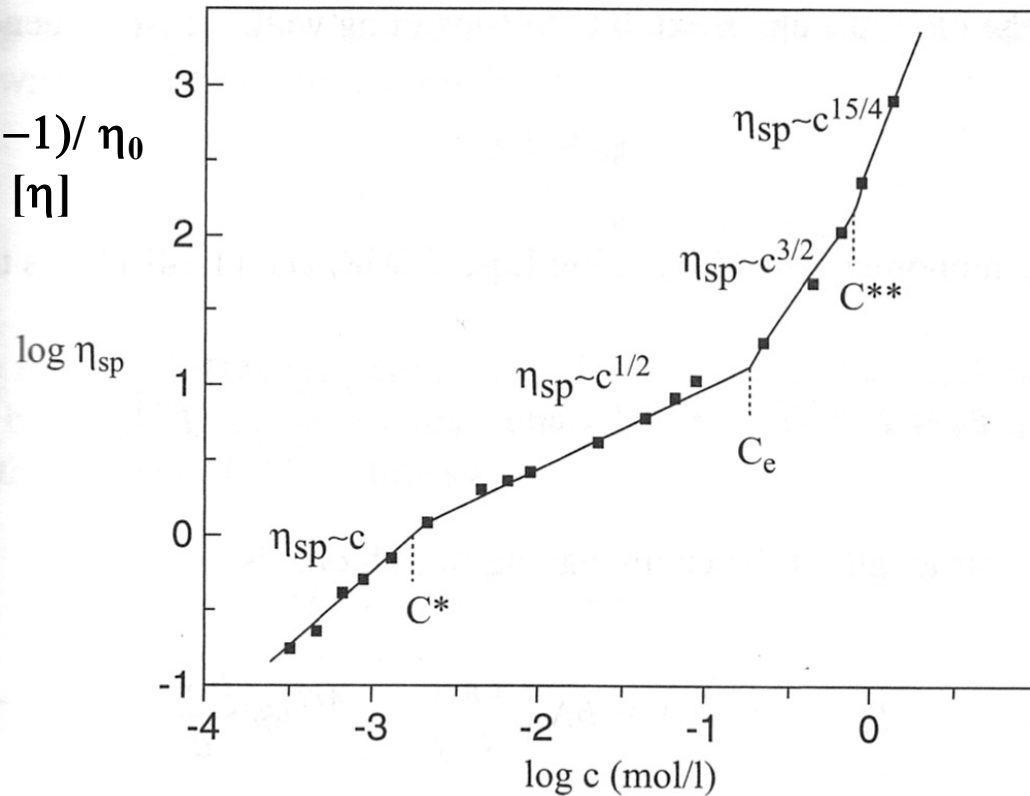
Initially rod structures, increasing concentration  
 Followed by charge screening  
 Finally uncharged chains



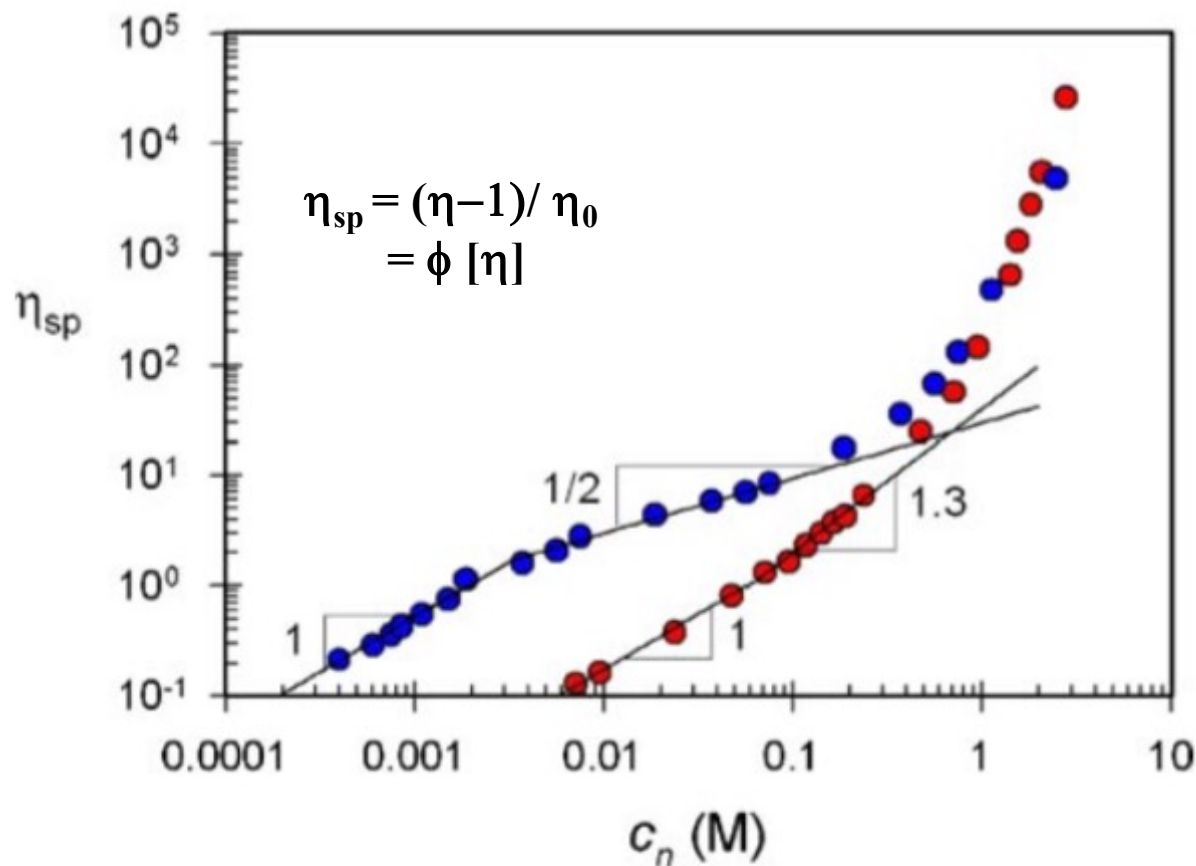
## Polyelectrolytes and Intrinsic Viscosity

$$\eta_{sp} = (\eta - 1) / \eta_0$$

$$= \phi [\eta]$$



**FIGURE 1.16** Determination of the chain overlap concentration  $c^*$ , the entanglement concentration  $c_e$ , the electrostatic blob overlap concentration  $c^{**}$  from the concentration dependence of specific viscosity for a 17%-quaternized P2VP copolymer (17PMVP-Cl) in solution in ethylene glycol at 25°C. Symbols are experimental data and solid lines represent the power laws predicted from scaling theory. (Adapted from Dou and Colby [2006].)



Structure and linear viscoelasticity of flexible polymer solutions: comparison of polyelectrolyte and neutral polymer solutions

Ralph H. Colby

Rheol Acta (2010) 49:425–442

**Fig. 10** Comparison of specific viscosity in the good solvent ethylene glycol of a neutral polymer (poly(2-vinyl pyridine), *red*) and the same polymer that has been 55% quaternized (poly(2-vinyl pyridine) chloride, *blue*; Dou and Colby 2006) plotted as functions of the number density of monomers with units of moles of monomer per liter. Slopes of unity for  $\eta_{sp} < 1$  are expected by the Zimm model in dilute solution ( $c < c^*$ ). Slopes of 1/2 and 1.3 for  $1 < \eta_{sp} < 20$  are expected by the Rouse model for semidilute unentangled solutions of polyelectrolytes and neutral polymers, respectively. At higher concentrations, entangled solution viscosity data are shown that are consistent with the  $3\times$  larger slopes predicted for entangled solutions

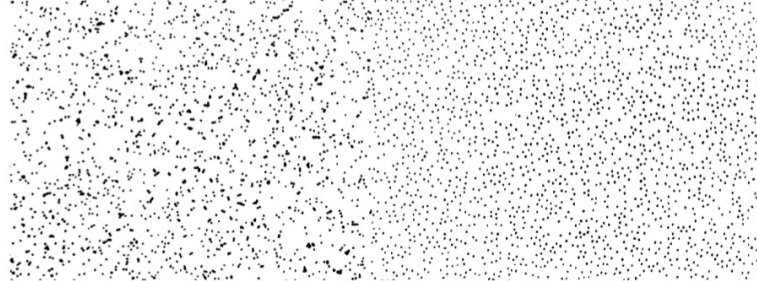
# Hydrodynamic Radius from Dynamic Light Scattering

<http://www.eng.uc.edu/~gbeaucag/Classes/Properties/HiemenzRajagopalanDLS.pdf>

<http://www.eng.uc.edu/~gbeaucag/Classes/Physics/DLS.pdf>

<http://www.eng.uc.edu/~gbeaucag/Classes/Properties/HydrodynamicRadius.pdf>

## Correlation Functions (Tadmor and Gogos pp. 381)



**Fig. 7.32** The two textures (left field and right field) have the same first-order statistics (the same number of black dots), but they differ in second-order statistics. In the left field the dots fall at random, whereas in the right field there are at least 10 dot diameters between dots. [Reprinted by permission from B. Julesz, “Experiments in the Visual Perception of Texture” *Sci. Am.*, **232**, 34 (1975).]



**Fig. 7.33** The two textures (left field and right field) made of black, dark gray, light gray, and white squares have the same first-order statistics, but different second-order statistics, which appear as a difference in granularity. [Reprinted by permission from B. Julesz, “Experiments in the Visual Perception of Texture” *Sci. Am.*, **232**, 34 (1975).]

Let random variable  $I$  represents the gray levels of image region. The first-order histogram  $P(I)$  is defined as:

$$P(I) = \frac{\text{number of pixels with gray level } I}{\text{total number of pixels in the region}} \quad (8)$$

Based on the definition of  $P(I)$ , the Mean  $m_1$  and Central Moments  $\mu_k$  of  $I$  are given by

$$m_1 = E[I^1] = \sum_{I=0}^{N_g-1} I^1 P(I) \quad (9)$$

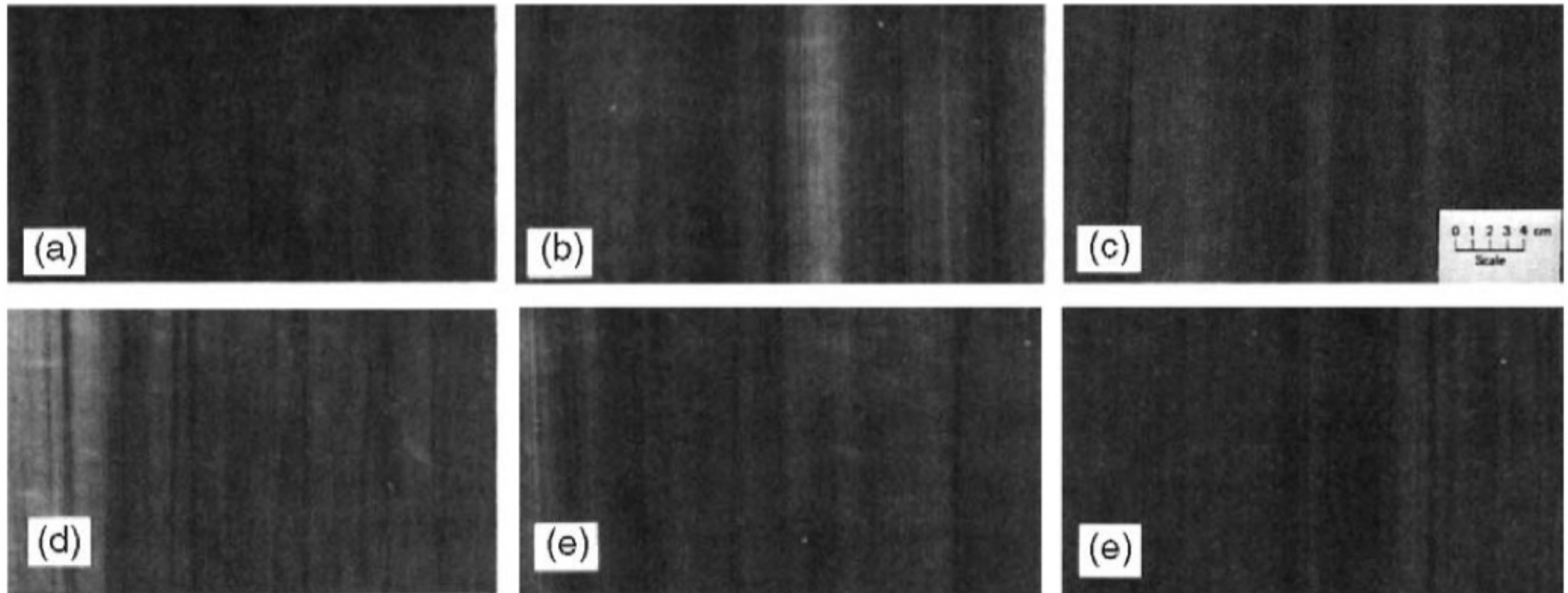
$$\mu_k = E[(I - E[I])^k] = \sum_{I=0}^{N_g-1} (I - m_1)^k P(I), \quad (10)$$

$$k = 2, 3, 4$$

where  $N_g$  is the number of possible gray levels.

$P_{\theta,d}(I_1, I_2)$ . It describes how frequently two pixels with gray-levels  $I_1, I_2$  appear in the window separated by a distance  $d$  in direction  $\theta$ . The information can be extracted from the co-occurrence matrix that measures second-order image statistics [17,24], where the pixels are considered in pairs. The co-occurrence matrix is a function of two parameters: relative distance measured in pixel numbers ( $d$ ) and their relative orientation  $\theta$ . The orientation  $\theta$  is quantized in four directions that represent horizontal, diagonal, vertical and anti-diagonal by  $0^\circ, 45^\circ, 90^\circ$  and  $135^\circ$  respectively.





**Fig. 7.34** Photographs of extruded LDPE films with carbon black concentrate extruded at various conditions. The barrel temperature ( $^{\circ}\text{C}$ ) and screw speed (rpm) are as follows: (a)  $160^{\circ}$ , 40; (b)  $160^{\circ}$ , 60; (c)  $160^{\circ}$ , 80; (d)  $180^{\circ}$ , 40; (e)  $180^{\circ}$ , 60; (f)  $180^{\circ}$ , 80. [Reprinted by permission from N. Nadav and Z. Tadmor “Quantitative Characterization of Extruded Film Texture,” *Chem. Eng. Sci.*, **28**, 2115 (1973).]

## Correlation Functions (Tadmor and Gogos pp. 381)

Gross Uniformity: Gaussian distribution of samples, First order

Scale of Segregation: Second order

### The Scale of Segregation

The *coefficient of correlation*,  $R(r)$ , measures the degree of correlation between the concentrations at two points separated by distance  $r$ . It is obtained by randomly “throwing” a dipole of length  $r$ , and is defined as follows:

$$0 \text{ to } 1 \quad R(r) = \frac{\sum_{i=1}^N (x'_i - \bar{x})(x''_i - \bar{x})}{NS^2} \quad (7.4-7) \quad S^2 = \frac{\sum_{i=1}^{2N} (x_i - \bar{x})^2}{2N - 1}$$

Diffusion/Gradient  
Non-reversible

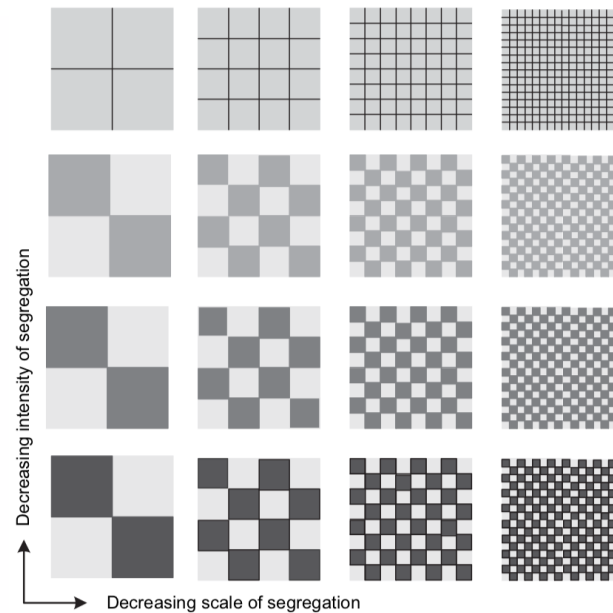


Fig. 7.36 Schematic representation of scale and intensity of segregation.

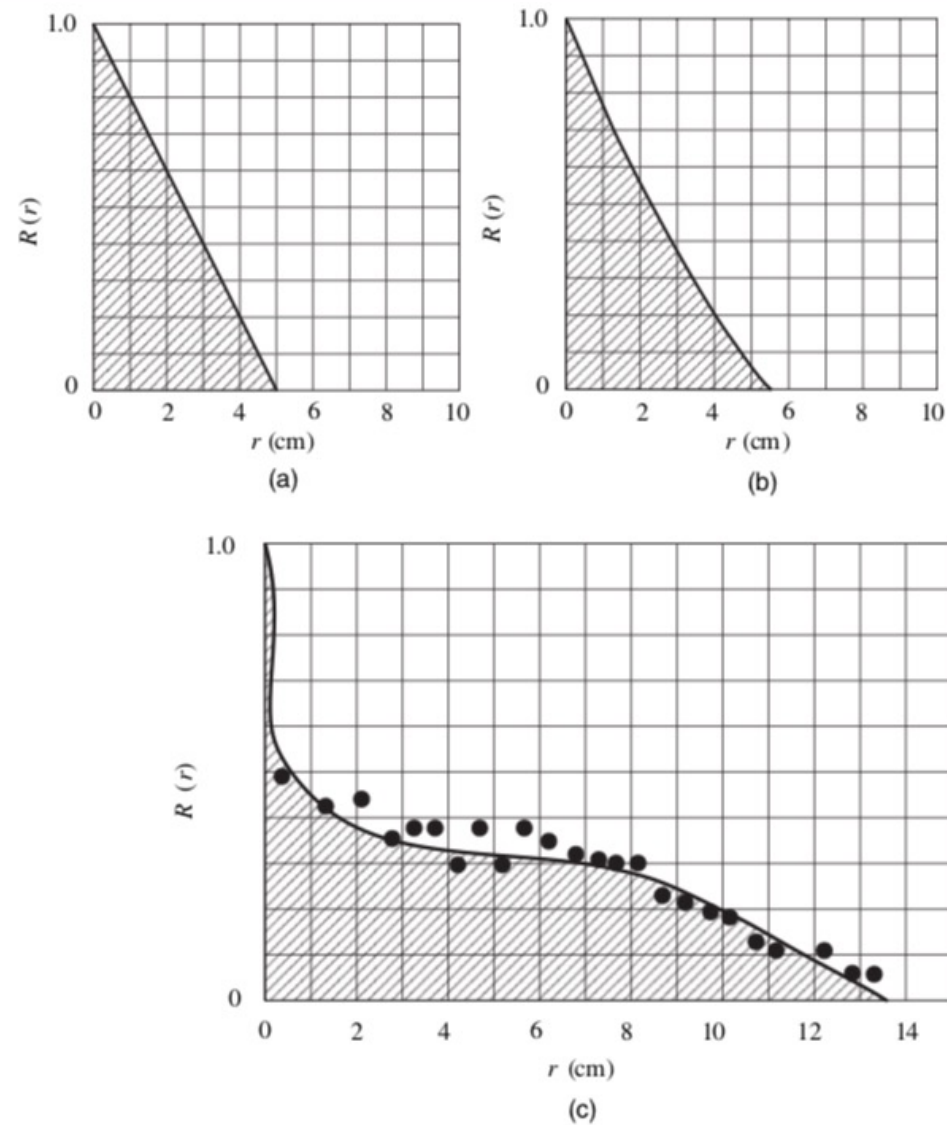
Shear strain  
Reversible

$$\sigma = \int_0^{\zeta} R(r) dr$$

Scale of Segregation

Laminar Flow  
Before/After

## Correlation Functions (Tadmor and Gogos pp. 381)

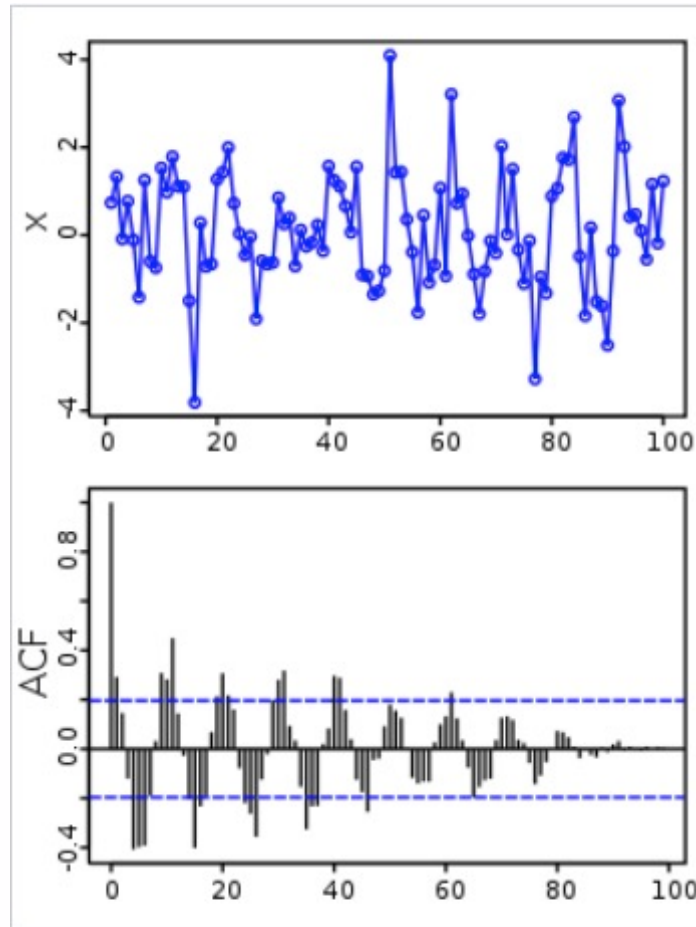


**Fig. 7.37** Typical correlograms. (a) Along a line perpendicular to an equally spaced striped texture. (b) Over an area of a checkered board texture. (c) Along a line of an extruded film, as shown in Fig. 7.34, perpendicular to the extrusion direction.



## Correlation Functions

DLS deals with a time correlation function at a given “ $q$ ” =  $2\pi/d$



Above: A plot of a series of 100 random numbers concealing a [sine](#) function. Below: The sine function revealed in a [correlogram](#) produced by autocorrelation.



LSU

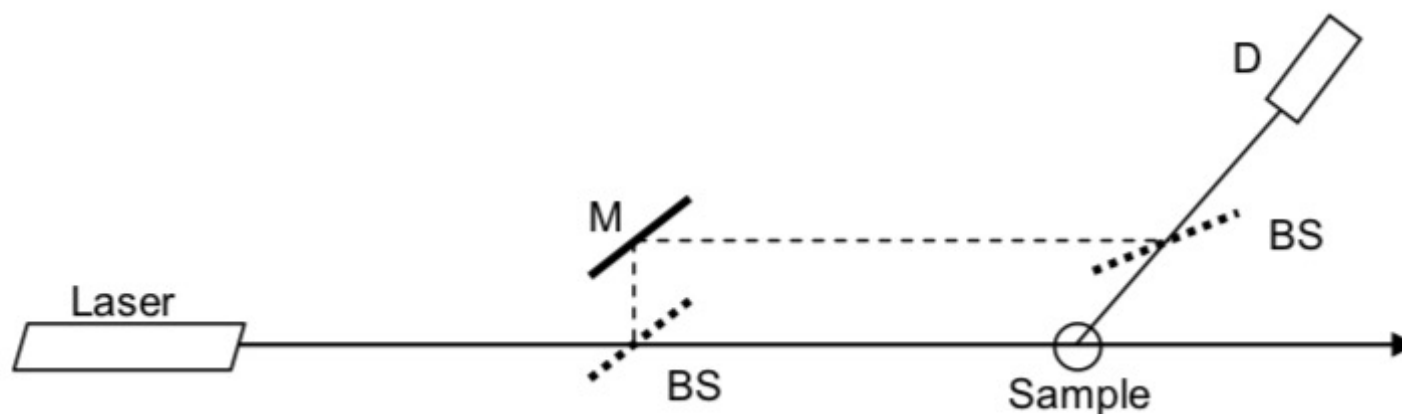


Figure 1. Heterodyne DLS apparatus. BS = beamsplitter; M = Mirror; D = detector. For a homodyne apparatus, just remove the two beamsplitters and mirror.

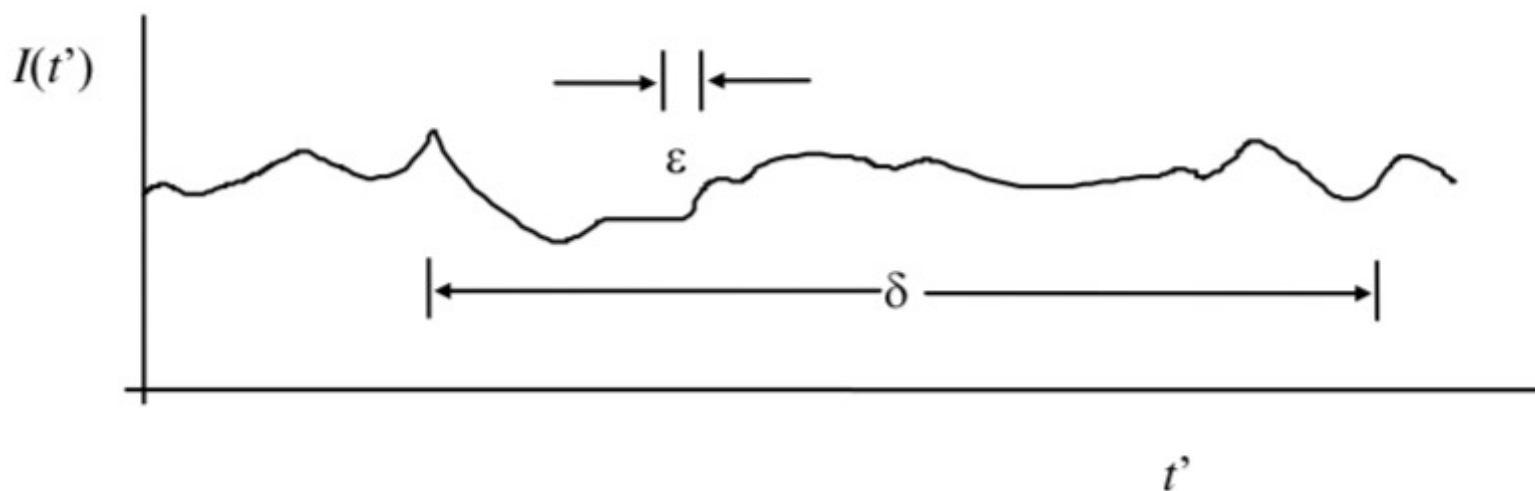


Figure 4. Intensity fluctuations are “random” on a time scale  $\delta$  but “correlated” on a time scale  $\epsilon$ .



Georgia Tech

## **Fick's Laws**

$$J = -D \frac{d\varphi}{dx}$$

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} \quad \varphi(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

## **Brownian Motion**

$$\text{MSD} \equiv \langle (\mathbf{x} - \mathbf{x}_0)^2 \rangle = 2nDt$$

$$G^{(2)}(t) = \langle I(0)I(t) \rangle = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T I(t') \cdot I(t'+t) dt' \quad \langle 1 \rangle$$

Not normalized second order correlation function (capital G, normalized is small g)

After some time, the signal in the correlator is well approximated<sup>2</sup> by:

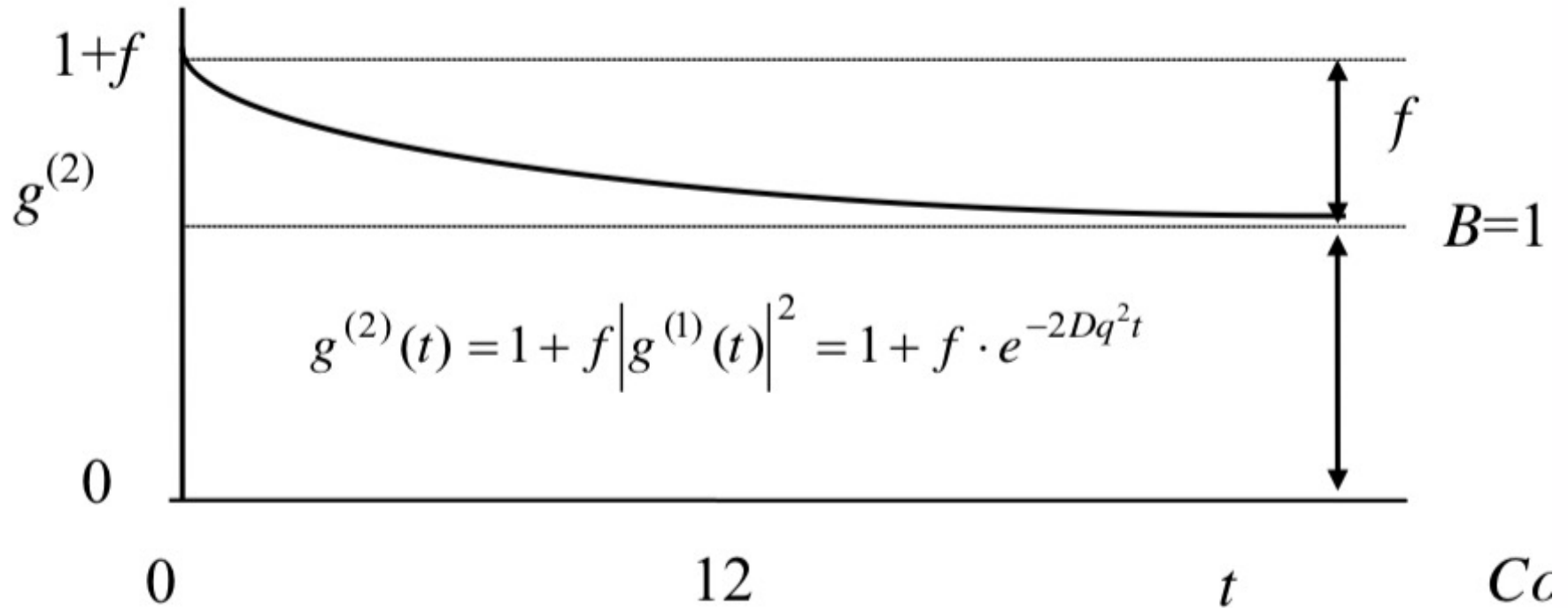
$$G^{(2)}(t) = B(1 + f|g^{(1)}(t)|^2) \quad \langle 2 \rangle$$

$$g^{(1)}(t) = e^{-\Gamma t} \quad \langle 3 \rangle$$

$$\Gamma = \tau^{-1} = q^2 D_m \quad \langle 4 \rangle \quad \text{MSD} = 2nDt$$

$$q = 4\pi \cdot n \cdot \sin(\theta/2) / \lambda_o \quad \langle 5 \rangle$$

$$g^{(2)}(t) = \frac{G^{(2)}(t)}{G^{(2)}(t = \infty)} = \frac{G^{(2)}(t)}{B}$$



$$\sqrt{\frac{g^{(2)}(t) - 1}{g^{(2)}(0) - 1}} \equiv \sqrt{\frac{g^{(2)}(t) - 1}{f}} \equiv g^{(1)}(t). \quad \langle 6.5 \rangle$$

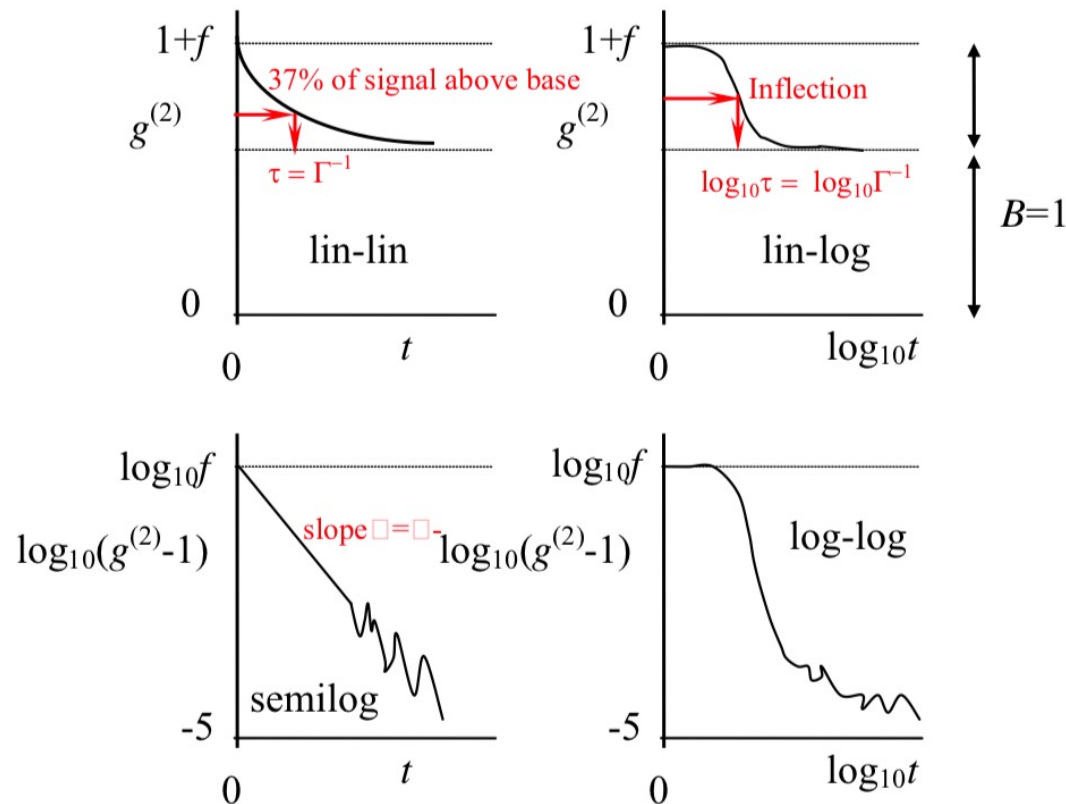


Figure 6. Various forms of autocorrelation function available

$$g^{(1)}(t) = e^{-\Gamma t} \quad \langle 3 \rangle$$

$$\Gamma = \tau^{-1} = q^2 D_m \quad \langle 4 \rangle$$

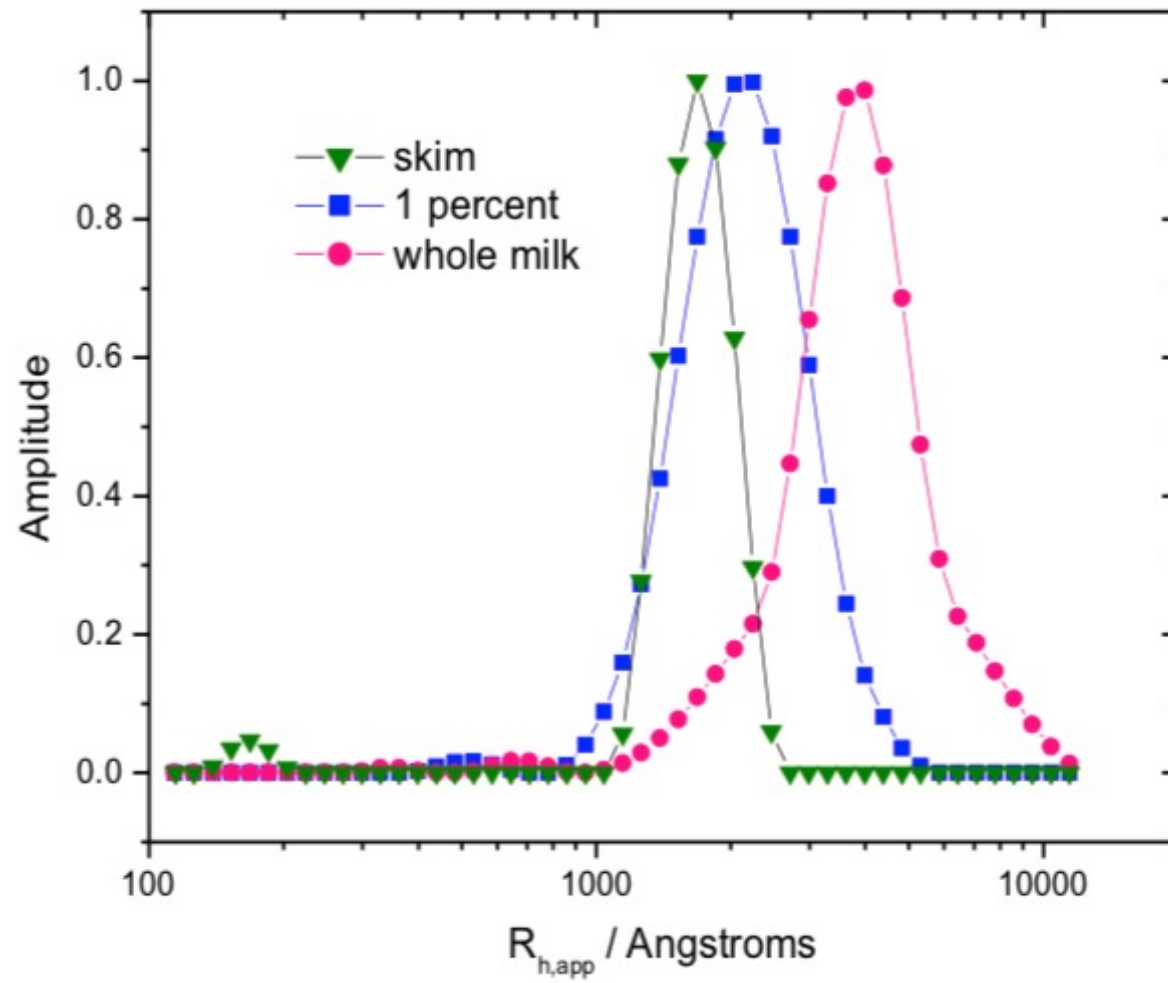
$$R_h = \frac{kT}{6\pi\eta_o D_o} \quad \langle 7 \rangle$$

What does  $R_h$  mean?

Sometimes newcomers to DLS do not know what  $R_h$  really means, so let's be very clear about that.

1. If your object is a solid sphere of radius  $R$ , then  $R_h = R$ .
2. If your object is spherical “bubble” (e.g., liposome) with *outer* radius  $R$ , then  $R_h = R$  (exception: some liposomes may “wobble” and that could alter  $R_h$ ).
3. If your object is a sphere on the outside, but has inclusions of any shape inside, then  $R_h = R$ .
4. If your object has some other shape—such as cylinder, cube, polymer chain or star—then  $R_h$  is the radius of some hypothetical sphere that diffuses as fast as your object does.
5. If your object is a semidilute solution, gel, etc., all bets are off.





## 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,  $D$

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

$$\langle x^2 \rangle = \sigma^2 = 2Dt$$

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

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

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) (<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  
 $g_1(q, \tau)$

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/Courses/Physics/DLS.pdf>)

$$I(\mathbf{R}, t) = Q_e \mathbf{E}_s^*(\mathbf{R}, t')^T \cdot \mathbf{E}_s(\mathbf{R}, t')$$

$Q_e$  = quantum efficiency

$$R = 2\pi/q$$

$E_s$  = amplitude of scattered wave

$$\langle I(\mathbf{R}) \rangle = Q_e \langle \mathbf{E}_s^*(\mathbf{R}, t')^T \cdot \mathbf{E}_s(\mathbf{R}, t') \rangle$$

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

If the intensity correlation function is normalized by  $\langle I(0)^2 \rangle$  the autocorrelation function results,

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

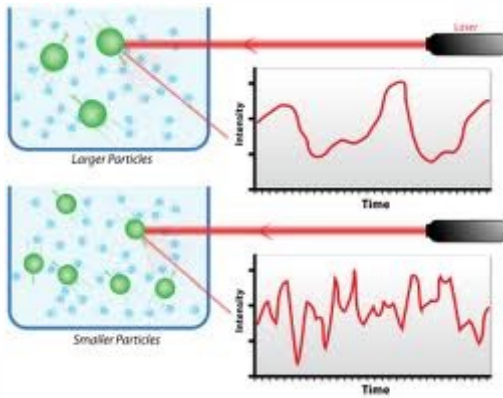
where  $g^{(2)}(t)$  is the square of the normalized autocorrelation function for electric field,  $g^{(2)}(t) = |g^{(1)}(t)|^2$ .

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

$$g^{(1)}(t) = g^{(1)}(\mathbf{K}, t) = \exp(-D_m K^2 t)$$

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

# Dynamic Light Scattering



$$g^2(q; \tau) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2}$$

$$g^2(q; \tau) = 1 + \beta [g^1(q; \tau)]^2$$

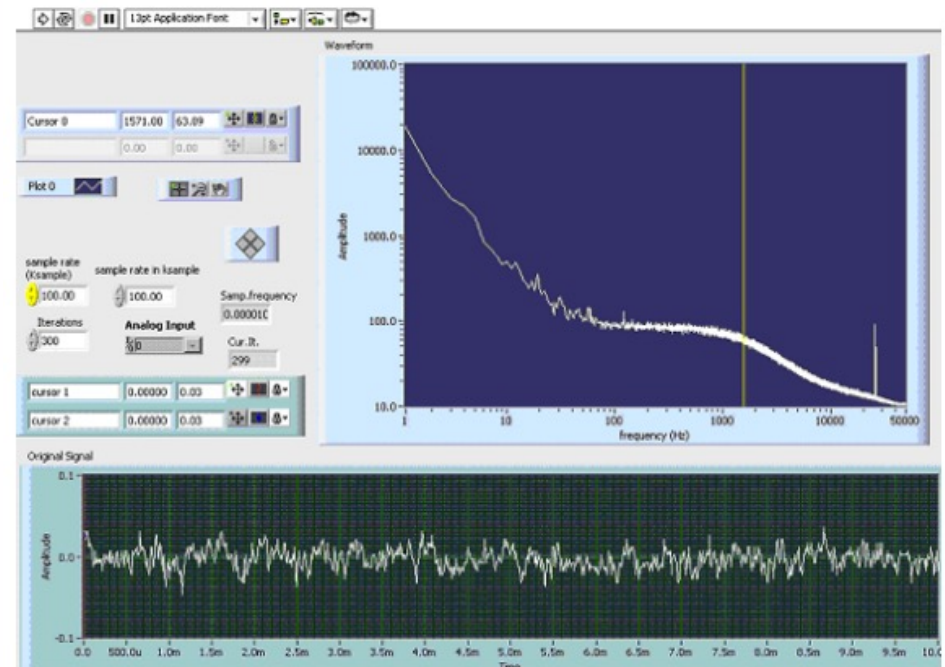
$$q = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

$$g^1(q; \tau) = \exp(-\Gamma\tau)$$

$$\Gamma = q^2 D_t$$

$$D = k_B T / 6\pi\eta a$$

$$a = R_H = \text{Hydrodynamic Radius}$$



The radius of an equivalent sphere following Stokes' Law

# Dynamic Light Scattering

## my DLS web page

<http://www.eng.uc.edu/~gbeaucag/Courses/Physics/DLS.pdf>

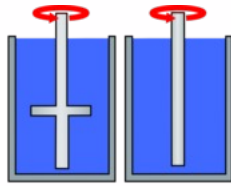
## Wiki

[https://en.wikipedia.org/wiki/Dynamic\\_light\\_scattering](https://en.wikipedia.org/wiki/Dynamic_light_scattering)

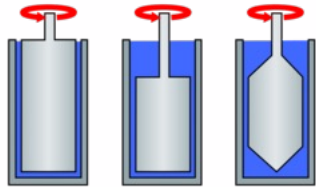
## Wiki Einstein Stokes

[http://webcache.googleusercontent.com/search?q=cache:yZDPRbqZ1BIJ:en.wikipedia.org/wiki/Einstein\\_relation\\_\(kinetic\\_theory\)+&cd=1&hl=en&ct=clnk&gl=us](http://webcache.googleusercontent.com/search?q=cache:yZDPRbqZ1BIJ:en.wikipedia.org/wiki/Einstein_relation_(kinetic_theory)+&cd=1&hl=en&ct=clnk&gl=us)

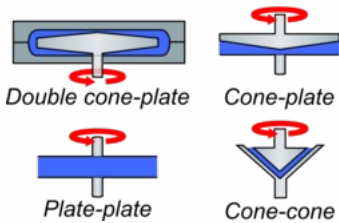
# Diffusing Wave Spectroscopy (DWS)



Spindle type

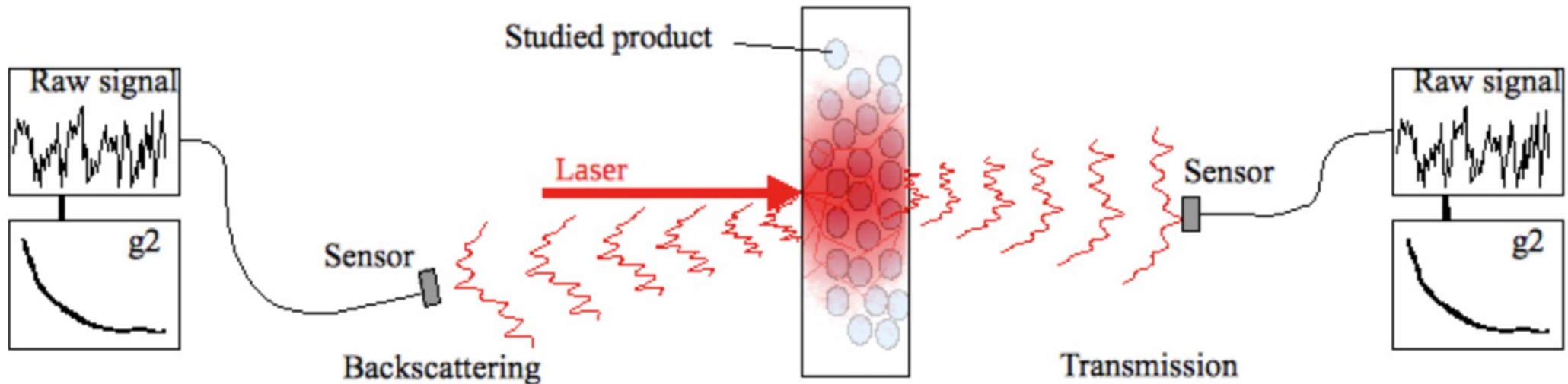


Concentric cylinder



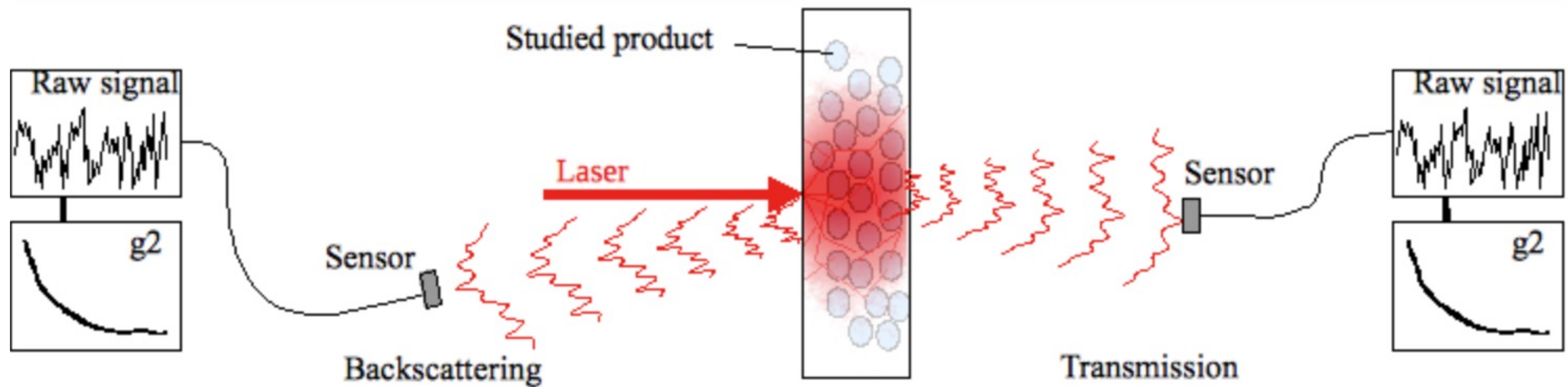
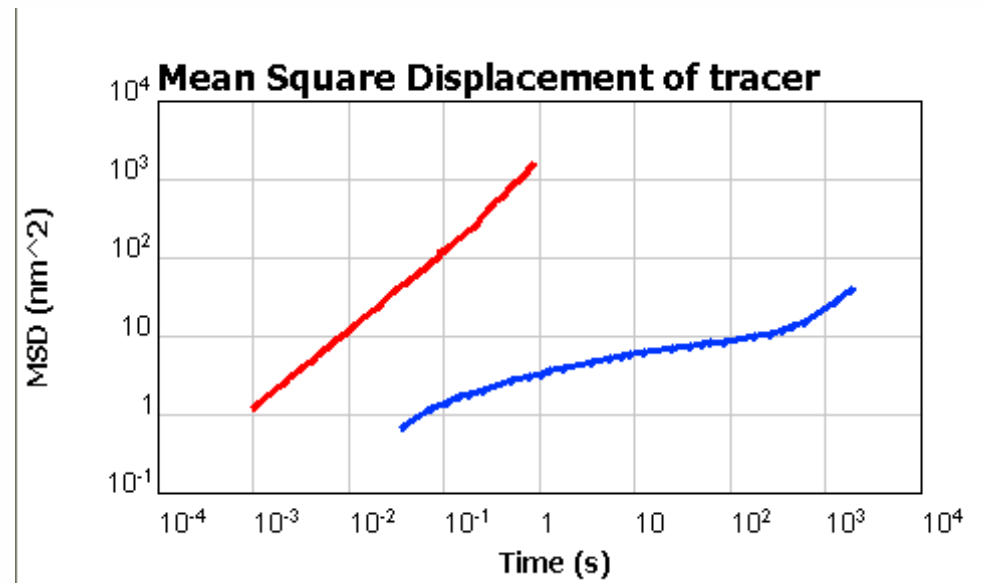
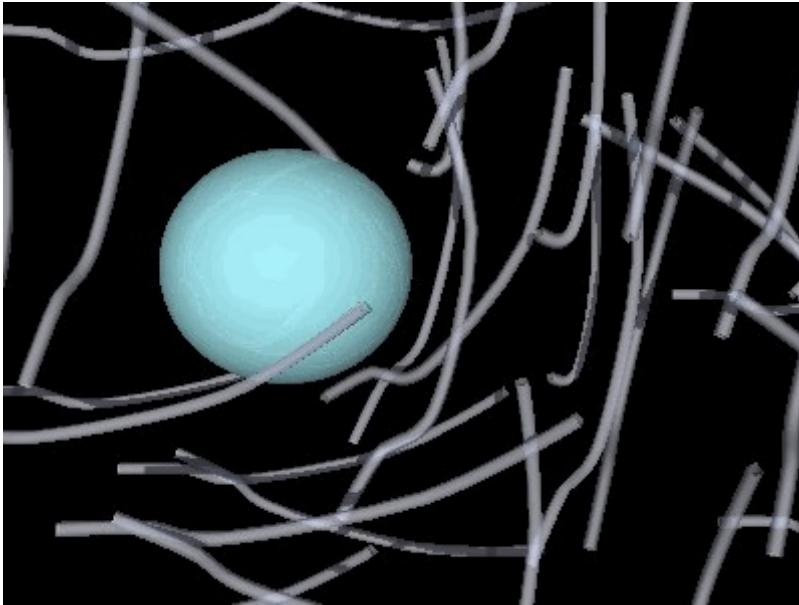
Traditional Rheology: Place a fluid in a shear field, measure torque/force and displacement

Microrheology: Observe the motion of a tracer.  
Two types, passive or active microrheology. DWS is passive.





## Diffusing Wave Spectroscopy (DWS)



## Diffusing Wave Spectroscopy (DWS)

Viscous Motion  $\langle \Delta r^2 \rangle = 4Dt$

Elastic Motion  $\langle \Delta r^2 \rangle = \text{Const}$

$$G(\omega) = G'(\omega) + iG''(\omega)$$

$$\tilde{G}(s) = \frac{k_B T}{\pi a s \langle \Delta \tilde{r}^2(s) \rangle}$$

$\tilde{G}(s)$ : Laplace transform of  $G$

$k_B$ : Boltzmann constant

$T$ : temperature in kelvins

$s$ : the Laplace frequency

$a$ : the radius of the tracer

$\langle \Delta \tilde{r}^2(s) \rangle$ : the Laplace transform of the mean squared displacement

$$F(s) = \int_0^\infty f(t) e^{-st} dt \quad (\text{Eq.1})$$

## Diffusing Wave Spectroscopy (DWS)

$$G(\omega) = G'(\omega) + iG''(\omega)$$

$$\tilde{G}(s) = \frac{k_B T}{\pi a s \langle \Delta \tilde{r}^2(s) \rangle}$$

$$g_2(\tau) - 1 = \left[ \int ds P(s) \exp(-(s/l^*) k_0^2 \langle \Delta r^2(\tau) \rangle) \right]^2$$

For back scatter:  $g_2(\tau) - 1 = \exp\left(-2\gamma \sqrt{\langle \Delta r^2(\tau) \rangle k_0^2}\right)$

## Diffusing Wave Spectroscopy (DWS)

$$G(\omega) = G'(\omega) + iG''(\omega)$$

$$k_B T$$

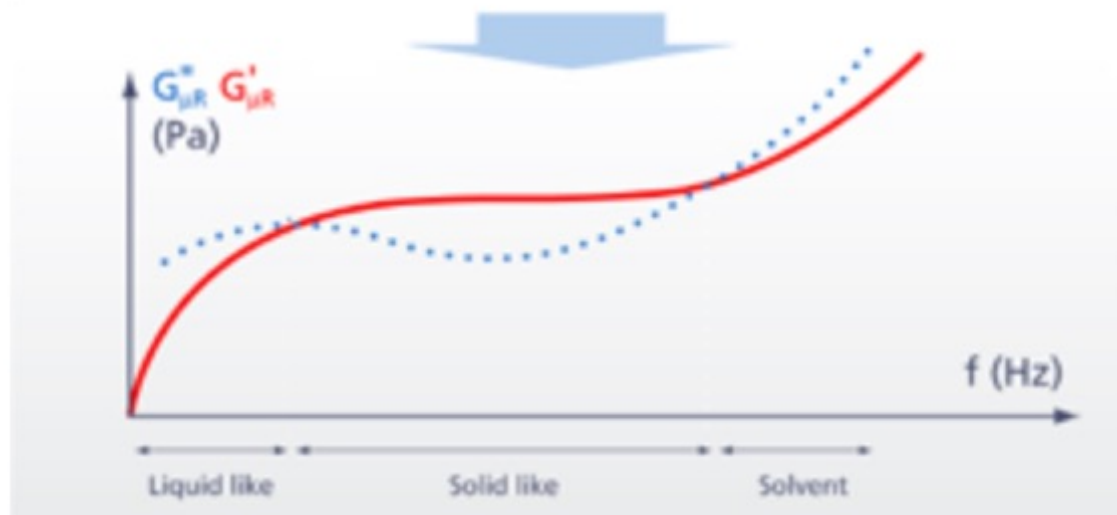
$$g_2(\tau)$$

For bac



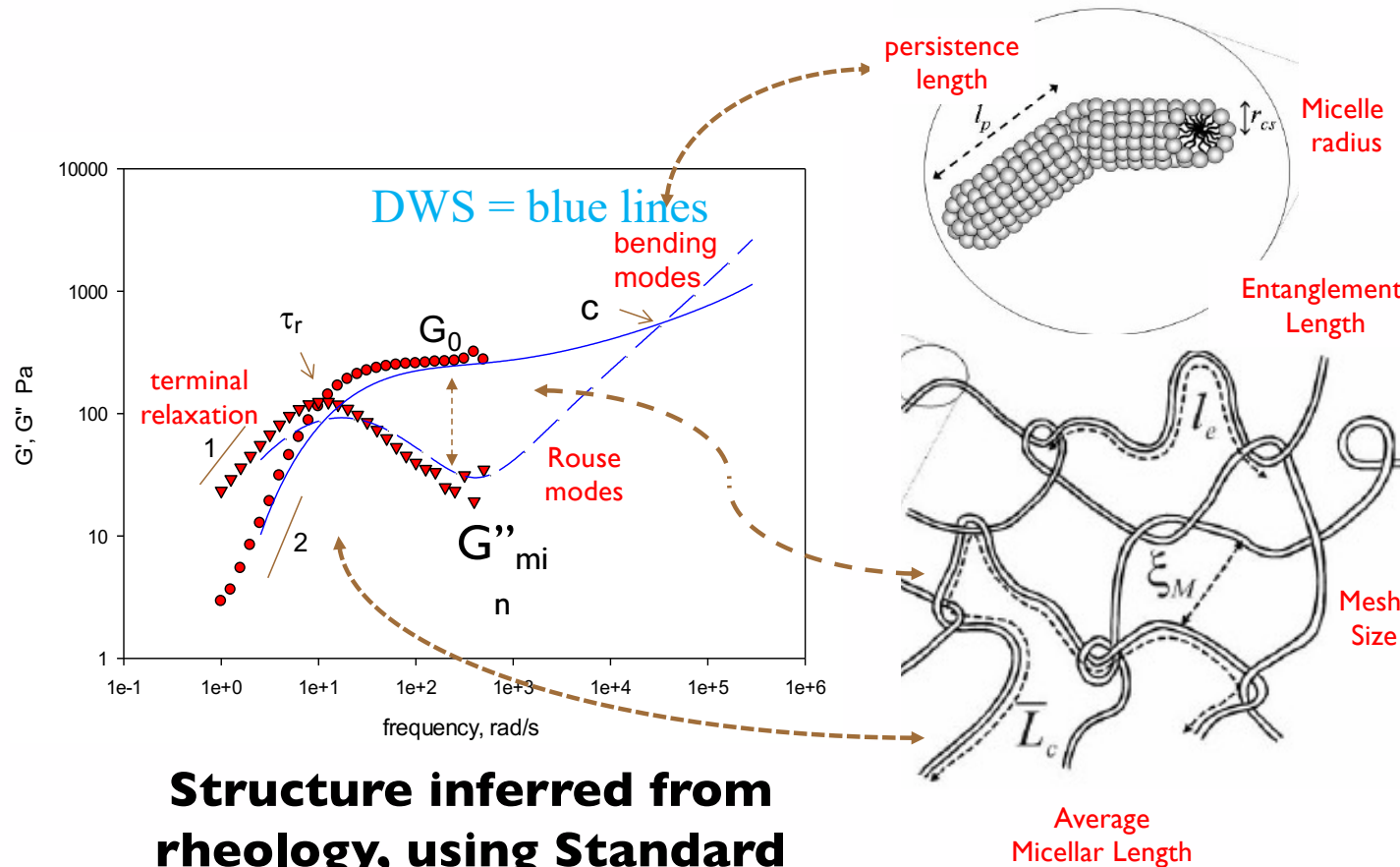
$$(\tau) \rangle \rangle \rangle]^2$$

$$(\tau) \rangle \rangle k_0^2)$$



# Link rheology to micelle structure

*Ron Larson/Mike Weaver*



**Structure inferred from  
rheology, using Standard  
Cates Model and newer  
developments (Larson group,  
others...)**

*Beth Schubert, 2003*

# Quasi-Elastic Neutron (and X-ray) Scattering

In the early days of DLS there were two approaches:

Laser light flickers creating a speckle pattern that can be analyzed in the time domain

The flickering is related to the diffusion coefficient through an exponential decay of the time correlation function

A more direct method is to take advantage of the Doppler effect. Train whistle appears to change pitch as the train passes since the speed of the train is close to  $1/\omega$  for the sound

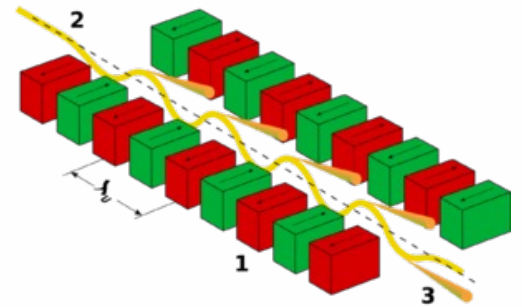
If we know the frequency of the sound, we can determine the speed of the train. Measuring the spectrum from a laser, and the broadening of this spectrum after interaction with particles the diffusion coefficient can be determined from an exponential decay in the frequency, peak broadening. This is called quasi-elastic light scattering and measures the same thing as DLS by a different method.

For Neutrons and X-rays the time involved is too fast for correlators, pico- to nanoseconds. But line broadening can be observed (though **there are no X-ray or neutron lasers** i.e., monochromatic and collimated).



## Neutron and X-ray “Lasers”

For X-rays a synchrotron with an undulator insertion device can produce close to monochromatic and fairly coherent radiation. NSLS II Brookhaven National Laboratory near Stony Brook, Long Island NY (near NYC)



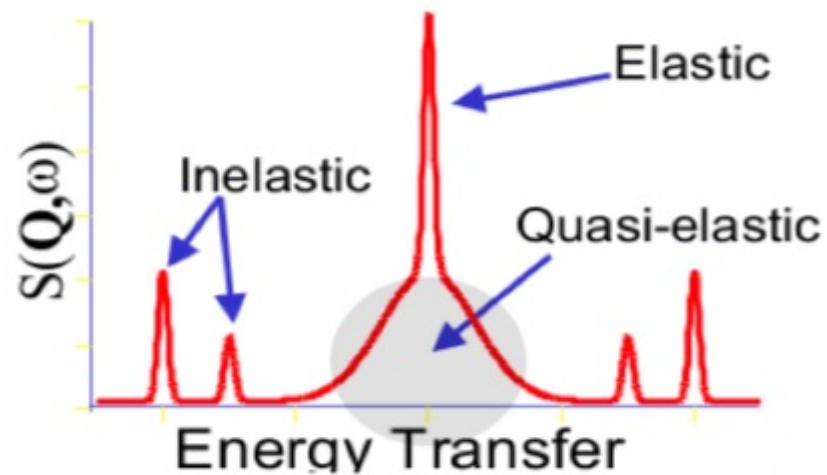


## Neutron and X-ray “Lasers”

For neutrons, a spallation source with a time-of-flight detection system or a reactor with a velocity selector can result in a reasonably coherent and monochromatic (spectral in time) beam. SNS at Oak Ridge National Laboratory, Tennessee (near Knoxville) and NCNR at NIST Gaithersburg MD (near Washington DC).



# Quasi Elastic Neutron Scattering QENS



- Quasi elastic neutron scattering is a limiting case of inelastic neutron scattering
- Doppler type of broadening of the elastic line due to a small energy transfer between the neutrons and the atoms in the sample

# What is QENS used for

Probes slow dynamics

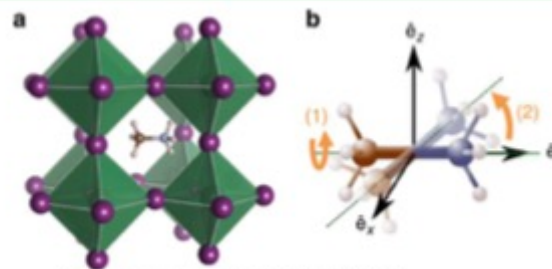
- Translational diffusion
- Molecular reorientations
- Relaxation processes

Applicable to wide range of scientific topics

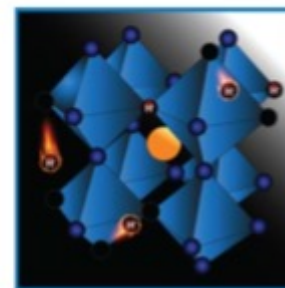
- **Materials science**: fuel cells, batteries, hydrogen storage,
- **Soft Matter**: polymer nanocomposites and blends, organic photovoltaics, polymer electrolytes
- **Biology**: hydration water, dynamics of proteins
- **Chemistry**: water interfaces, ionic liquids, clays, porous media, complex fluids, surface interactions

Results are comparable to Molecular Dynamics simulations

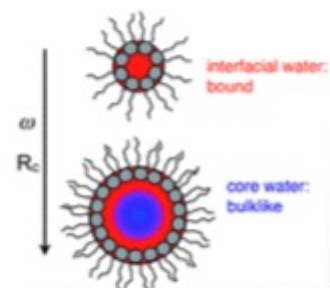
6 Presentation\_name



Nature Communications 6, 7124 (2015)



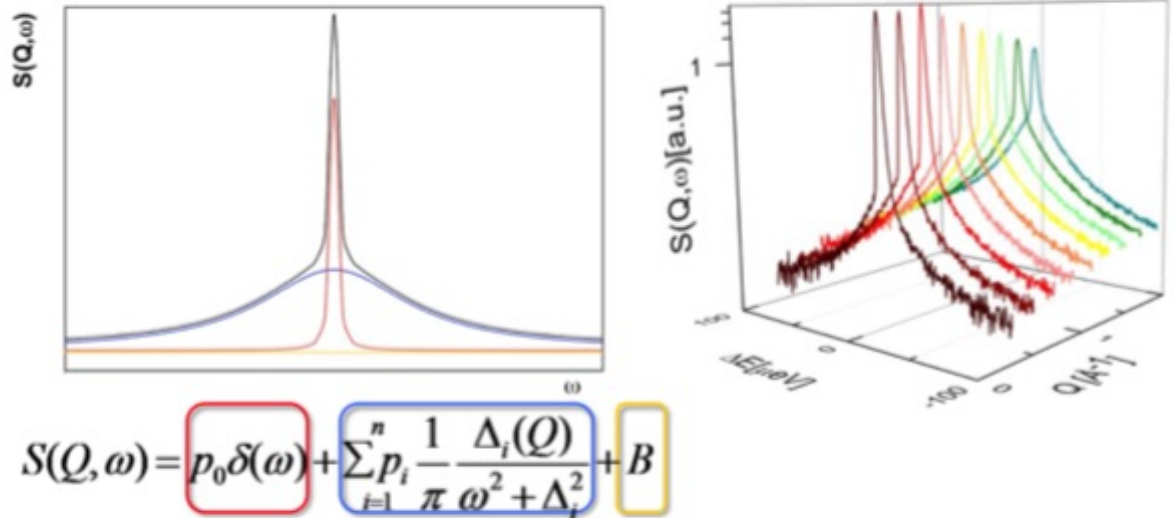
Journal of Physical Chemistry C, 123, 2019 (2019).



Soft Matter, 7, 12, 5745-5755 (2011)

 **OAK RIDGE**  
National Laboratory

## QENS spectra

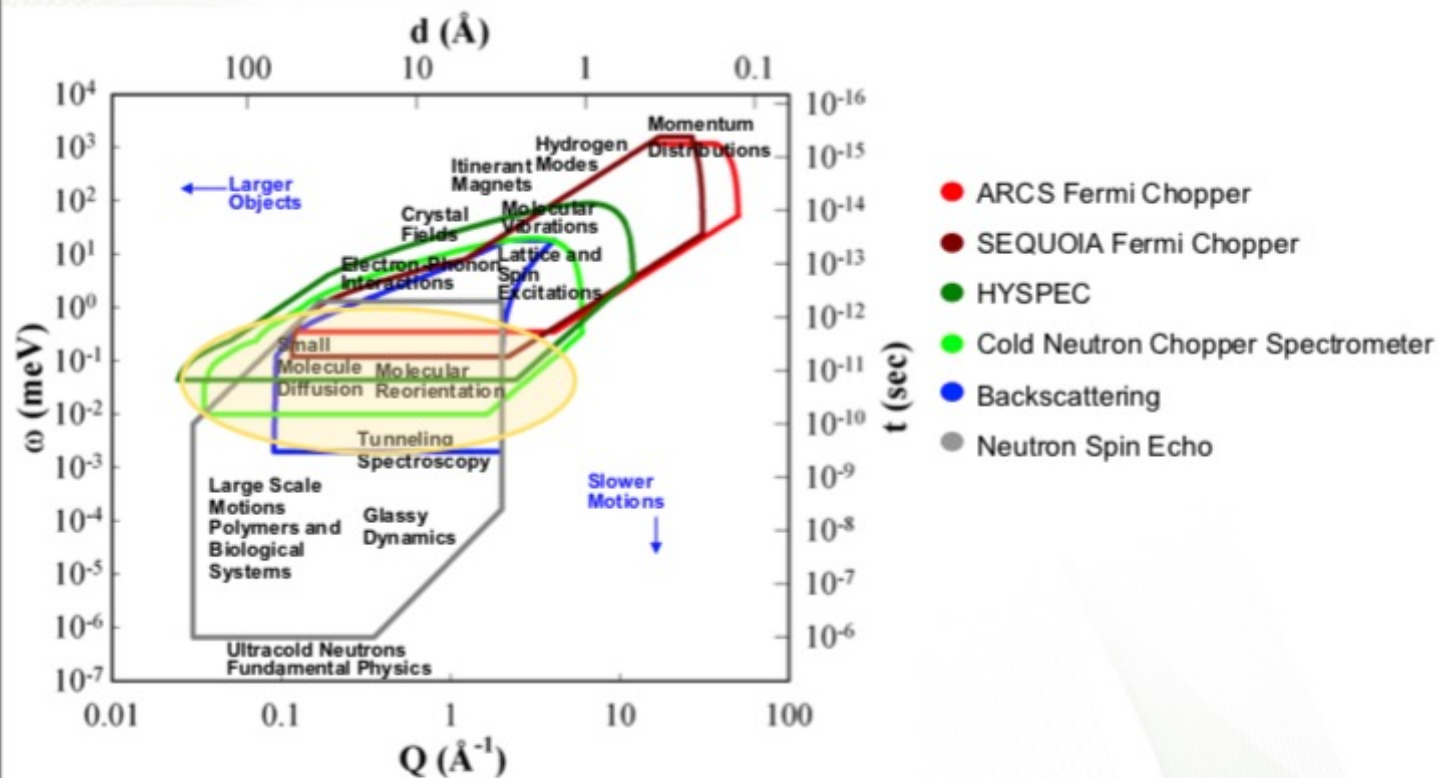


Dynamic scattering function provides information on the sample states

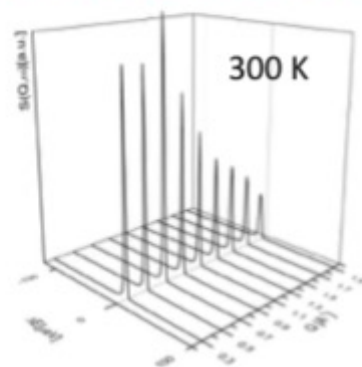
- Elastic intensity** → Debye-Waller factor: Vibrational amplitudes
- Quasielastic intensity** →  $A_0 = \text{EISF (ratio elastic/total)}$ : Geometry of motion
- Quasielastic broadening** → Width: Characteristic time scale / diffusion



# The SNS Inelastic Instrument Suite

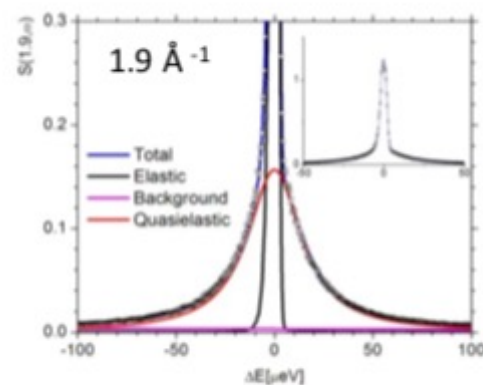
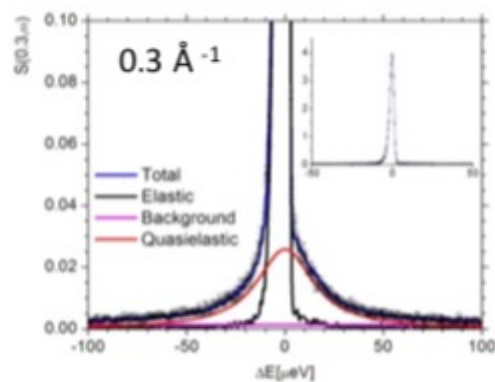


# Science Example 1: Molecular Reorientation



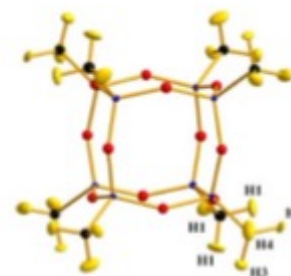
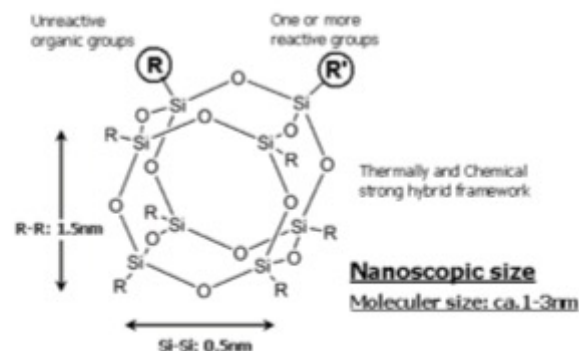
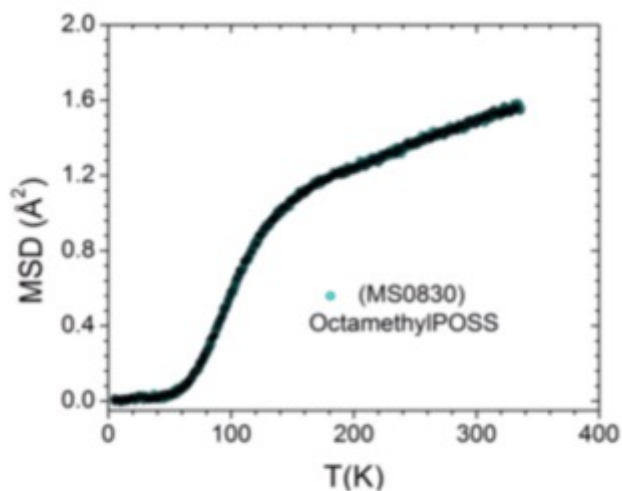
Octamethyl POSS @ BASIS

$$S(Q, \omega) = f \left[ p_0 \delta(\omega) + \sum_{i=1}^n p_i \frac{1}{\pi} \frac{\Delta_i(Q)}{\omega^2 + \Delta_i^2} \right] \otimes R(Q, \omega) + B$$



# Science Example 1: Molecular Reorientation

- Polyoligosilsesquioxane Ligand Dynamics
- How do ligand dynamics contribute to the functionalities of POSS?





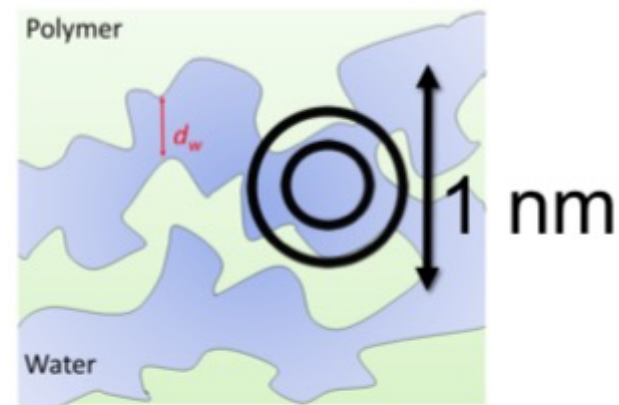
## Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

Ionic conductivity and water transport are key properties for applications

Depends on water content

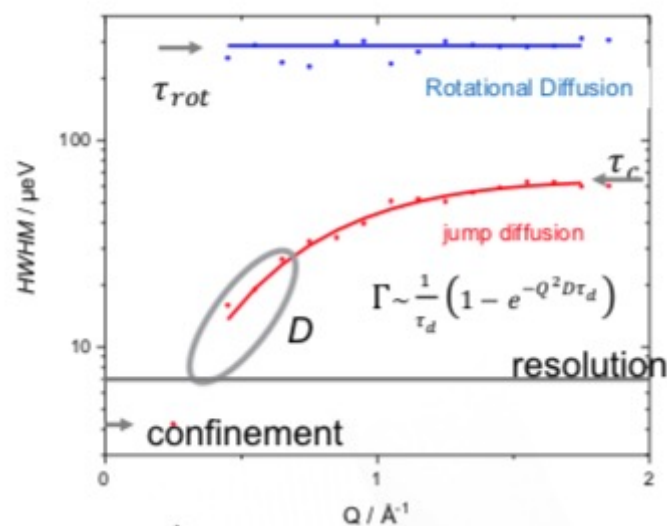
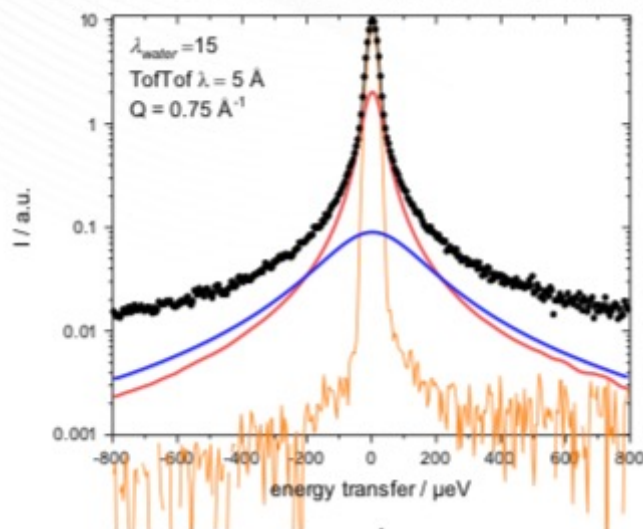
Water transport in AEM  
multiscale problem

Investigation of transport in multiple  
time- and length scales for structure –  
function insight



# Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

TOFTOF: time-of-flight spectrometer

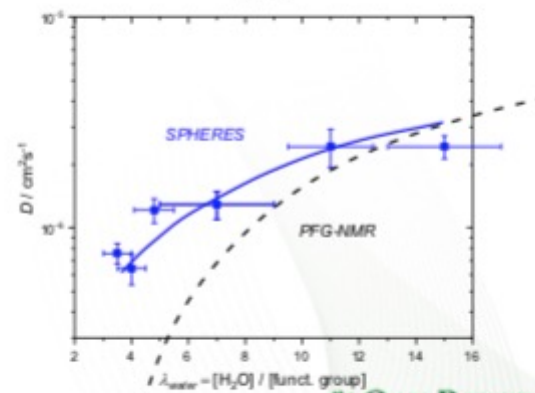
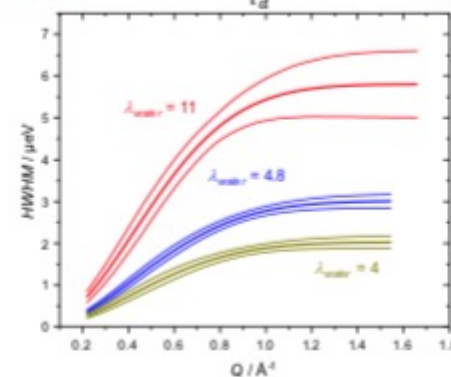
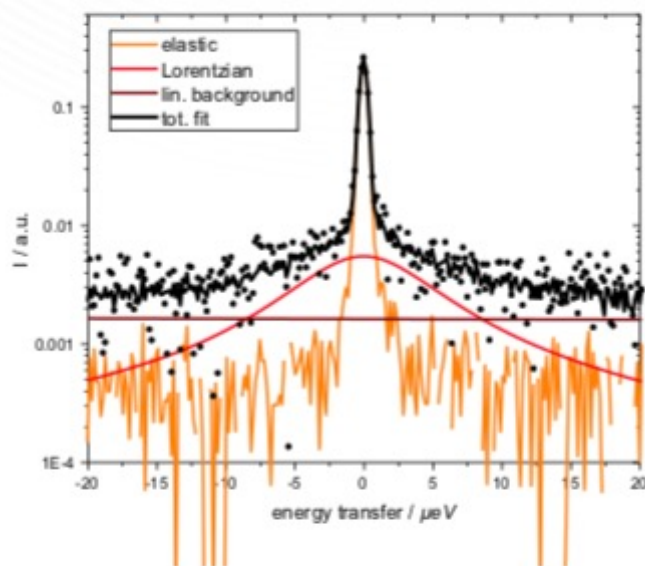


$$S(Q, \omega) = f \left( a_0(Q) \delta + \sum_n \frac{a_n(Q)}{\pi} \left( \frac{\Gamma}{\omega^2 + \Gamma^2} \right) \right) \otimes \text{Res} + \text{Backg}$$

# Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

$$\Gamma \sim \frac{1}{\tau_d} (1 - e^{-Q^2 D \tau_d})$$

**SPHERES: high-resolution  
backscattering spectrometer**

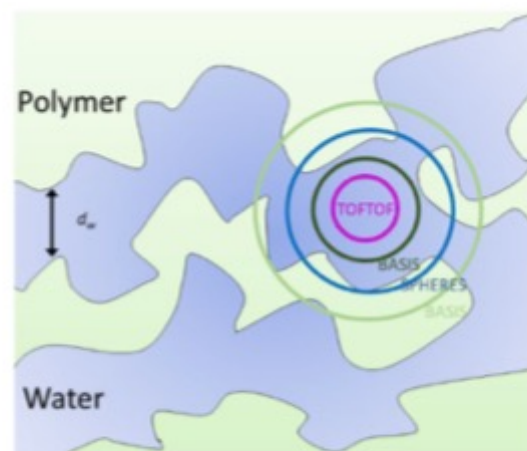
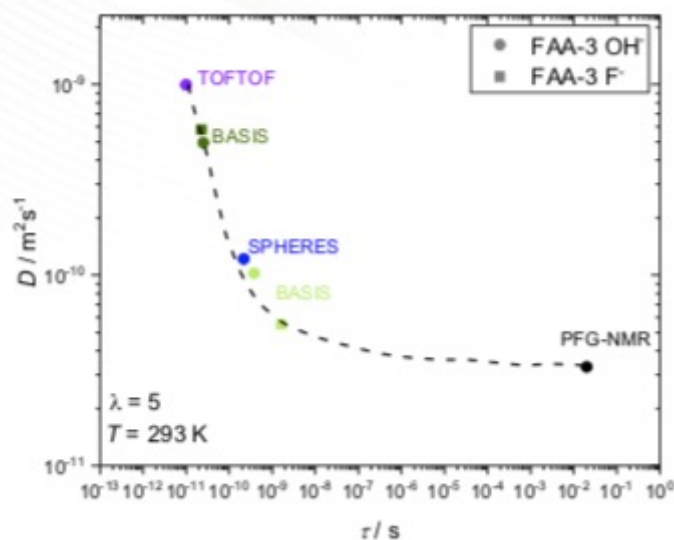


37 Presentation\_name

J. Melchior, *et al.*, Journal of Membrane Science 586, Pages 240-247 (2019)

**OAK RIDGE**  
National Laboratory

## Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS



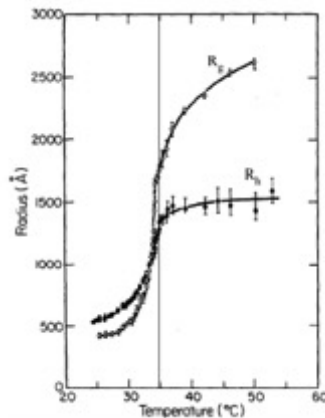
## $R_g/R_H$ Ratio

$R_g$  reflects spatial distribution of structure

$R_H$  reflects 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 some way, the structural connectivity, that is, how the structure is put together.



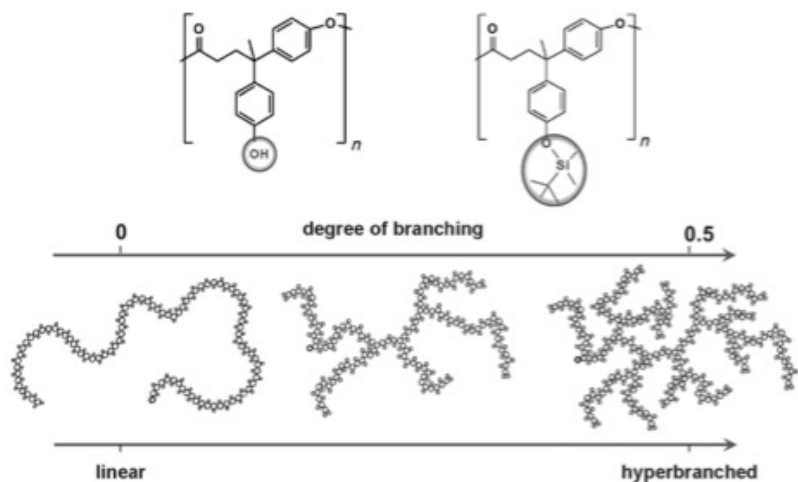
This can also be considered in the context of the “universal constant”

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

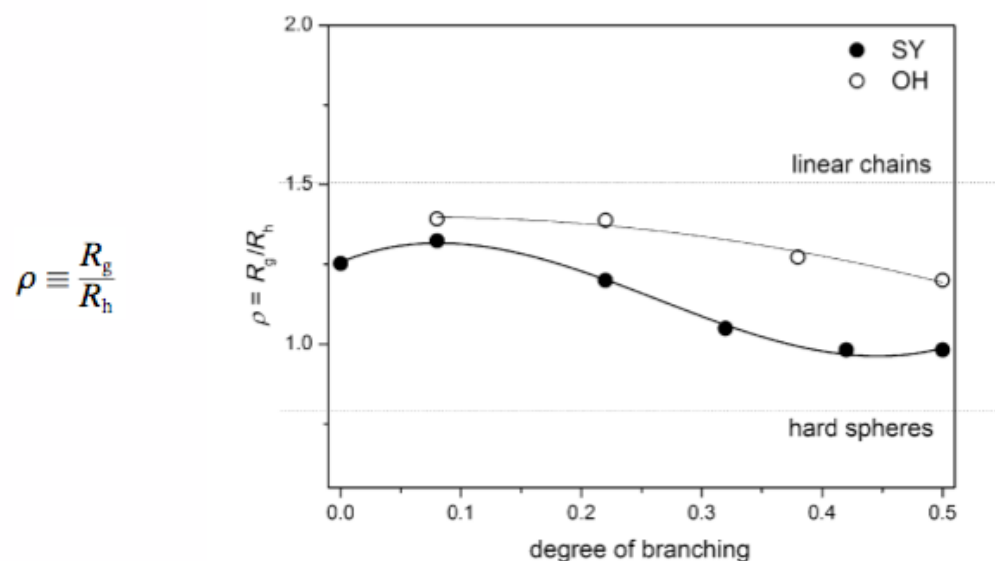
Lederer A et al. Angewandte Chemi 52 4659 (2013).

([http://www.eng.uc.edu/~gbeauca/Classes/Properties/DresdenRgbyRh4659\\_ftp.pdf](http://www.eng.uc.edu/~gbeauca/Classes/Properties/DresdenRgbyRh4659_ftp.pdf))

## $R_g/R_h$ Ratio



**Scheme 1.** Variation of the branching degree from linear to hyperbranched structures for polyesters with different functional groups.



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

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

where  $D$ ,  $T$  and  $L$  are the fractions of dendritic, terminal or linearly incorporated monomers in the resulting hyperbranched 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)



# $R_g/R_H$ Ratio

Table III  
 $\rho$  Factor and Molecular Polydispersity  $P_w/P_n$  for Some Selected Models<sup>a</sup>

model	$\rho$	$P_w/P_n$
linear chains		
monodisperse	1.5	$8/3\pi^{1/2}$
polydisperse ( $m = 1$ )		$3^{1/2}$
polydisperse ( $m$ coupled chains)		$\frac{(m+2)^{1/2}}{m+1} 2\Sigma \left(1 + \frac{k-1}{m}\right) c(k)$
star molecules		
regular stars		$\left(\frac{3f-2}{f\pi}\right)^{1/2} \frac{8}{3} \frac{(2-f) + 2^{1/2}(f-1)}{f}$
polydisperse stars		$\left(\frac{6f}{f+1}\right)^{1/2} \frac{f+3}{2(f+1)}$
polycondensates		
$A_f$ type	1.73	$3^{1/2}$
ABC type		$\left(\frac{3}{4} \frac{1+2B}{1+B}\right)^{1/2} \left(\frac{2+B}{1+B}\right)$
randomly cross-linked chains (polydisperse ( $m = 1$ ) primary chains)		$3^{1/2}$
monodisperse spheres	0.77	$(3/5)^{1/2}$

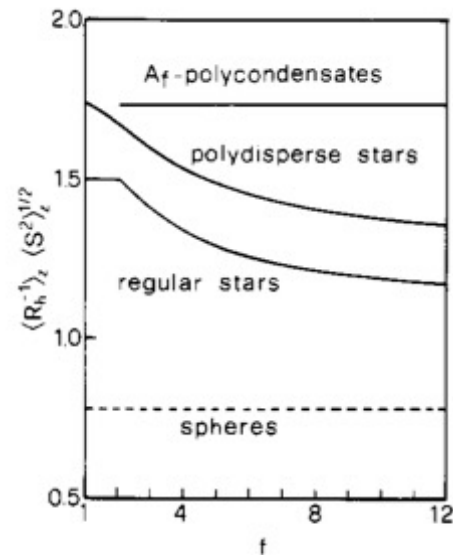
<sup>a</sup>  $\rho = \langle 1/R \rangle_z \langle S^2 \rangle_z^{1/2}$ ; all other notation is as in Tables I and II.

[Burchard, Schmidt, Stockmayer, Macro. 13 1265 \(1980\)](http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhRatioBurchardma60077a045.pdf)

(<http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhRatioBurchardma60077a045.pdf>)



## $R_g/R_H$ Ratio

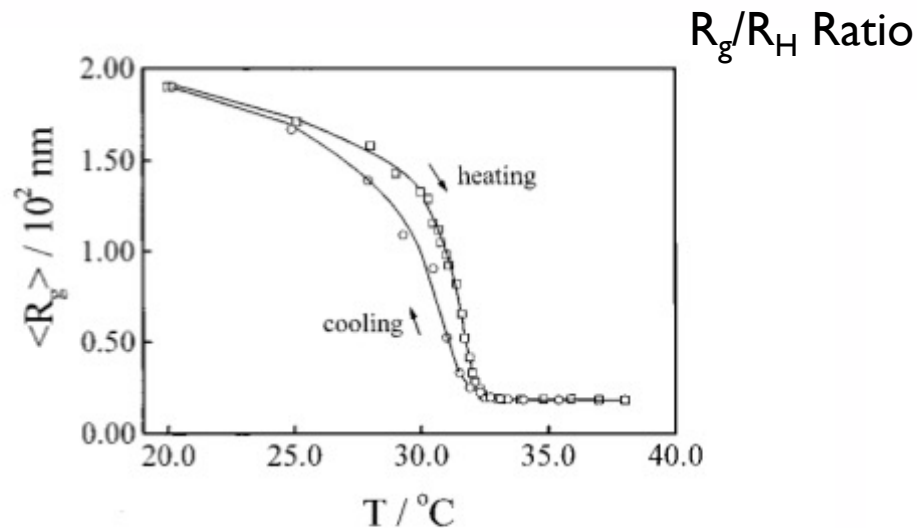


**Figure 3.** Dimensionless parameter  $\rho = \langle R_h^{-1} \rangle_z R_g$  for three branching models and for compact spheres.

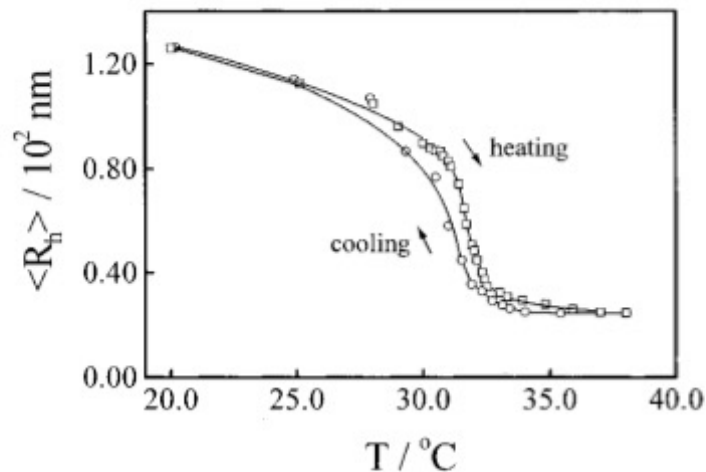
	$f$		$B$
	reg stars	polydisp stars	ABC poly- condensate
$g = 0.77 \pm 14\%$	$3 \pm 0.8$	$5.5 \pm 1.4$	$2.25 \pm 0.6$
$h = 0.94 \pm 5\%$	$3 \pm 0.8$	$4.3 \pm 0.9$	$1.65 \pm 0.35$
$\rho = 1.4 \pm 6\%$	$3 \pm 0.9$	$8.0 \pm 2.5$	$3.5 \pm 1.1$
$C = 0.158 \pm 10\%$	$3 \pm 1.5$	$10.0 \pm 5$	$4.5 \pm 2.3$

[Burchard, Schmidt, Stockmayer, Macro. 13 1265 \(1980\)](http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhRatioBurchardma60077a045.pdf)

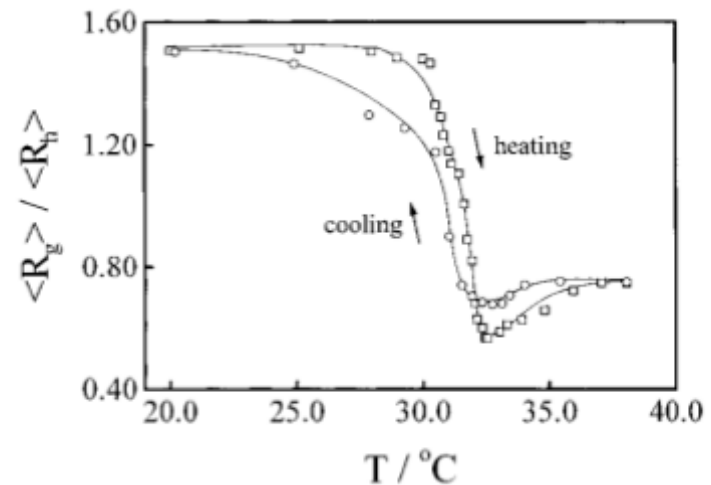
(<http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhRatioBurchardma60077a045.pdf>)



**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 ( $\langle R_g \rangle / \langle R_h \rangle$ ) 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

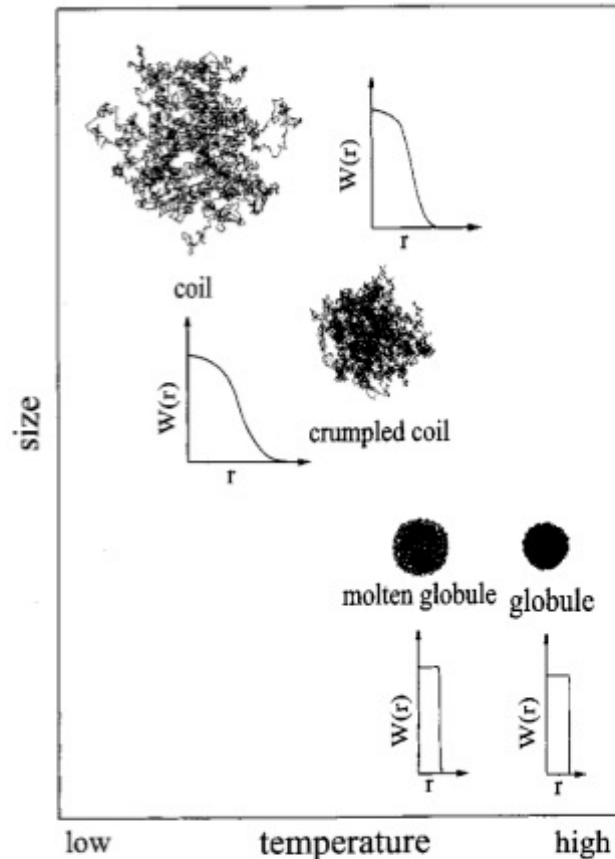
Globule to Coil => Smooth Transition

Coil to Globule => Intermediate State

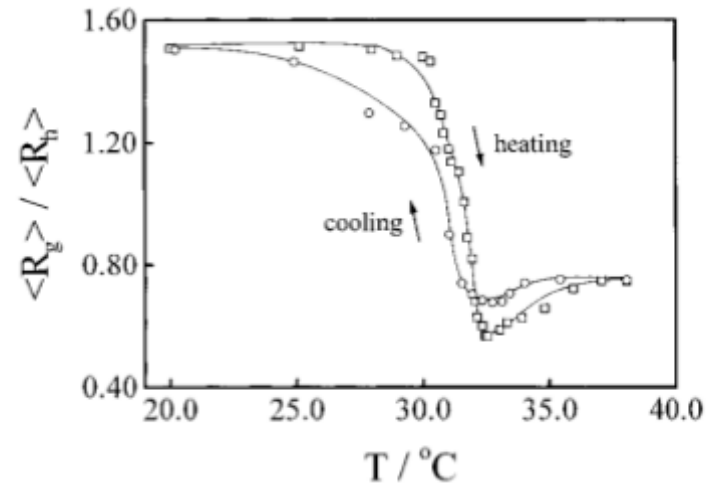
Less than  $(3/5)^{1/2} = 0.77$  (sphere)

[Wang X., Qiu X., Wu C. Macro. 31 2972 \(1998\).](http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhPNIPAAMma971873p.pdf)  
[\(http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhPNIPAAMma971873p.pdf\)](http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhPNIPAAMma971873p.pdf)

$R_g/R_H$  Ratio



**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 ( $\langle R_g \rangle / \langle R_h \rangle$ ) 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

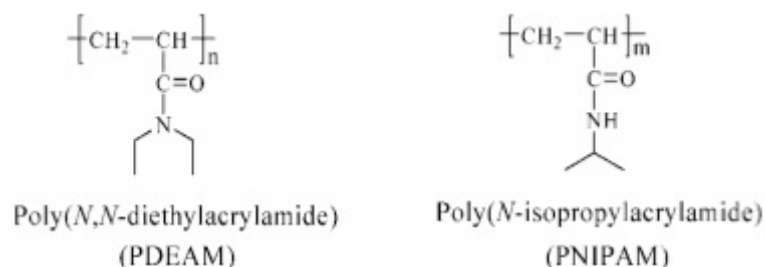
Coil to Globule => Intermediate State

Less than  $(3/5)^{1/2} = 0.77$  (sphere)

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

(<http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhPNIPAAMma971873p.pdf>)

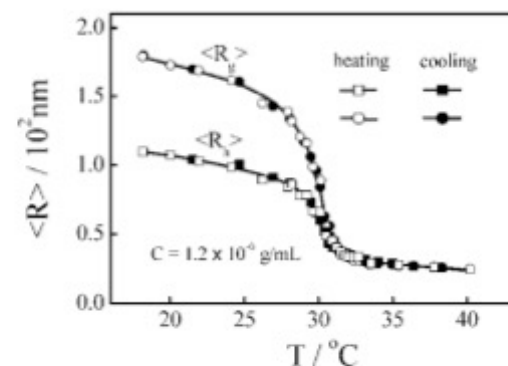
## $R_g/R_H$ Ratio



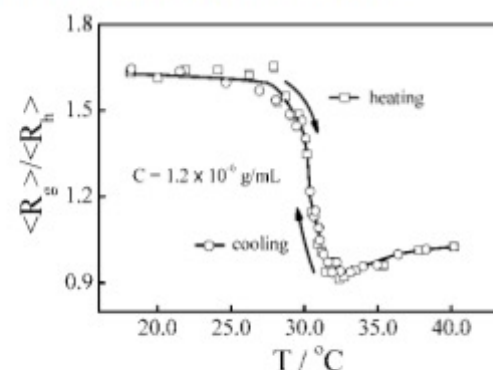
The objectives of the current study are to find whether the intrachain hydrogen bonding plays a role in stabilizing individual collapsed single-chain globules, in the formation of the molten globular state during the coil-to-globule transition, and in the hysteresis of the globule-to-coil transition.

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  $\sim 1.0$ , higher than 0.774 predicted for a uniform nondraining sphere. This means that individual PDEAM single-chain 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  $\sim 0.78$  at high temperatures.<sup>21</sup> We can attribute such a difference to the lacking of intrachain hydrogen bonding in PDEAM. It has been known that the hydrogen



**Figure 4.** Temperature dependence of average radius of gyration ( $\langle R_g \rangle$ ) and hydrodynamic radius ( $\langle R_h \rangle$ ) of poly(*N,N*-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 ( $\langle R_g \rangle / \langle R_h \rangle$ ) of poly(*N,N*-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/RgbyRhCoiltoGlobulema8019128.pdf>)

## $R_g/R_H$ Ratio

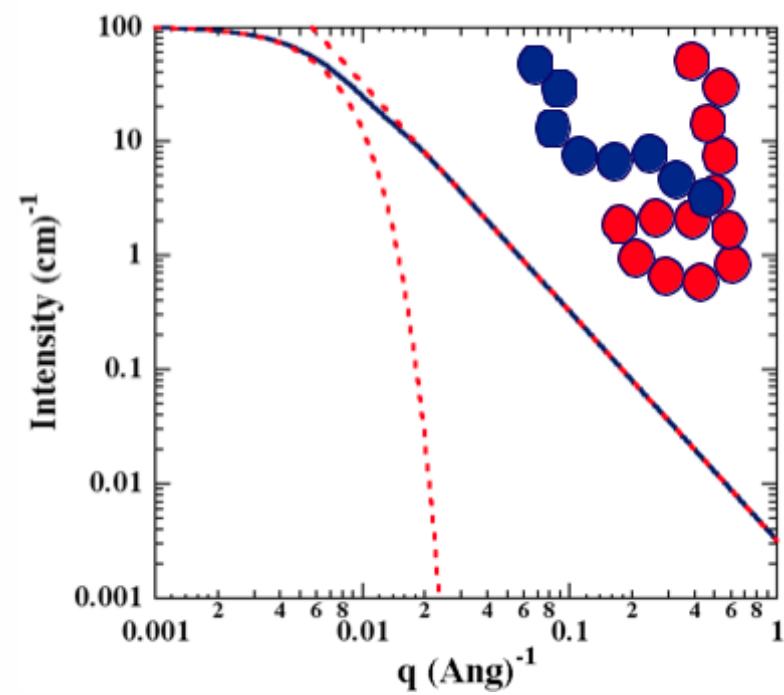
This ratio has also  
been related to the  
shape of a  
colloidal particle



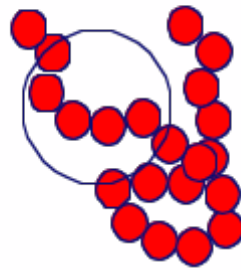




## Static Scattering for Fractal Scaling



At intermediate sizes the chain is “self-similar”



$$Mass \sim Size^{d_f}$$

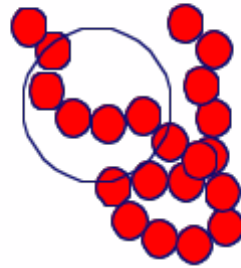
$$z \sim \left( \frac{R_2}{R_1} \right)^{d_f}$$

At intermediate sizes the chain is “self-similar”

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

$N$  = Number of  
Intermediate  
Spheres in the  
Aggregate

$n_e$  = Mass of inter.  
sphere



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

$$N \sim \left( \frac{R_2}{r_{\text{int}}} \right)^{d_f}$$

$$n_e \sim \left( \frac{r_{\text{int}}}{R_1} \right)^{d_f}$$

$$N n_e^2 \sim \left( \frac{r_{\text{int}}}{R_1} \right)^{d_f} \left( \frac{R_2}{R_1} \right)^{d_f} \Rightarrow I(q) \sim \left( \frac{R_2}{R_1} \right)^{d_f} q^{-d_f}$$

## The Debye Scattering Function for a Polymer Coil

$$I(Q) = \frac{2}{Q^2} (Q - 1 + \exp(-Q))$$

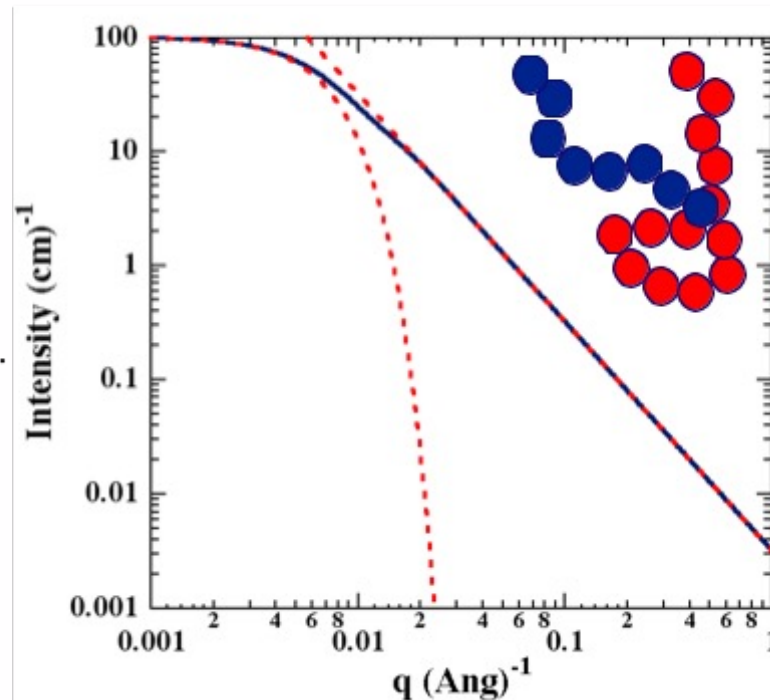
$$Q = q^2 R_g^2$$

For  $qR_g \ll 1$

$$\exp(-Q) = 1 - Q + \frac{Q^2}{2!} - \frac{Q^3}{3!} + \frac{Q^4}{4!} - \dots$$

$$I(q) = 1 - \frac{Q}{3} + \dots \approx \exp\left(-\frac{q^2 R_g^2}{3}\right)$$

Guinier's Law!



## The Debye Scattering Function for a Polymer Coil

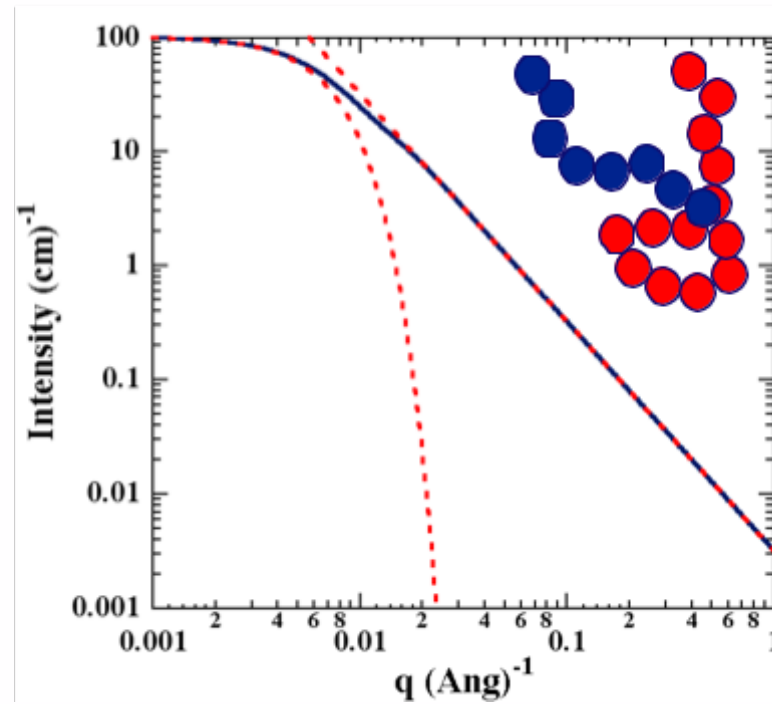
$$I(Q) = \frac{2}{Q^2} (Q - 1 + \exp(-Q))$$

$$Q = q^2 R_g^2$$

For  $qR_g \gg 1$

$$I(Q) = \frac{2}{Q} = \frac{2}{q^2 R_g^2} \sim q^{-d_f}$$

$$d_f = 2$$



## Ornstein-Zernike Equation

$$I(q) = \frac{G}{1 + q^2 \xi^2} \qquad I(q \Rightarrow \infty) = \frac{G}{q^2 \xi^2}$$

Has the correct functionality at high q  
Debye Scattering Function  $\Rightarrow$

$$I(q) = \frac{2}{q^2 R_g^2} (q^2 R_g^2 - 1 + \exp(-q^2 R_g^2)) \qquad I(q \Rightarrow \infty) = \frac{2G}{q^2 R_g^2}$$

So,  $R_g^2 = 2\xi^2$

## Ornstein-Zernike Equation

$$I(q) = \frac{G}{1 + q^2 \xi^2} \quad I(q \Rightarrow 0) = G \exp(-q^2 \xi^2)$$

Has the correct functionality at low q  
Debye =>

$$I(q) = \frac{2}{q^2 R_g^2} (q^2 R_g^2 - 1 + \exp(-q^2 R_g^2)) \quad I(q \Rightarrow 0) = G \exp\left(-\frac{q^2 R_g^2}{3}\right)$$

$$R_g^2 = 3\xi^2$$

The relationship between  $R_g$  and correlation length differs for the two regimes.





**How does a polymer chain respond to external perturbation?**

# The Gaussian Chain

Boltzman Probability  
For a Thermally Equilibrated System

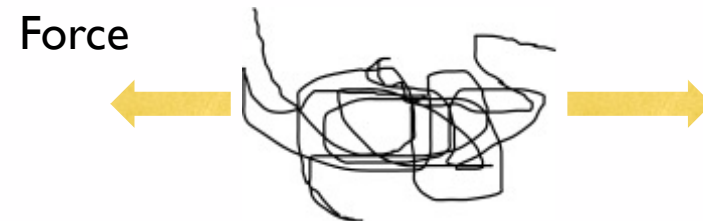
$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability  
For a Chain of End to End Distance R

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

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

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



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

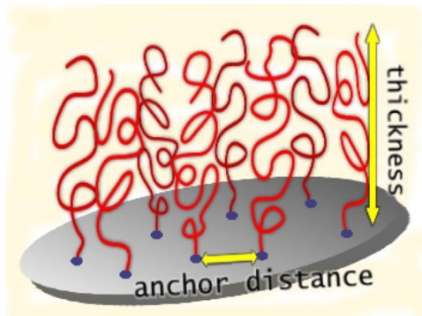
Assumptions:

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

## Tensile Blob

For **Larger Perturbations** of Structure

- 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  $\xi$



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

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

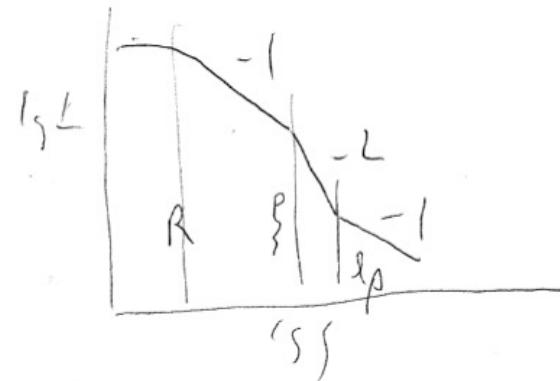
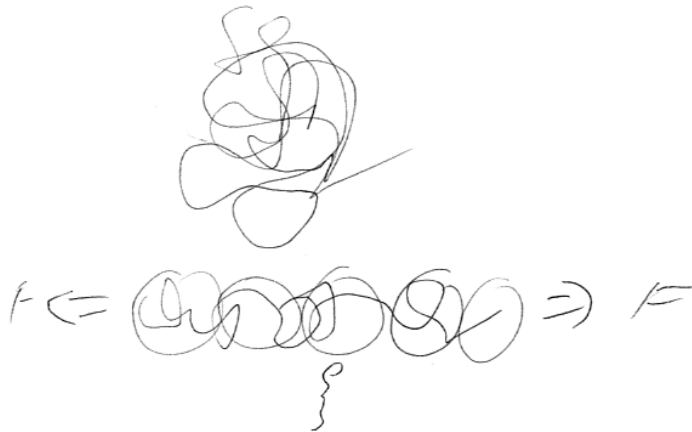
For weak perturbations of the chain  $R \approx n^{1/2}l_K \equiv \xi_{Tensile}$

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

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.

$$F = k_{spr} R = \frac{3kT}{R^{*2}} R$$

$$\xi_{Tensile} \sim \frac{R^{*2}}{R} = \frac{3kT}{F}$$



For sizes larger than the blob size the structure is linear, one conformational state so the conformational entropy is 0. For sizes smaller the blob has the minimum spring constant so the weakest link governs the mechanical properties and the chains are random below this size.

# Semi-Dilute Solution Chain Statistics

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

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

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 ( $c \gg c^*$ ),  $d_f = 2$ . At small sizes the coil acts as if it were in a dilute solution,  $d_f = 5/3$ . There is a size scale,  $\xi$ , 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  $\xi$ ?

$\xi$  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

$$\xi = b \left( \frac{N}{n_\xi} \right)^{3/5} \sim \left( \frac{c}{c^*} \right)^{-3/4}$$

$$n_\xi \sim \left( \frac{c}{c^*} \right)^{(3/4)(5/3)} = \left( \frac{c}{c^*} \right)^{(5/4)}$$

$$R = \xi n_\xi^{1/2} \sim \left( \frac{c}{c^*} \right)^{-3/4} \left( \frac{c}{c^*} \right)^{(5/8)} = \left( \frac{c}{c^*} \right)^{-1/8}$$

$$R = \xi n_\xi^{1/2} = R_{F0} (c/c^*)^{-3/4} (c/c^*)^{5/8} = R_{F0} (c/c^*)^{-1/8}$$

This is called the “Concentration Blob”

## Three regimes of chain scaling in concentration.

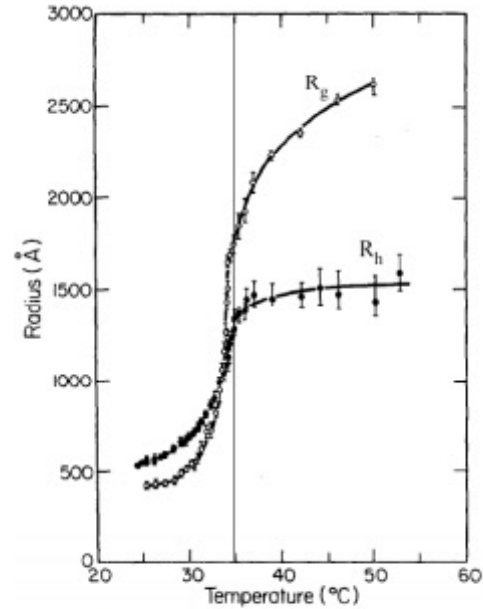
In dilute solution the chain displays good solvent scaling in most cases,  $d_f = 5/3$ . When the concentration is increased above the overlap concentration,  $c^*$ , a concentration blob,  $\xi_c$ , is introduced between  $R_g$  and  $l_p$ . For sizes larger than the blob size, screening of interactions leads to Gaussian scaling,  $d_f = 2$ . For sizes smaller than the screening length of blob size, the chains are not screened and good solvent scaling is observed. The blob size follows

$\xi \sim R \left( \frac{c}{c^*} \right)^{-3/4}$  until a concentration where  $\xi = l_p$ . At that concentrations above  $c^{**}$ ,

$c^{**} \sim c^* \left( \frac{R}{l_p} \right)^{4/3}$ , the chain is in a concentrated condition and all interactions are screened so

that the chain has a Gaussian configuration,  $d_f = 2$ .

## Thermal Blob



**Figure 3.** Radius of gyration,  $R_g$ , and hydrodynamic 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).

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

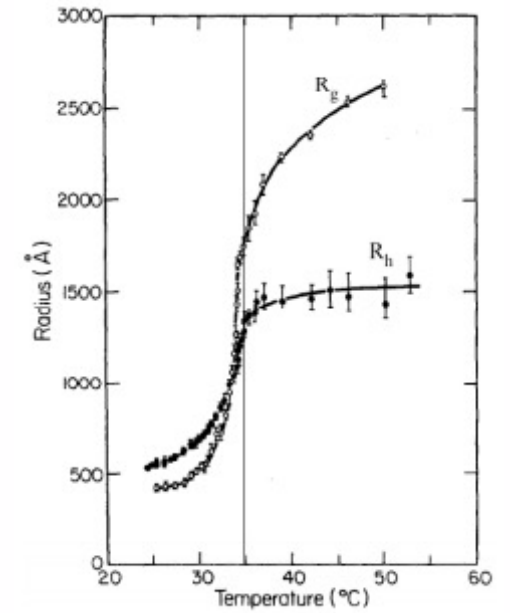
$$E = kT \left( \frac{3R^2}{2nl_K^2} + \frac{n^2 V_c (1 - 2\chi)}{2R^3} \right)$$

## Thermal Blob

$$\Delta\varepsilon = (\varepsilon_{PP} + \varepsilon_{SS})/2 - \varepsilon_{PS}$$

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

$$V_{c,enthalpic} = V_c(1 - 2\chi)$$



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

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

## Thermal Blob

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

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 = 100  
The 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.

## Thermal Blob

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

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

By equating these:

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

Classification  
 Physics Abstracts  
 36.20 — 64.00 — 61.40

# CROSS-OVER IN POLYMER SOLUTIONS

B. FARNOUX, F. BOUÉ, J. P. COTTON, M. DAOUD, G. JANNINK, M. NIERLICH

and

P. G. DE GENNES (\*)

DPh-G/PSRM, CEN Saclay, Boîte Postale n° 2, 91190 Gif sur Yvette, France

(Reçu le 18 avril 1977, révisé le 21 juillet 1977, accepté le 8 septembre 1977)

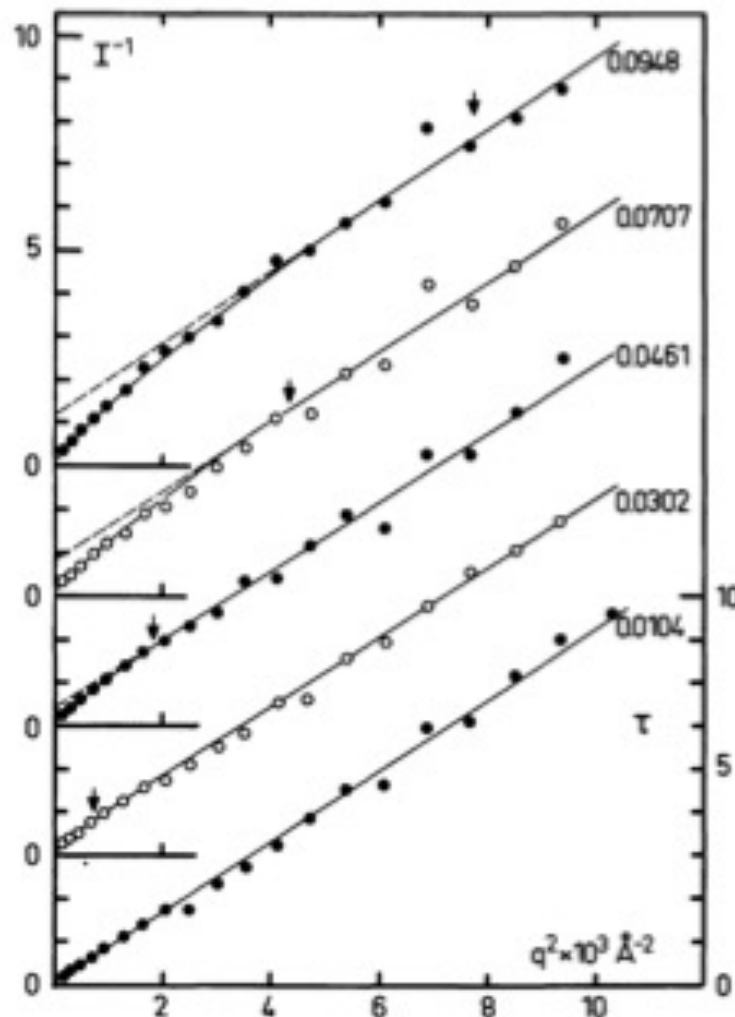
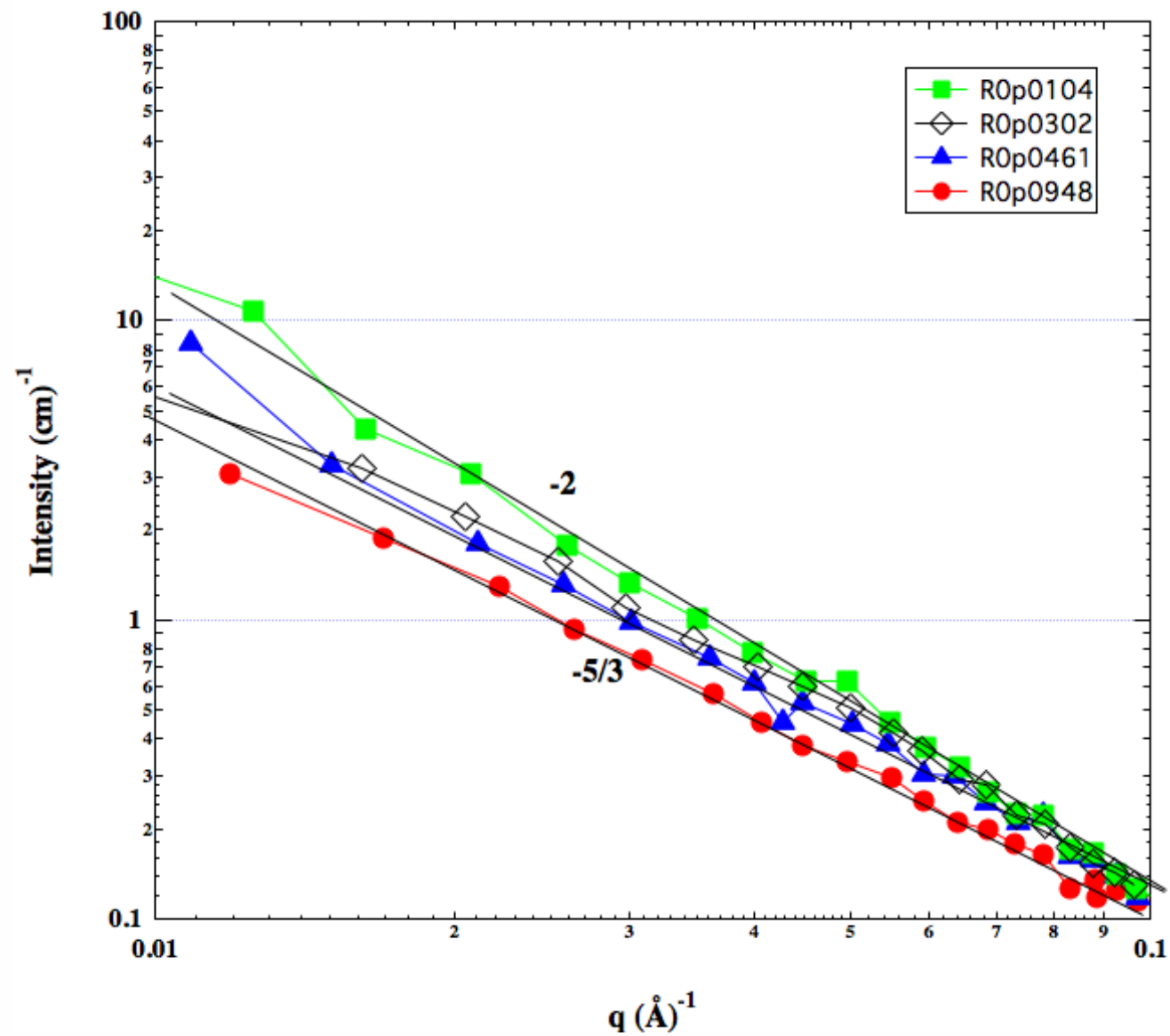


FIG. 7. — Inverse of the scattered intensity *versus* the square of the scattering vector. Points are experimental data recorded at different reduced temperatures  $\tau$  as indicated on the right. The solid curves are the results of calculation using the formula (3.16).

Vertical arrows show the theoretical cross-over point.



# Digitized from Farnoux





## Growth of Nanoparticles

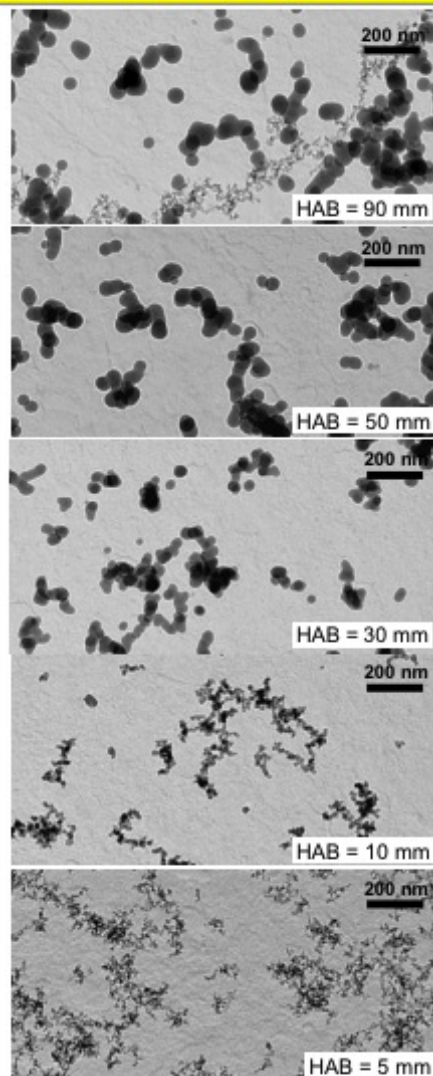


Fig. 1: Silica particles as collected by conventional thermophoretic sampling (TS) along the axis of a premixed flame of hexamethyldisiloxane and oxygen [1,2]. Using aluminum foil in-stead of TEM grids and performing multiple sampling from the same location in the flame, the Al-probe was covered with a silica monolayer [1] (as indicated in Fig. 2).

## Spray Flame Appearance

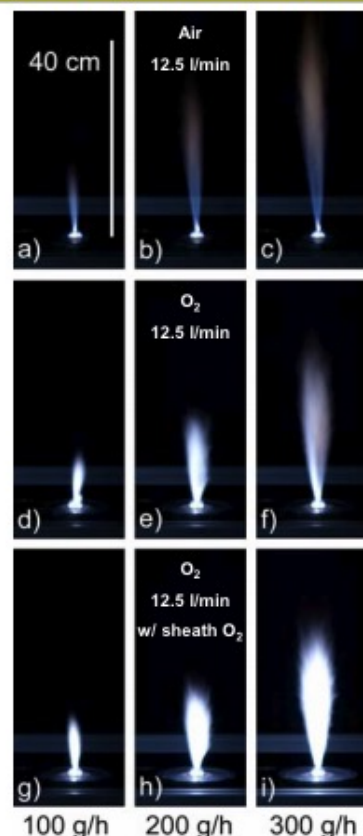


Fig. 3: Spray flames (1.26 M HMDSO in EtOH) producing 100, 200 and 300 g/h of silica using 12.5 l/min air (a-c) or O<sub>2</sub> as dispersion gas without (d-f) and with (g-i) additional 25 l/min of O<sub>2</sub> sheath flow at 1 bar pressure drop across the nozzle tip.

## Powder Morphology

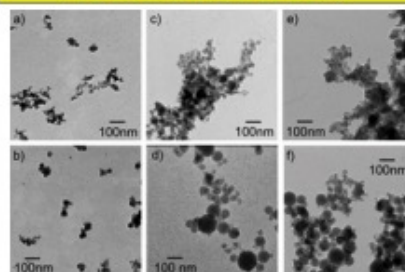


Fig. 4: Transmission electron micrographs of silica nanoparticles at production rates of 150 (top row) and 300 g/h (bottom row) using 12.5 l/min air (a,b) or O<sub>2</sub> as dispersion gas without (c,d) and with (e,f) additional 25 l/min of O<sub>2</sub> sheath flow using 1.26 M HMDSO in EtOH.

# Fractal Aggregates and Agglomerates

## Powder Morphology

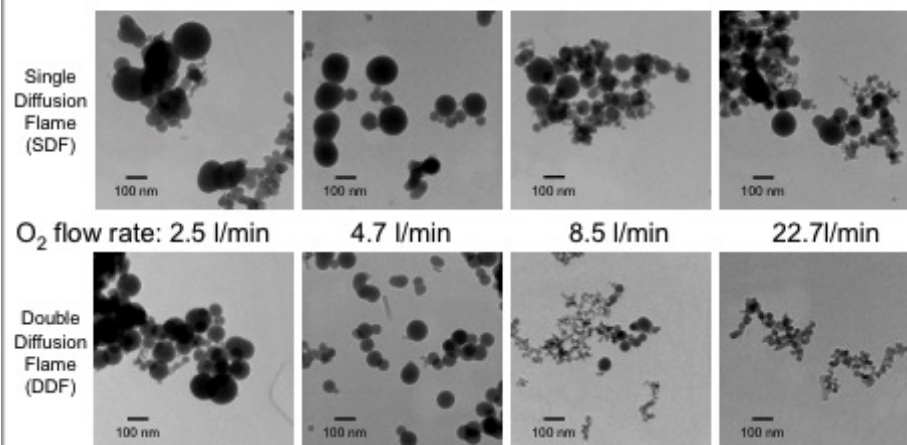


Fig. 5: Transmission Electron Micrographs (TEM) of SiO<sub>2</sub> synthesized in SDF and DDF at different oxygen flow rates. Particles made in flames at low oxygen flow rates stay longer at high temperatures leading to the formation of rather big spherical, non-agglomerated particles with diameters of about 100 nm. At high oxygen flow rates the particles are agglomerates of small primary particles. Particles synthesized in DDF have narrower size distributions indicated by TEM compared to those made in SDF.

## Flame Structure

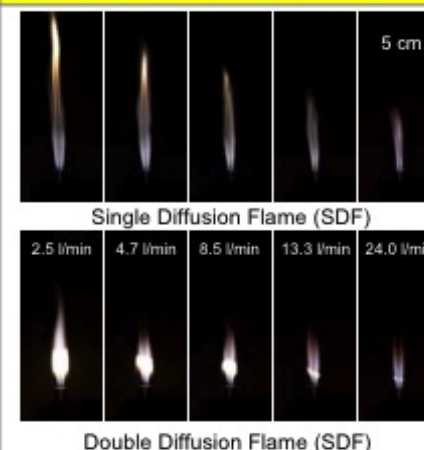


Fig. 3: Effect of oxygen flow rate on flame structure of a SDF and DDF. Increasing the oxygen flow rate decreases the flame height of the HMDSO-methane-oxygen diffusion flame as turbulence accelerates the mixing of fuel and oxidant.

## Polymer Chains are Mass-Fractals

$$R_{\text{RMS}} = n^{1/2} l$$

$$\text{Mass} \sim \text{Size}^2$$

3-d object

$$\text{Mass} \sim \text{Size}^3$$

2-d object

$$\text{Mass} \sim \text{Size}^2$$

1-d object

$$\text{Mass} \sim \text{Size}^1$$

df-object

$$\text{Mass} \sim \text{Size}^{\text{df}}$$

This leads to odd properties:

$$\text{density} \quad \rho = \frac{\text{Mass}}{\text{Volume}} = \frac{\text{Mass}}{\text{Size}^3} = \frac{\text{Size}^{\text{df}}}{\text{Size}^3} \sim \text{Size}^{\text{df}-3}$$

For a 3-d object density doesn't depend on size,

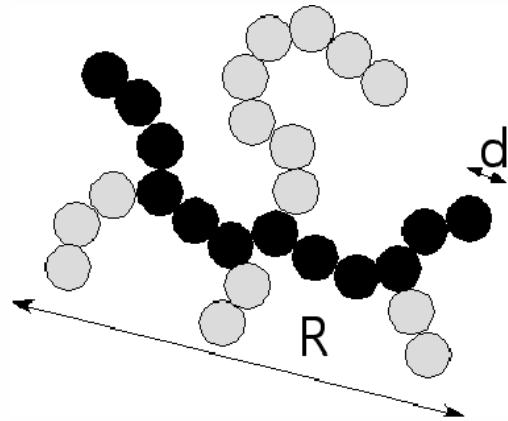
For a 2-d object density drops with Size

Larger polymers are less dense





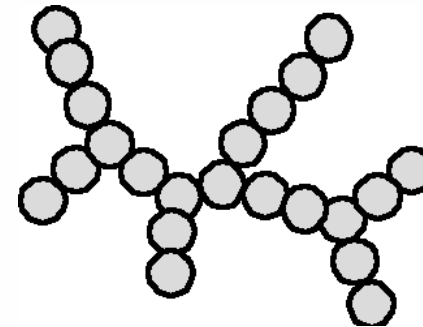
# How Complex Mass Fractal Structures Can be Decomposed



Tortuosity



Connectivity



$$z \sim \left(\frac{R}{d}\right)^{d_f} \sim p^c \sim s^{d_{\min}}$$

$$p \sim \left(\frac{R}{d}\right)^{d_{\min}}$$

$$s \sim \left(\frac{R}{d}\right)^c$$

$$d_f = d_{\min} c$$

z	d <sub>f</sub>	p	d <sub>min</sub>	s	c	R/d
27	1.36	12	1.03	22	1.28	11.2





## Disk

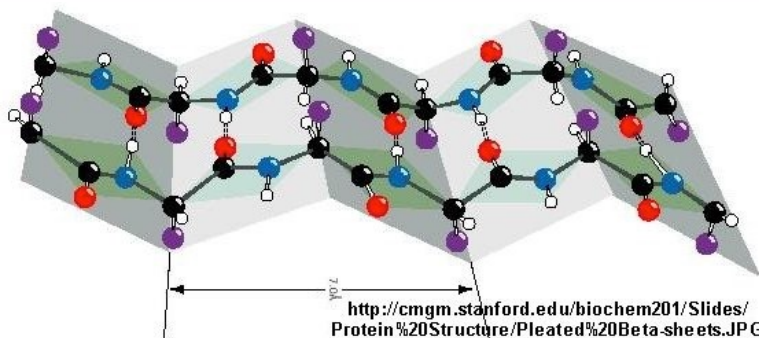


$$d_f = 2$$

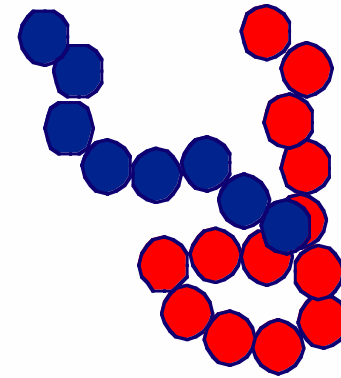
$$d_{\min} = 1$$

$$c = 2$$

Extended  $\beta$ -sheet  
(misfolded protein)



## Random Coil



$$d_f = 2$$

$$d_{\min} = 2$$

$$c = 1$$

Unfolded Gaussian chain

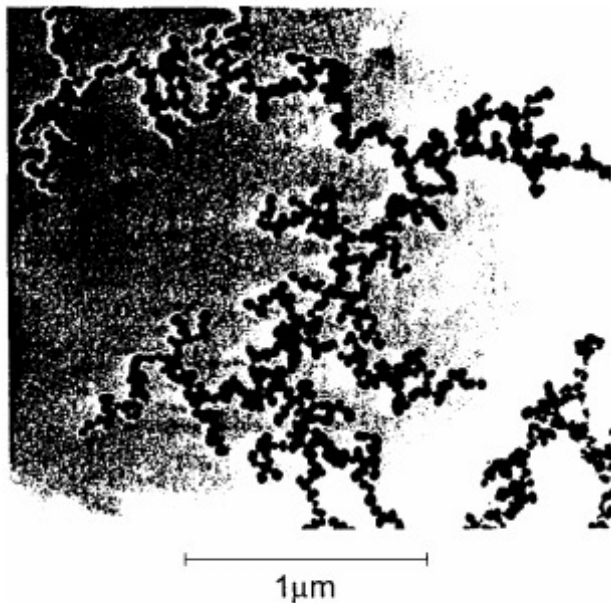


### **Primary Size for Fractal Aggregates**

# Fractal Aggregates and Agglomerates

## Primary Size for Fractal Aggregates

- Particle counting from TEM
- Gas adsorption  $V/S \Rightarrow d_p$
- Static Scattering  $R_g, d_p$
- Dynamic Light Scattering

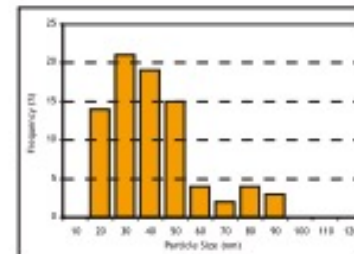
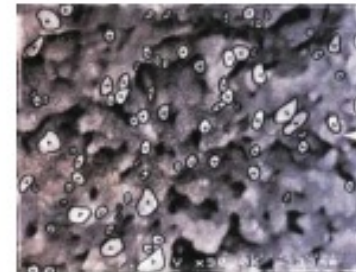


**Figure 2.** TEM picture of titania ( $\text{TiO}_2$ ) fractal aggregates with  $D \simeq 1.8$  produced by pyrolysis of Titanium Isopropoxide.

<http://www.phys.ksu.edu/personal/sor/publications/2001/light.pdf>

### Cryo Scanning Electron Microscopy

A scanning electron micrograph of a frozen sample was taken. The sizes of the particles visible on the picture were measured individually with a ruler and used to calculate a number-mean,  $D(1,0)$ , a volume-mean,  $D(4,3)$  and a number-distribution.



Number Mean -  $D(1,0) = 45.2$  nm  
Volume Mean -  $D(4,3) = 68.0$  nm

*Note : due to the limited number (82) of particles measured this result is only indicative.*

<http://www.koboproductsinc.com/Downloads/PS-Measurement-Poster-V40.pdf>

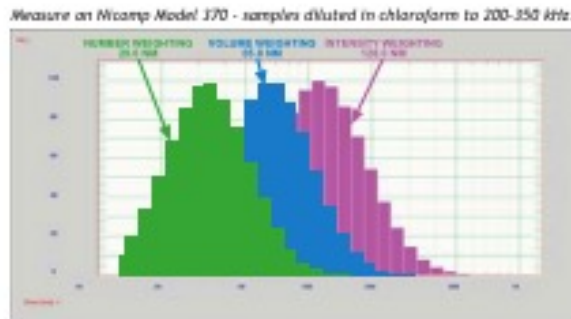
# Fractal Aggregates and Agglomerates

## Primary Size for Fractal Aggregates

- Particle counting from TEM
- Gas adsorption  $V/S \Rightarrow d_p$
- Static Scattering  $R_g, d_p$
- Dynamic Light Scattering

### Dynamic Light Scattering

To evaluate repeatability and robustness, the measure was made 8 times, using 3 different dilutions. The following graph presents one of these measures, expressed as intensity-distribution, volume-distribution and number (length)-distribution.



The following table shows the averaged results for the 8 measurements. Precision is calculated as the Relative Standard Deviation of the measurements.

Mean Calculation	Particle Size	Precision
Intensity Weighting	127.9 nm	2 %
Volume Weighting	71.6 nm	16 %
Number Weighting	36.2 nm	25 %

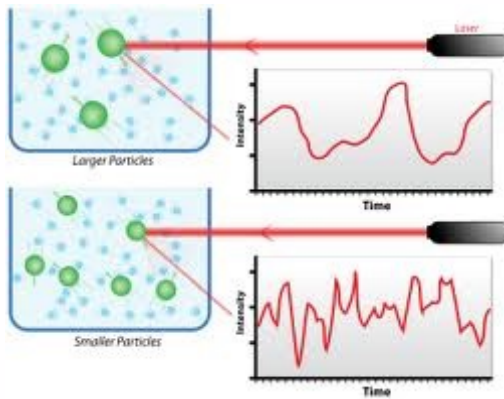
For static scattering  $p(r)$  is the binary spatial auto-correlation function

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

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



$$g^2(q; \tau) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2}$$

$$g^2(q; \tau) = 1 + \beta [g^1(q; \tau)]^2$$

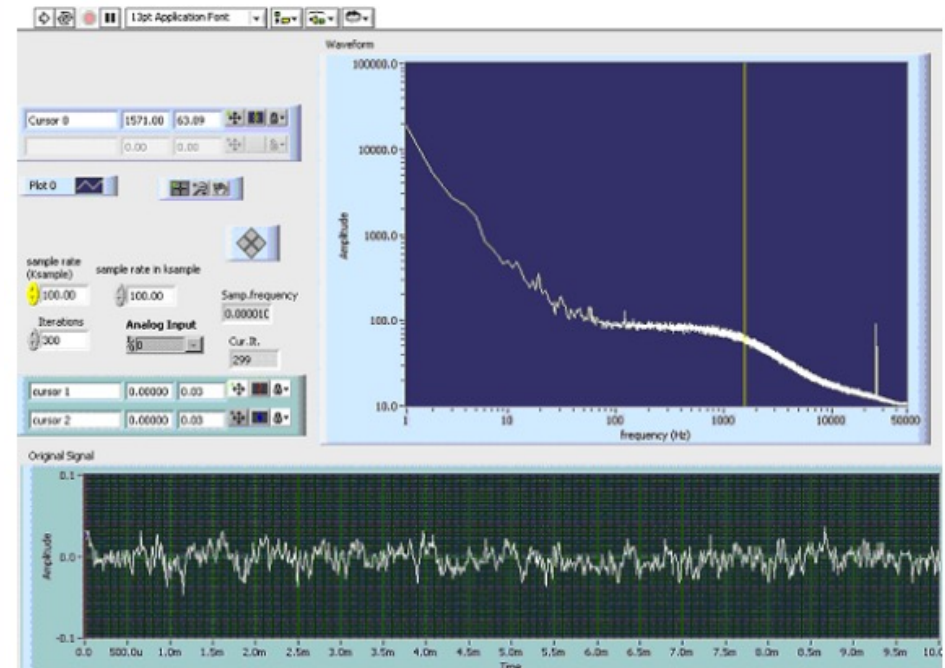
$$q = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

$$g^1(q; \tau) = \exp(-\Gamma\tau)$$

$$\Gamma = q^2 D_t$$

$$D = k_B T / 6\pi\eta a$$

$a = R_H = \text{Hydrodynamic Radius}$



# Dynamic Light Scattering

## my DLS web page

<http://www.eng.uc.edu/~gbeaucag/Courses/Physics/DLS.pdf>

## Wiki

[http://webcache.googleusercontent.com/search?q=cache:eY3xhiX117IJ:en.wikipedia.org/wiki/Dynamic\\_light\\_scattering+&cd=1&hl=en&ct=clnk&gl=us](http://webcache.googleusercontent.com/search?q=cache:eY3xhiX117IJ:en.wikipedia.org/wiki/Dynamic_light_scattering+&cd=1&hl=en&ct=clnk&gl=us)

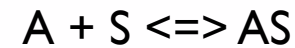
## Wiki Einstein Stokes

[http://webcache.googleusercontent.com/search?q=cache:yZDPRbqZ1BIJ:en.wikipedia.org/wiki/Einstein\\_relation\\_\(kinetic\\_theory\)+&cd=1&hl=en&ct=clnk&gl=us](http://webcache.googleusercontent.com/search?q=cache:yZDPRbqZ1BIJ:en.wikipedia.org/wiki/Einstein_relation_(kinetic_theory)+&cd=1&hl=en&ct=clnk&gl=us)



# Gas Adsorption

$$\theta = \frac{\text{adsorbed sites}}{\text{total sites (N)}}$$



Adsorption

$$\frac{d\theta}{dt} = k_a p N (1 - \theta)$$

Equilibrium

=

Desorption

$$\frac{d\theta}{dt} = k_d N \theta$$

$$\theta = \frac{Kp}{1 + Kp}$$

$$K = \frac{k_a}{k_d}$$

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_{abs}}{RT^2}$$

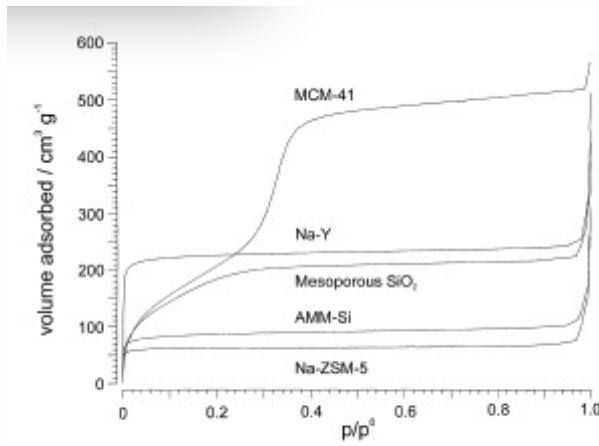
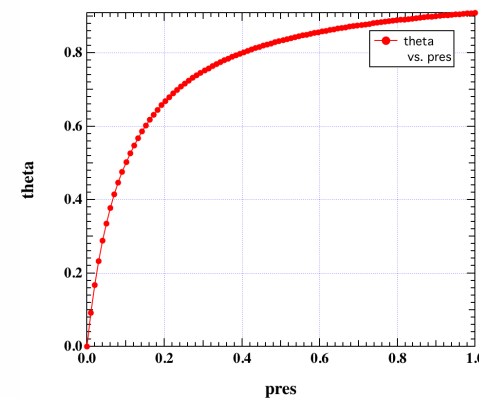


Fig. 2. Adsorption isotherms of the samples tested with Ar at 87.5 K.

[http://www.chem.ufl.edu/~iti/44111\\_f00/ads/ads\\_1.html](http://www.chem.ufl.edu/~iti/44111_f00/ads/ads_1.html)



# Gas Adsorption

## Multilayer adsorption

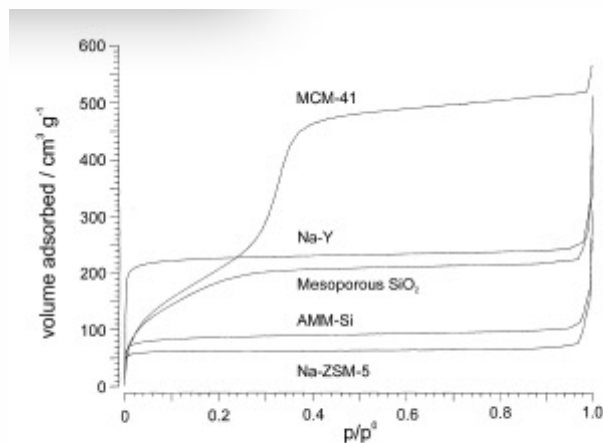
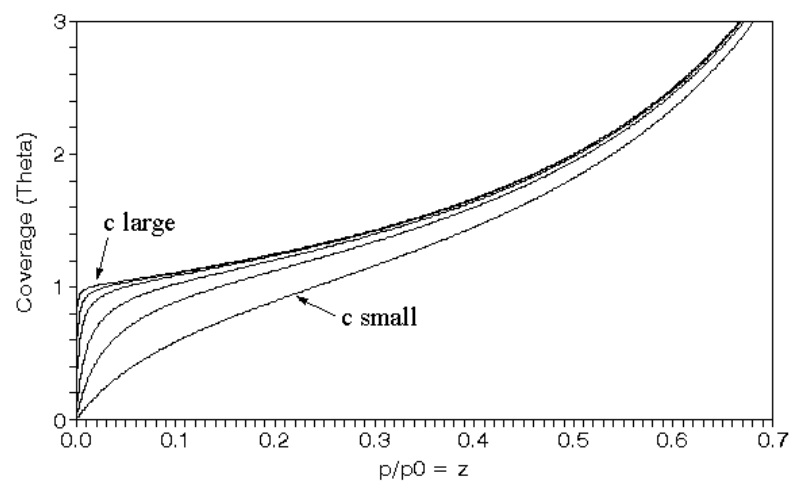


Fig. 2. Adsorption isotherms of the samples tested with Ar at 87.5 K.

## BET Isotherm

Various Values of  $c$



$$\frac{n}{n_{\text{mono}}} = \frac{cZ}{(1-Z)[1 - Z(1-c)]} = (\theta)$$

$$c \approx \frac{e^{-\Delta H_{\text{ads}}/RT}}{e^{\Delta H_{\text{vap}}/RT}}$$

[http://www.chem.ufl.edu/~itl/4411L\\_f00/ads/ads\\_1.html](http://www.chem.ufl.edu/~itl/4411L_f00/ads/ads_1.html)

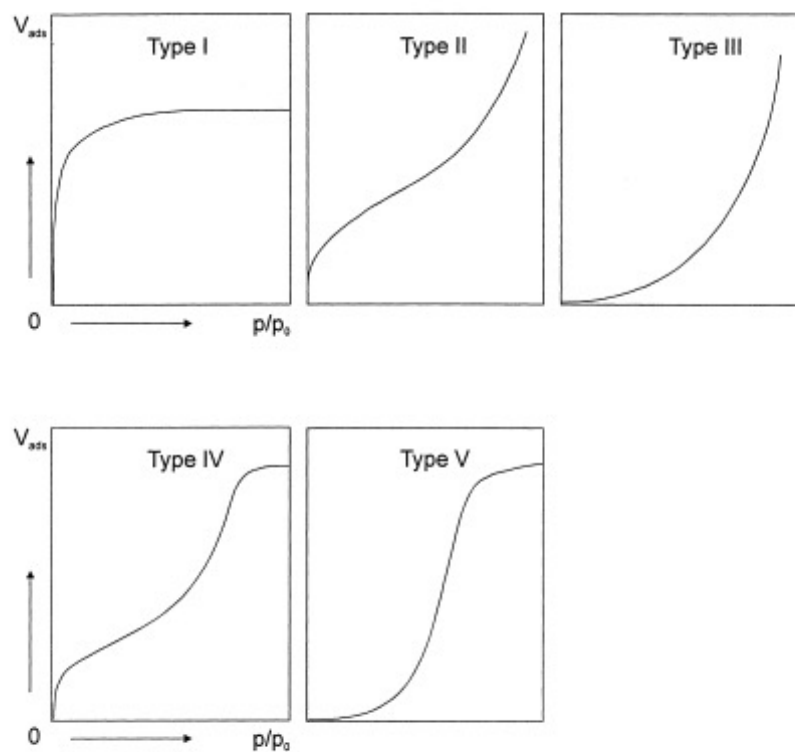


Fig. 1. Adsorption isotherm types defined by Brunauer [6].

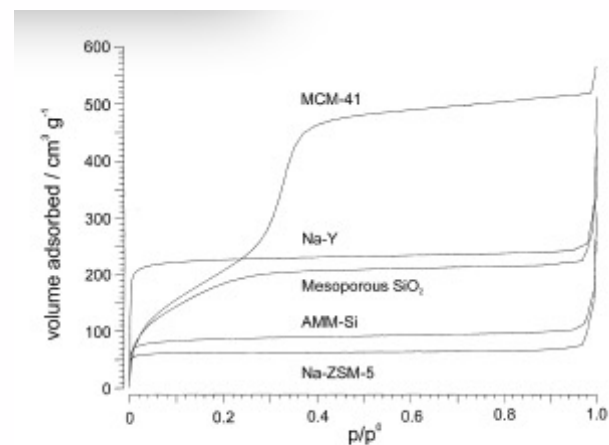


Fig. 2. Adsorption isotherms of the samples tested with Ar at 87.5 K.

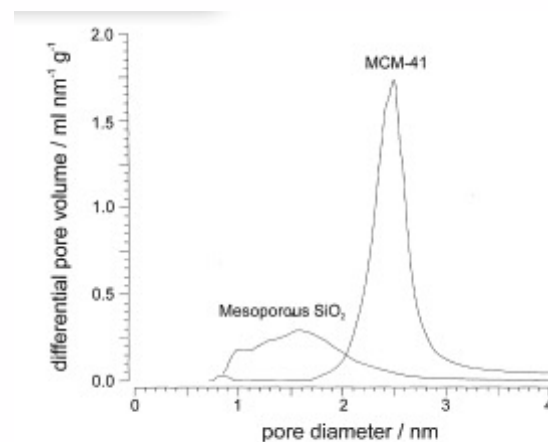


Fig. 3. Pore-size distribution according to the BJH method.

From gas adsorption obtain surface area by number of gas atoms times an area for the adsorbed gas atoms in a monolayer

Have a volume from the mass and density.

So you have  $S/V$  or  $V/S$

Assume sphere  $S = 4\pi R^2$ ,  $V = 4/3 \pi R^3$

So  $d_p = 6V/S$

Sauter Mean Diameter  $d_p = \langle R^3 \rangle / \langle R^2 \rangle$

# Log-Normal Distribution

$$f(R) = \frac{1}{R\sigma(2\pi)^{1/2}} \exp\left\{-\frac{[\log(R/m)]^2}{2\sigma^2}\right\},$$

$$\langle R^r \rangle = m^r \exp(r^2 \sigma^2 / 2) = \exp(r\mu + r^2 \sigma^2 / 2)$$

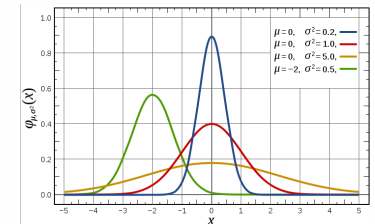
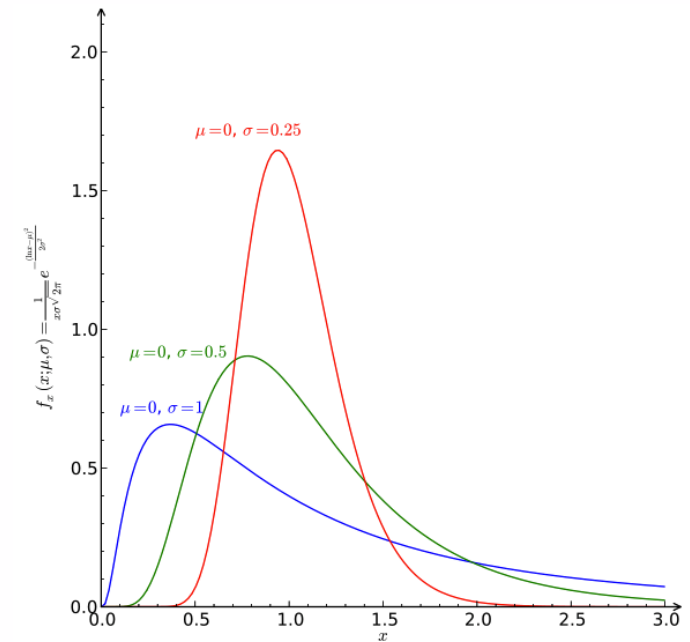
$$\langle R \rangle = m \exp(\sigma^2 / 2)$$

Mean

$$\sigma_g = \exp(\sigma) \quad x_g = \exp(m)$$

Geometric standard deviation and geometric mean (median)

Gaussian is centered at the Mean and is symmetric. For values that are positive (size) we need an asymmetric distribution function that has only values for greater than 1. In random processes we have a minimum size with high probability and diminishing probability for larger values.



<http://www.eng.uc.edu/~gbeaucag/PDFPapers/ks5024%20|applcryst%20Beaucage%20PSD.pdf>

[http://en.wikipedia.org/wiki/Log-normal\\_distribution](http://en.wikipedia.org/wiki/Log-normal_distribution)

## Log-Normal Distribution

$$f(R) = \frac{1}{R\sigma(2\pi)^{1/2}} \exp\left\{-\frac{[\log(R/m)]^2}{2\sigma^2}\right\},$$

$$\langle R^r \rangle = m^r \exp(r^2 \sigma^2 / 2) = \exp(r\mu + r^2 \sigma^2 / 2)$$

$$\langle R \rangle = m \exp(\sigma^2 / 2)$$

Mean

$$\sigma_g = \exp(\sigma) \quad x_g = \exp(m)$$

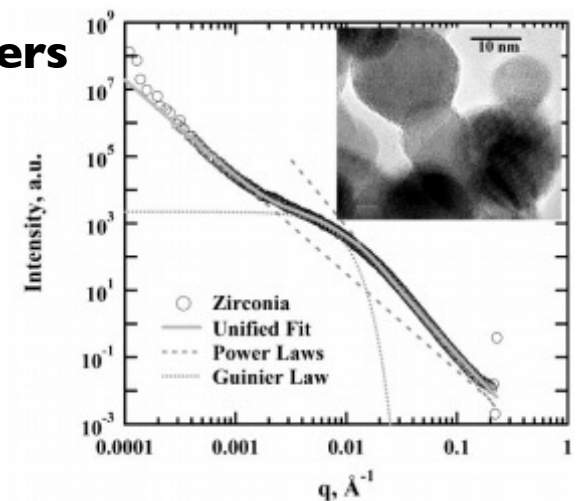
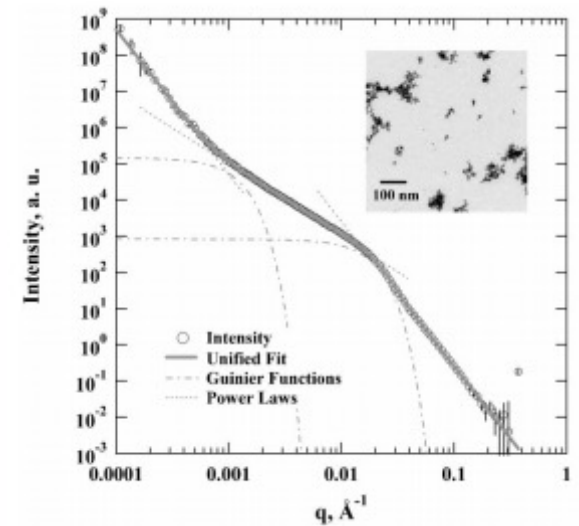
Geometric standard deviation and geometric mean (median)

## Static Scattering Determination of Log Normal Parameters

$$\ln \sigma_g = \sigma = \left\{ \frac{\ln [B(R_g^2)^2 / (1.62G)]}{12} \right\}^{1/2} = \left( \frac{\ln \text{PDI}}{12} \right)^{1/2} \quad (17)$$

and

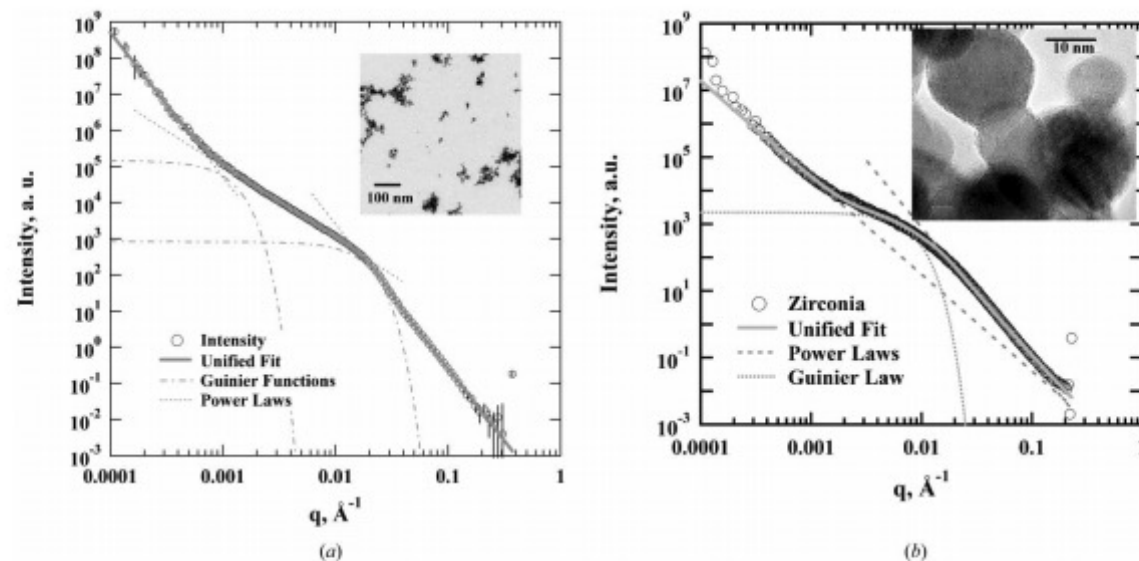
$$m = \{5R_g^2 / [3 \exp(14\sigma^2)]\}^{1/2}, \quad (18)$$



# Fractal Aggregates and Agglomerates

## Primary Size for Fractal Aggregates

- Particle counting from TEM
- Gas adsorption  $V/S \Rightarrow d_p$
- Static Scattering  $R_g, d_p$
- Dynamic Light Scattering



**Figure 2**

USAXS data from aggregated nanoparticles (circles) showing unified fits (bold grey lines), primary particle Guinier and Porod functions at high  $q$ , the intermediate mass fractal scaling regime and the aggregate Guinier regime (dashed lines). (a) Fumed titania sample with multi-grain particles and low- $q$  excess scattering due to soft agglomerates.  $d_{V/S} = 16.7 \text{ nm}$  (corrected to  $18.0 \text{ nm}$ ),  $\text{PDI} = 3.01$  ( $\sigma_g = 1.35$ ),  $R_g = 11.2 \text{ nm}$ ,  $d_t = 1.99$ ,  $z_{\pm 1} = 175$ ,  $z_{R_g} = 226$ ,  $R_{g2} = 171 \text{ nm}$ . From gas adsorption,  $d_p = 16.2 \text{ nm}$ . (b) Fumed zirconia sample (Mueller *et al.*, 2004) with single-grain particles, as shown in the inset. The primary particles for this sample have high polydispersity leading to the observed hump near the primary particle scattering regime.  $d_{V/S} = 20.3 \text{ nm}$ ,  $\text{PDI} = 10.8$  ( $\sigma_g = 1.56$ ),  $R_g = 26.5 \text{ nm}$ ,  $d_t = 2.90$ . From gas adsorption,  $d_p = 19.7 \text{ nm}$ .

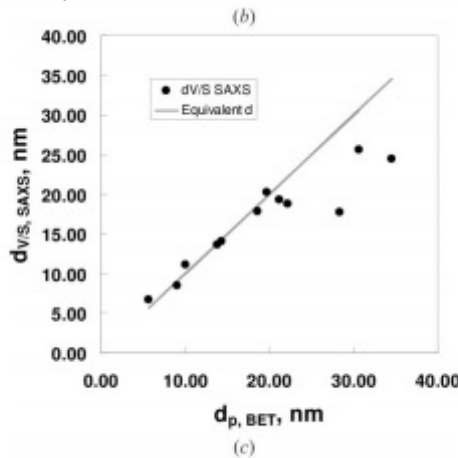
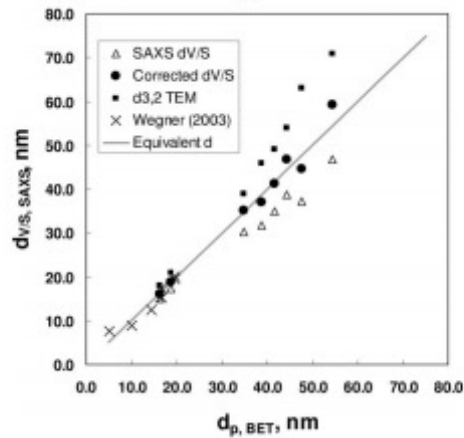
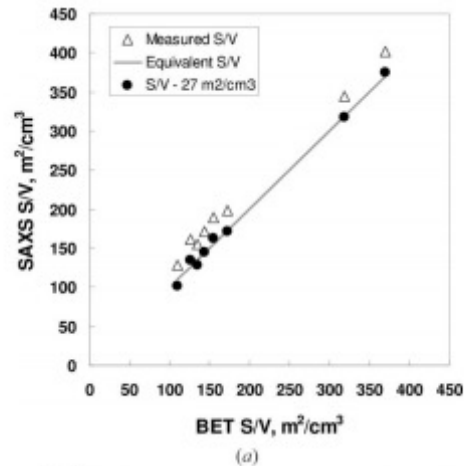
[http://www.eng.uc.edu/~gbeauca/PDFPapers/ks5024%20\[appliedcryst%20Beaucage%20PSD\].pdf](http://www.eng.uc.edu/~gbeauca/PDFPapers/ks5024%20[appliedcryst%20Beaucage%20PSD].pdf)

# Fractal Aggregates and Agglomerates

## Primary Size for Fractal Aggregates

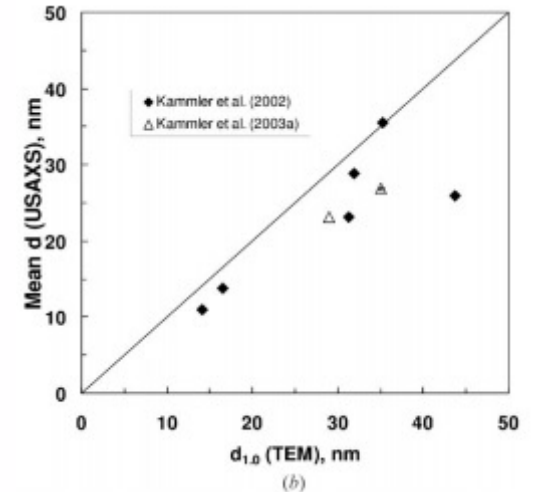
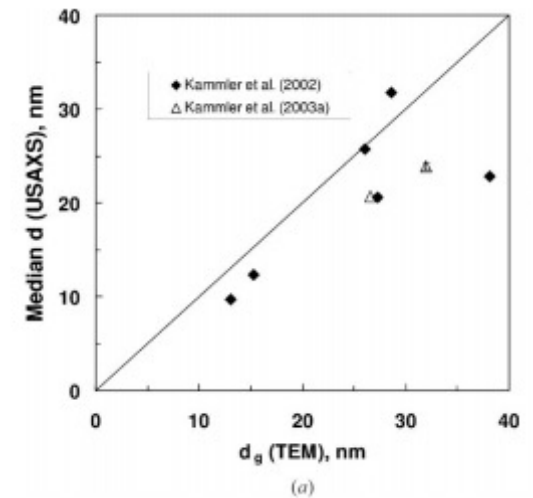
- Particle counting from TEM
- Gas adsorption  $V/S \Rightarrow d_p$
- Static Scattering  $R_g, d_p$

*Smaller Size = Higher S/V  
(Closed Pores or similar issues)*



**Figure 3**

(a)  $S/V$  from SAXS for titania particles produced by vapor-phase pyrolysis of titania tetraisopropoxide by Kammler *et al.* (2002, 2003). The SAXS  $S/V$  can be made to agree with the BET value by subtraction of  $27 \text{ m}^2 \text{ cm}^{-3}$ . (b)  $d_{V/S}$  from USAXS [and corrected from (a)] versus  $d_p$  from BET analysis of gas adsorption data for a series of titania samples produced by Kammler (triangles and filled circles), and samples made in a quenched-spray flame from Wegner & Pratsinis (2003) (crosses, single-grain particles). The calculated  $d_{3,2}$  from TEM micrographs for the Kammler samples is also shown (filled squares). (c)  $d_{V/S}$  from USAXS versus  $d_p$  from BET for fumed zirconia samples of Mueller *et al.* (2004).



**Figure 4**

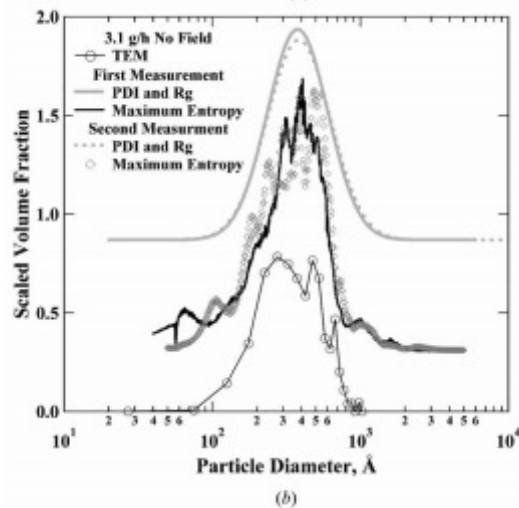
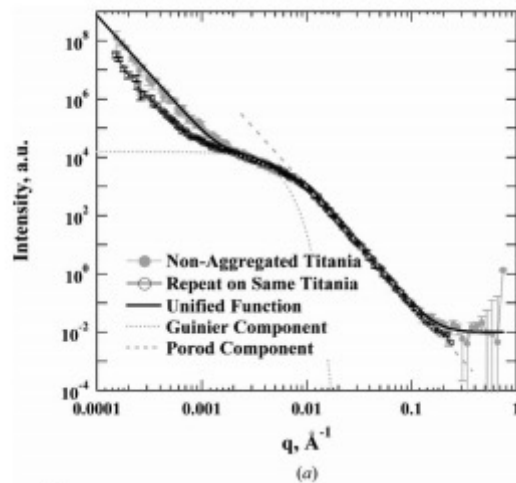
(a) Comparison of the median particle size from  $xpm$ , with  $m$  defined by equation (18), and the median particle size calculated from an analysis of TEM data on  $\text{TiO}_2$ . (b) Mean particle size,  $\langle R \rangle$  from USAXS, equation (2) with  $r = 1$ , and from TEM (Kammler *et al.*, 2003) for the same samples as Figs. 3(a) and 3(b).

[http://www.eng.uc.edu/~gbeaucag/PDFPapers/ks5024%20\[ap\]lcryst%20Beaucage%20PSD.pdf](http://www.eng.uc.edu/~gbeaucag/PDFPapers/ks5024%20[ap]lcryst%20Beaucage%20PSD.pdf)

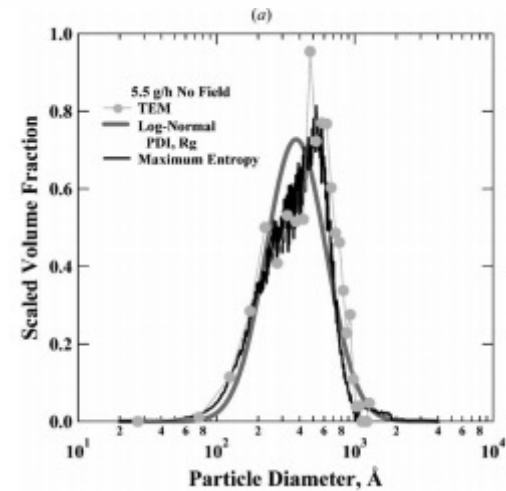


# Fractal Aggregates and Agglomerates

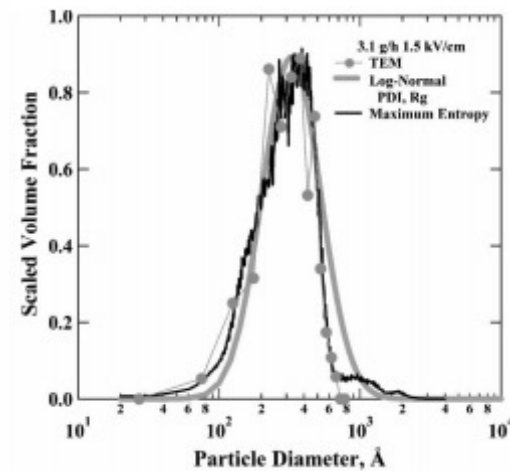
## Primary Size for Fractal Aggregates



**Figure 5**  
3.1 g h<sup>-1</sup> titania. (a) Repeat USAXS runs on a non-aggregated titania powder (Fig. 1). (b) Particle size distributions from TEM (circles; Kammler *et al.*, 2003), equations (1), (2), (17) and (18) using PDI and  $R_g$ , and using the maximum-entropy program of Jemian (Jemian *et al.*, 1991). Distribution curves are shifted vertically for clarity.  $d_{V/S} = 34.9$  nm, PDI = 14.4 ( $\sigma_g = 1.60$ ),  $R_g = 44.2$  nm.



## Fractal Aggregate Primary Particles



# **Fractal Aggregates and Agglomerates**

## **Aggregate growth**

### ***Some Issues to Consider for Aggregation/Agglomeration***

Path of Approach, Diffusive or Ballistic (Persistence of velocity for particles)

Concentration of Monomers

*persistence length of velocity compared to mean separation distance*

*Branching and structural complexity*

What happens when monomers or clusters get to a growth site:

Diffusion Limited Aggregation

Reaction Limited Aggregation

Chain Growth (Monomer-Cluster), Step Growth (Monomer-Monomer to Cluster-Cluster)  
or a Combination of Both (mass versus time plots)

Cluster-Cluster Aggregation

Monomer-Cluster Aggregation

Monomer-Monomer Aggregation

DLCA Diffusion Limited Cluster-Cluster Aggregation

RLCA Reaction Limited Cluster Aggregation

Post Growth: Internal Rearrangement/Sintering/Coalescence/Ostwald Ripening

<http://www.eng.uc.edu/~gbeaucag/Courses/Nanopowders/AggregateGrowth.pdf>

# Fractal Aggregates and Agglomerates

## Aggregate growth

Consider what might effect the dimension of a growing aggregate.

Transport Diffusion/Ballistic

Growth Early/Late (0-d point => Linear 1-d => Convoluted  
2-d => Branched 2+d)

Speed of Transport Cluster, Monomer

Shielding of Interior

Rearrangement

Sintering

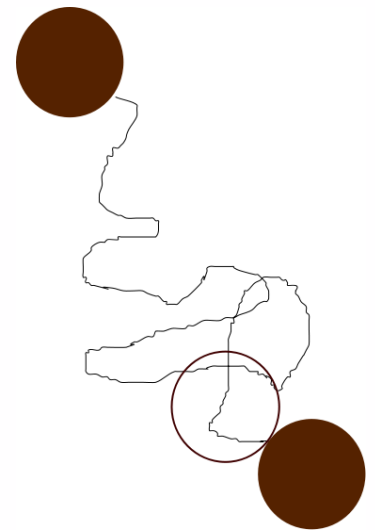
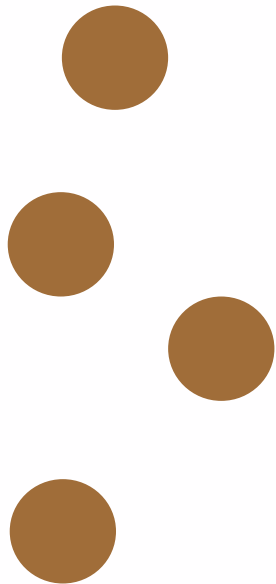
Primary Particle Shape

DLA  $df = 2.5$  Monomer-Cluster (Meakin 1980 Low  
Concentration)

DLCA  $df = 1.8$  (Higher Concentration Meakin 1985)

Ballistic Monomer-Cluster (low concentration)  $df = 3$

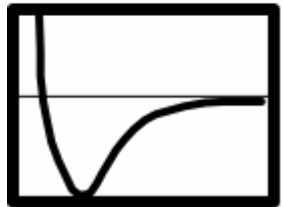
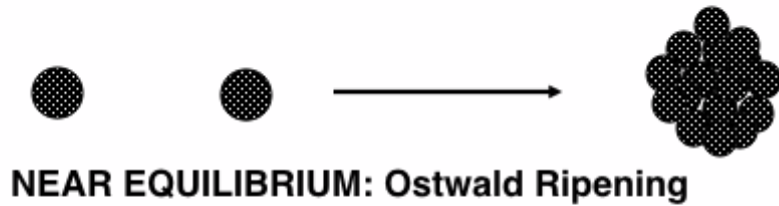
Ballistic Cluster-Cluster (high concentration)  $df = 1.95$



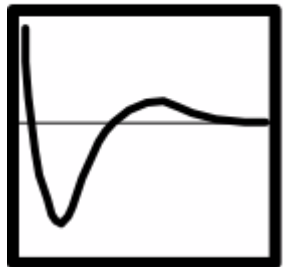
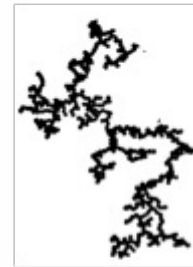
# Fractal Aggregates and Agglomerates

## Aggregate growth

### Colloids with Strongly attractive forces



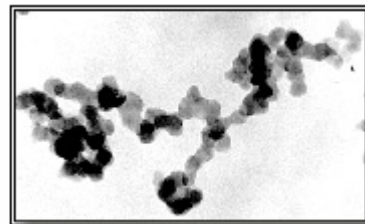
Kinetic Growth: DIFFUSION LIMITED



Kinetic Growth: CHEMICALLY LIMITED



Reaction Limited,  
Short persistence of velocity



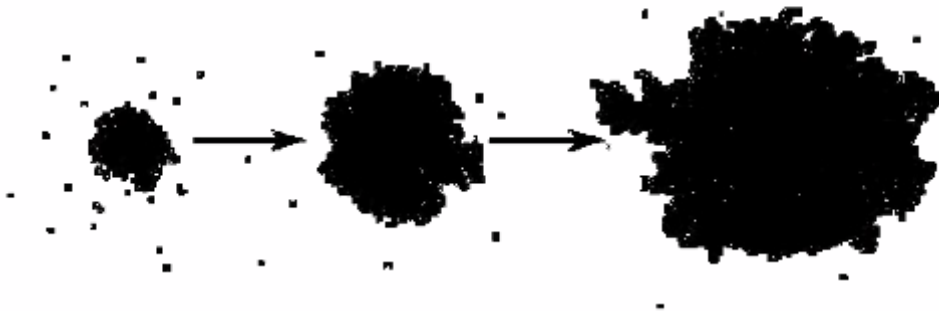
Precipitated Silica

# Fractal Aggregates and Agglomerates

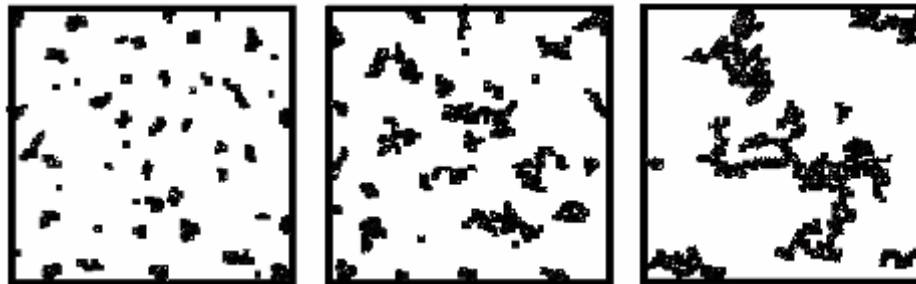
## Aggregate growth

### Sticking Law

Particle-Cluster Growth



Cluster-Cluster Growth

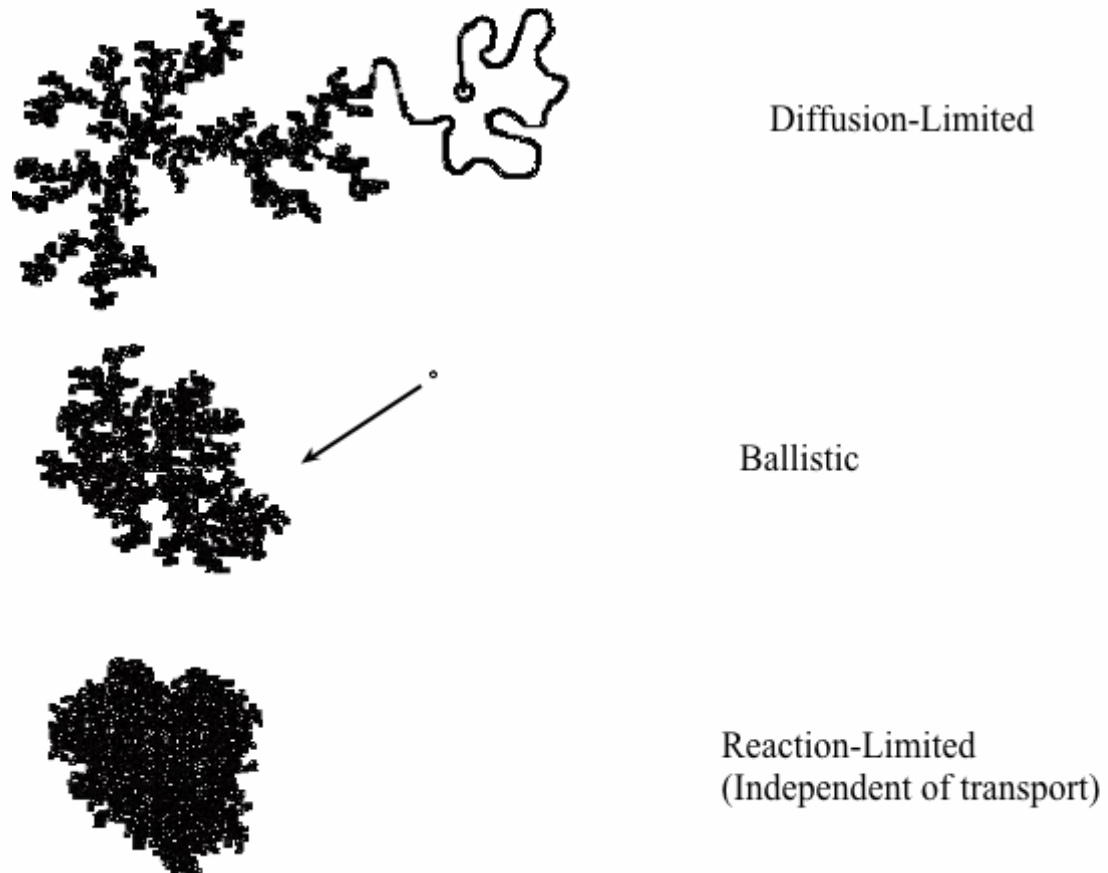


From DW Schaefer Class Notes

# Fractal Aggregates and Agglomerates

## Aggregate growth

### Transport



From DW Schaefer Class Notes

# Fractal Aggregates and Agglomerates







## Aggregate growth

### Aggregation Models

Eden Model particles are added at random with equal probability to any unoccupied site adjacent to one or more occupied sites (Surface Fractals are Produced)

Vold-Sutherland Model particles with random **linear** trajectories are added to a growing cluster of particles at the position where they first contact the cluster

Witten-Sander Model particles with random **Brownian** trajectories are added to a growing cluster of particles at the position where they first contact the cluster

		Transport		
		Reaction-Limited	Ballistic	Diffusion-Limited
Sticking Law	Monomer-Cluster	<b>EDEN</b>  $D = 3.00$	<b>VOLD</b>  $D = 3.00$	<b>WITTEN-SANDER</b>  $D = 2.50$
	Cluster-Cluster	<b>RLCA</b>  $D = 2.09$	<b>SUTHERLAND</b>  $D = 1.95$	<b>DLCA</b>  $D = 1.80$

In RLCA a “sticking probability is introduced in the random growth process of clusters. This increases the dimension.

Sutherland Model pairs of particles are assembled into randomly oriented dimers. Dimers are coupled at random to construct tetramers, then octamers etc. This is a step-growth process except that all reactions occur synchronously (monodisperse system).

In DLCA the “sticking probability is 1. Clusters follow random walk.

2

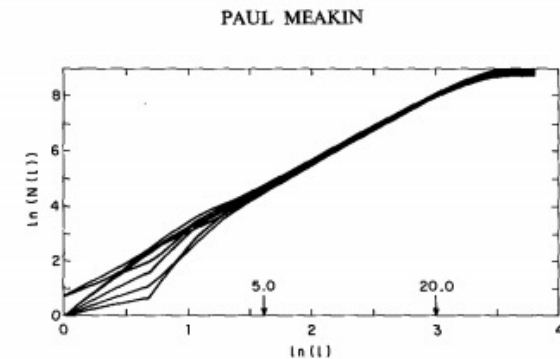


FIG. 8. Dependence of  $\ln(N(l))$  on  $\ln(l)$  for eight clusters grown using the WS model of diffusion-limited cluster formation on a three-dimensional cubic lattice.

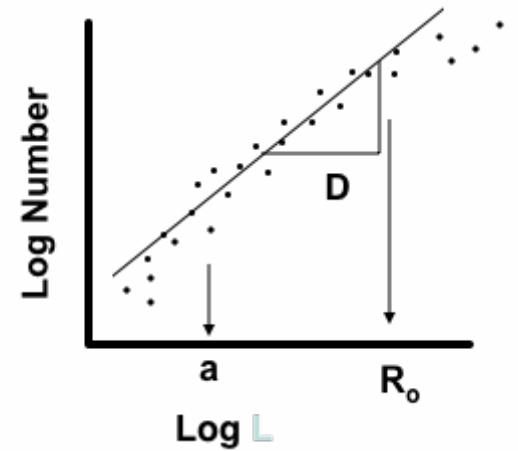
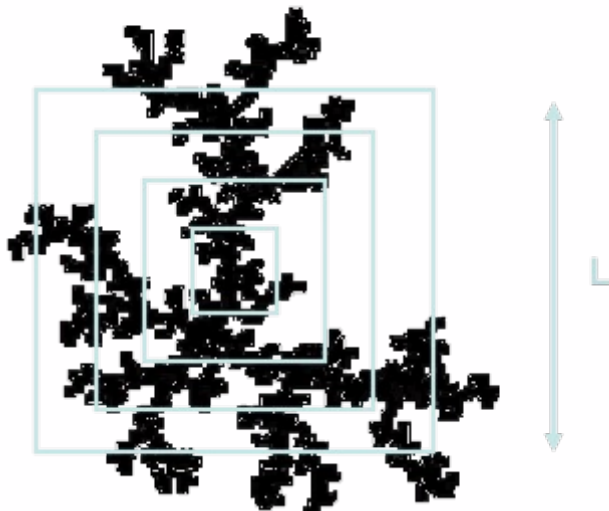
<http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/MeakinVoldSunderlandEdenWittenSanders.pdf>

# Fractal Aggregates and Agglomerates

## Aggregate growth

### Analysis of Fractals

$$\text{Log}(N) = D \text{Log}(R)$$



From DW Schaefer Class Notes

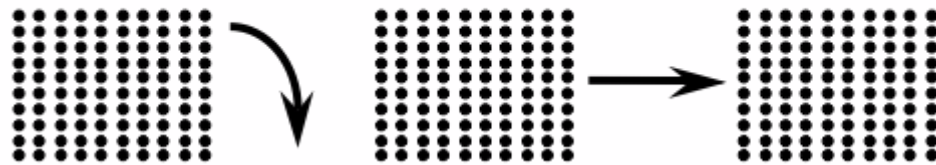


# Fractal Aggregates and Agglomerates

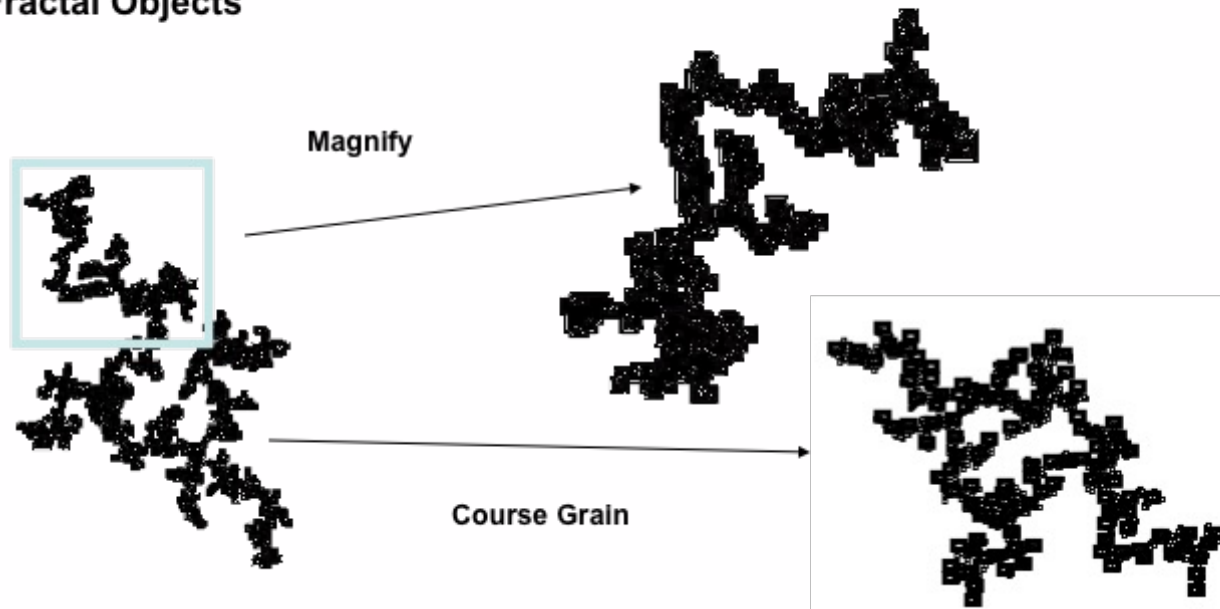
## Aggregate growth

### Self Similarity

Euclidian Objects

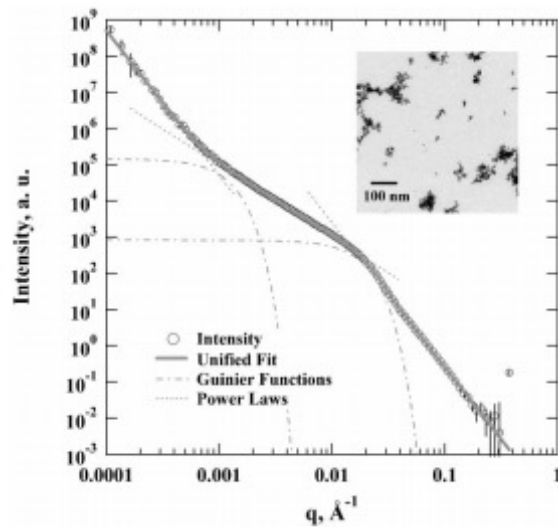


Fractal Objects

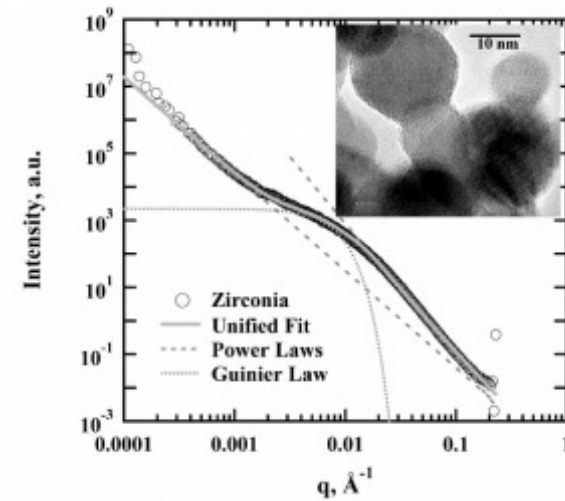


From DW Schaefer Class Notes

# Fractal Aggregates and Agglomerates



Primary: Primary Particles  
Secondary: Aggregates  
Tertiary: Agglomerates



Primary: Primary Particles  
Tertiary: Agglomerates

From DW Schaefer Class Notes

<http://www.eng.uc.edu/~gbeaucag/PDFPapers/ks5024%20applcryst%20Beaucage%20PSD.pdf>

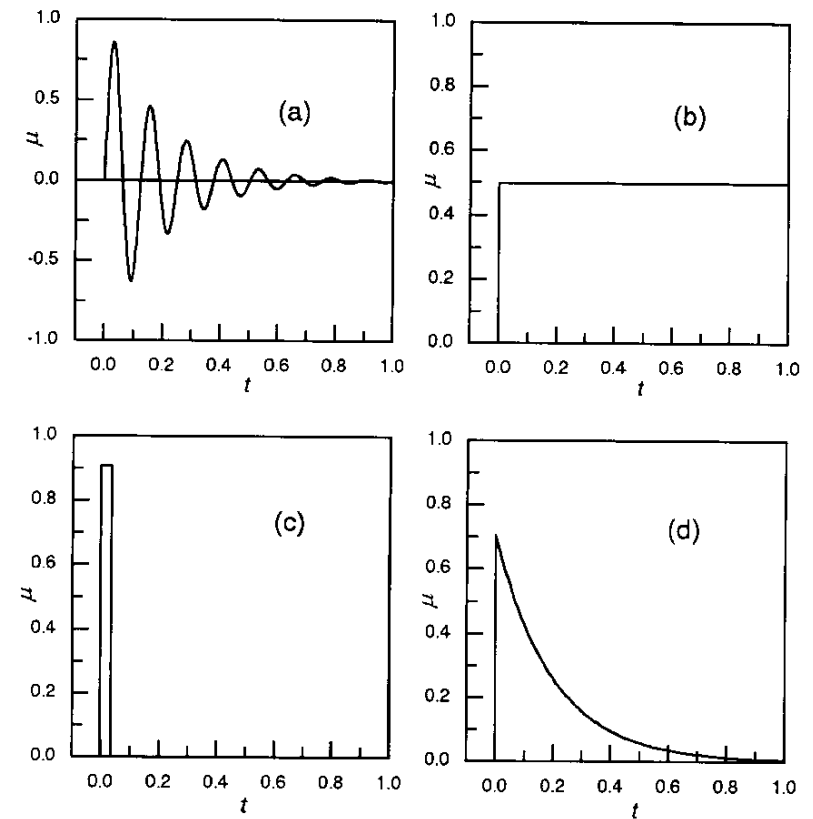
## **Hierarchy of Polymer Chain Dynamics**

# Dilute Solution Chain

## Dynamics of the chain

### 5.1 Response Functions

199



**Fig. 5.4.** Primary response function of a damped harmonic oscillator (a), a perfectly viscous body (b), a Hookean solid (c), a simple relaxatory system (d)

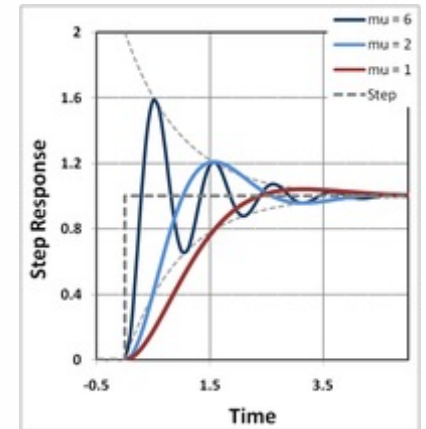
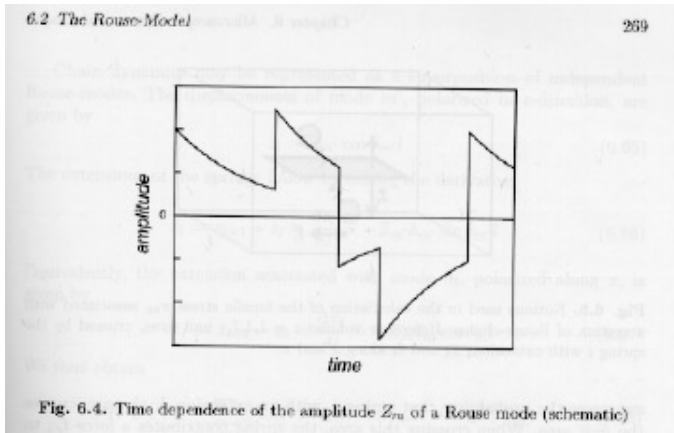
$$x(t) = \int_{-\infty}^t dt' \exp(-k_{spr}(t-t')/\xi) g(t')$$

The exponential term is the “response function”  
response to a pulse perturbation

## Dilute Solution Chain Dynamics of the chain

### Damped Harmonic Oscillator

$$x(t) = \int_{-\infty}^t dt' \exp(-k_{spr}(t-t')/\xi) g(t')$$



For Brownian motion  
of a harmonic bead in a solvent  
this response function can be used to calculate the  
time correlation function  $\langle x(t)x(0) \rangle$   
for DLS for instance

$$\langle x(t)x(0) \rangle = \int_{-\infty}^t dt_1 \int_{-\infty}^0 dt_2 \exp[-k_{spr}(t-t_1-t_2)/\xi] \langle g(t_1)g(t_2) \rangle$$

$$\langle g(t_1)g(t_2) \rangle = \frac{2kT}{\xi} \delta(t_1 - t_2)$$

$$\langle x(t)x(0) \rangle = \frac{kT}{k_{spr}} \exp(-t/\tau)$$

$\tau$  is a relaxation time.

$$\tau = \frac{\xi}{k_{spr}}$$

# Dilute Solution Chain

## Dynamics of the chain

### Rouse Motion



Beads 0 and N are special

For Beads 1 to N-1

$$E = \frac{k_{spr}}{2} \sum_{i=1}^N (R_i - R_{i-1})^2$$

$$\frac{dR_i}{dt} = \frac{-(dE/dR_i)}{\xi} + g_i(t)$$

$$\frac{dR_i}{dt} = \frac{-k_{spr}}{\xi} (R_{i+1} + R_{i-1} - 2R_i) + g_i(t)$$

For Bead 0 use  $R_{-1} = R_0$  and for bead N  $R_{N+1} = R_N$

This is called a closure relationship

$$\xi = 6\pi\eta_{solvent}a$$

## Dilute Solution Chain

### Dynamics of the chain

#### Rouse Motion



$$\frac{dR_i}{dt} = \frac{-k_{spr}}{\xi} (R_{i+1} + R_{i-1} - 2R_i) + g_i(t)$$

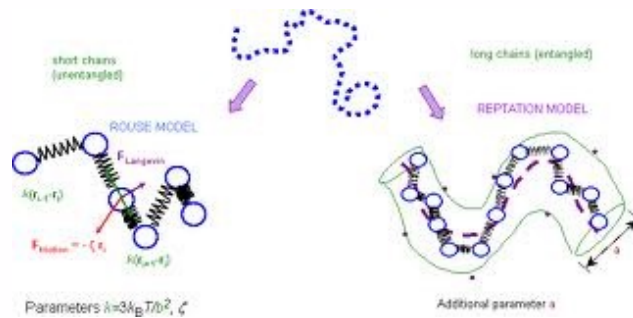
The Rouse unit size is arbitrary so we can make it very small and:

$$\frac{dR}{dt} = \frac{-k_{spr}}{\xi} \frac{d^2 R}{di^2} + g_i(t)$$

With  $dR/dt = 0$  at  $i = 0$  and  $N$

$$\frac{d^2 R}{di^2}$$

Reflects the curvature of  $R$  in  $i$ ,  
it describes modes of vibration like on a guitar string



## Dilute Solution Chain Dynamics of the chain Rouse Motion

$$\frac{d^2 R}{dt^2} \quad \text{Describes modes of vibration like on a guitar string}$$

For the “p’ th” mode (0’ th mode is the whole chain (string))

$$k_{spr,p} = \frac{2p^2 \pi^2 k_{spr}}{N} = \frac{6\pi^2 kT}{Nb^2} p^2 \quad \xi_p = 2N\xi \quad \xi_0 = N\xi$$

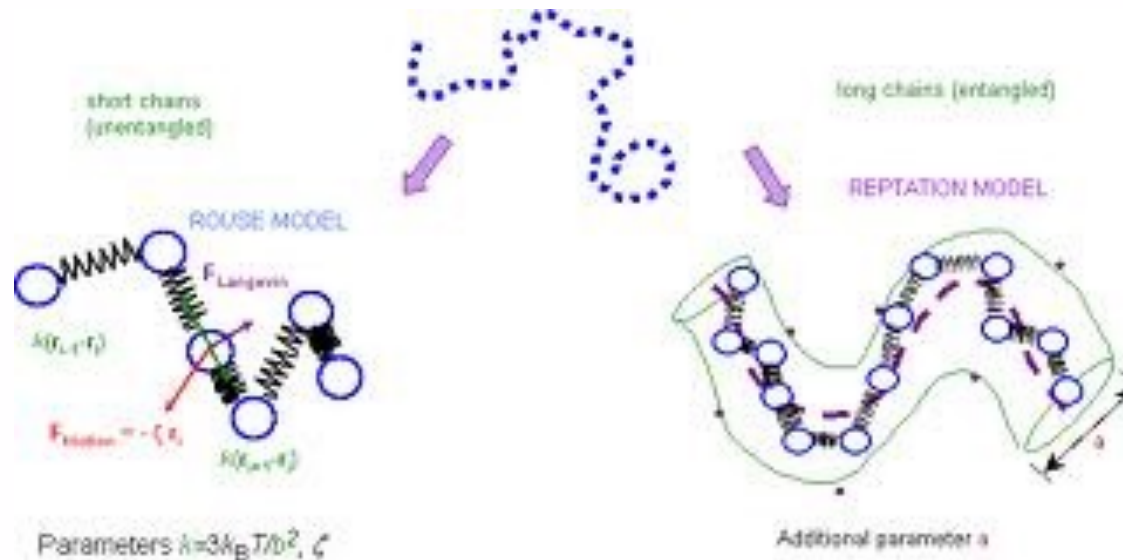
$$\tau_p = \frac{\xi_p}{k_{spr,p}} = \frac{2N^2 b^2 \xi}{3\pi^2 p^2 kT}$$



## Dilute Solution Chain

### Dynamics of the chain

#### Rouse Motion



Predicts that the viscosity will follow  $N$  which is true for low molecular weights in the melt and for fully draining polymers in solution

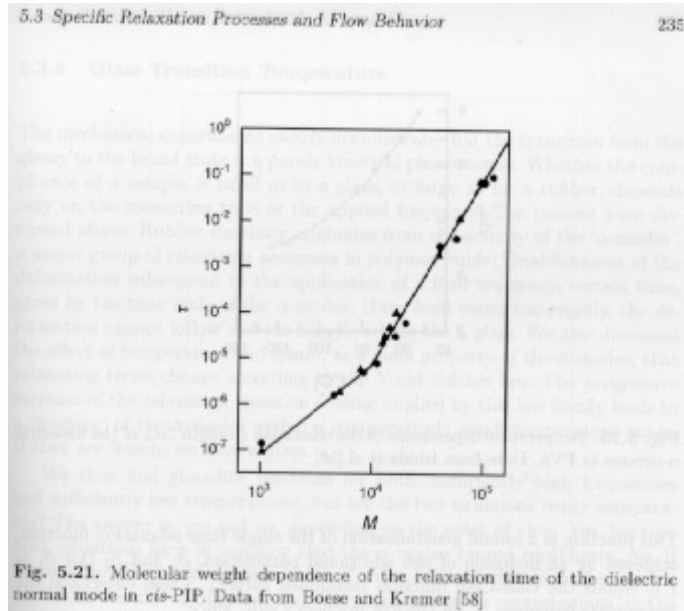
Rouse model predicts

Relaxation time follows  $N^2$  (actually follows  $N^3/df$ )

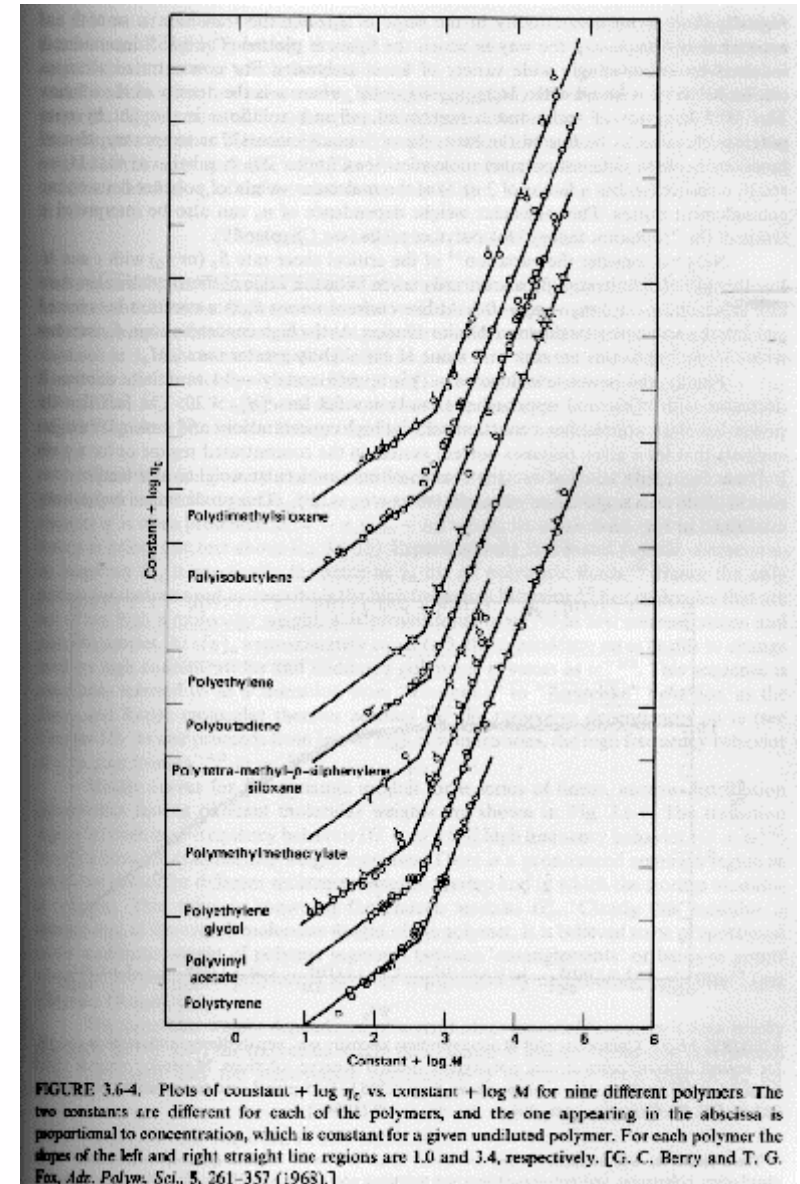
Diffusion constant follows  $1/N$  (zeroth order mode is translation of the molecule) (actually follows  $N^{-1/df}$ )

Both failings are due to hydrodynamic interactions (incomplete draining of coil)

## Dilute Solution Chain Dynamics of the chain Rouse Motion



Predicts that the viscosity will follow  $N$  which is true for low molecular weights in the melt and for fully draining polymers in solution



Rouse model predicts  
Relaxation time follows  $N^2$  (actually follows  $N^3/df$ )

## Hierarchy of Entangled Melts

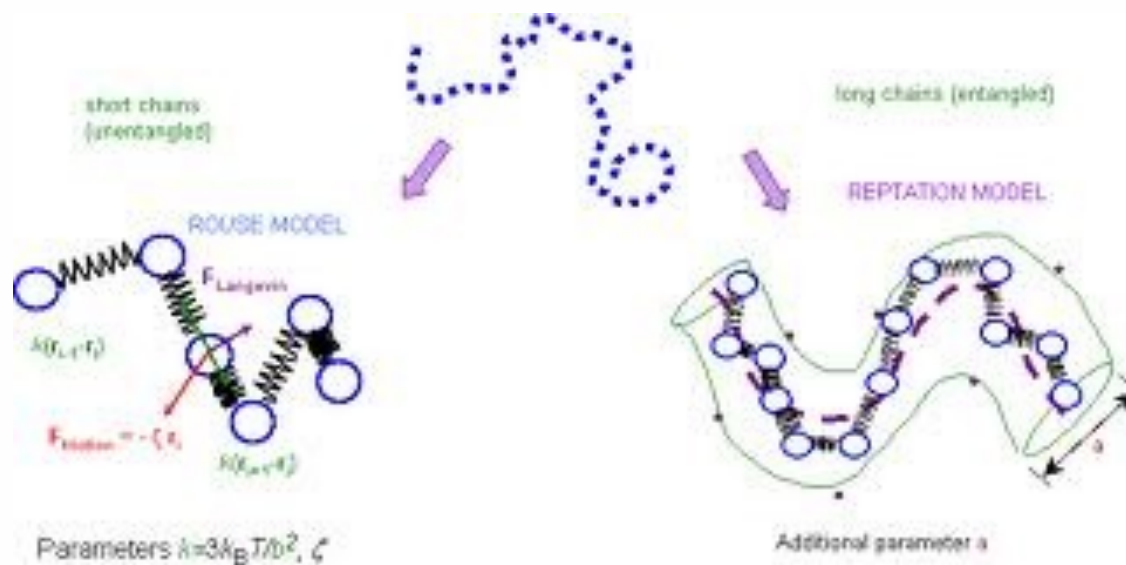
# Hierarchy of Entangled Melts

Chain dynamics in the melt can be described by a small set of “physically motivated, material-specific parameters”

Tube Diameter  $d_T$

Kuhn Length  $l_K$

Packing Length  $p$



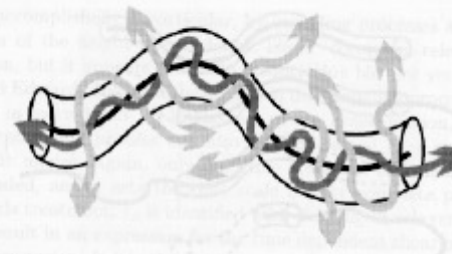


Fig. 6.10. Modelling the lateral constraints on the chain motion imposed by the entanglements by a 'tube'. The average over the rapid wriggling motion within the tube defines the 'primitive path' (continuous dark line)

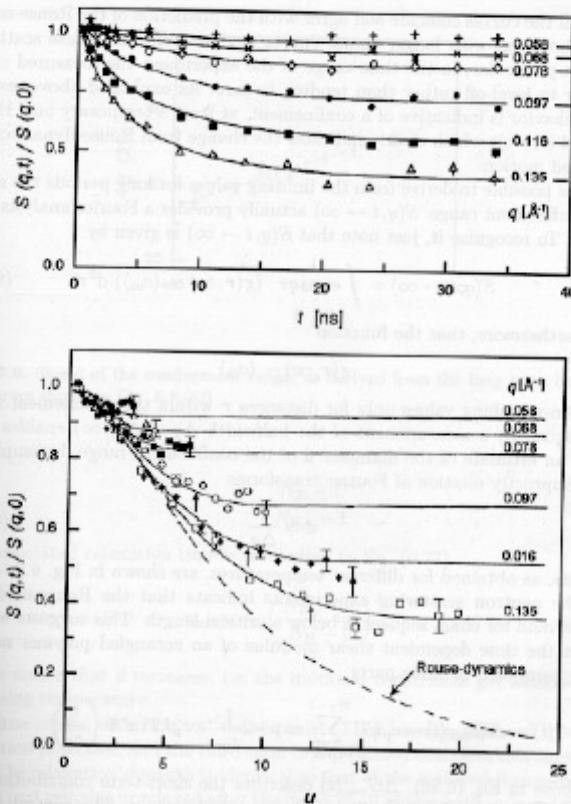


Fig. 6.8. Results of a quasielastic neutron scattering experiment on a melt of poly(ethylene-co-propylene) at 199°C (10% protonated chains dissolved in a deuterated matrix;  $M = 8.6 \cdot 10^4$ ): Intermediate scattering laws measured at the indicated scattering vectors (top); data representation using the dimensionless variable  $u = q^2(12kT a_R^2 t / \zeta_R)^{1/2}$  (bottom). From Richter et al.[67]

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

Unconstrained motion  $\Rightarrow S(q)$  goes to 0 at very long times

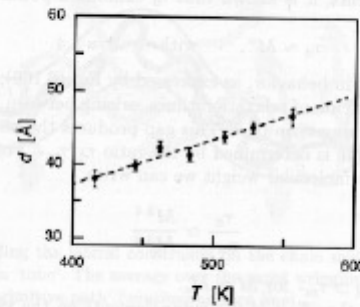
Each curve is for a different  $q = 1/\text{size}$

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

$dT$



**Fig. 6.9.** Size  $d$  of the confinement range, as derived from the long term limits of the curves shown in Fig. 6.8 [67]

There are two regimes of hierarchy in time dependence

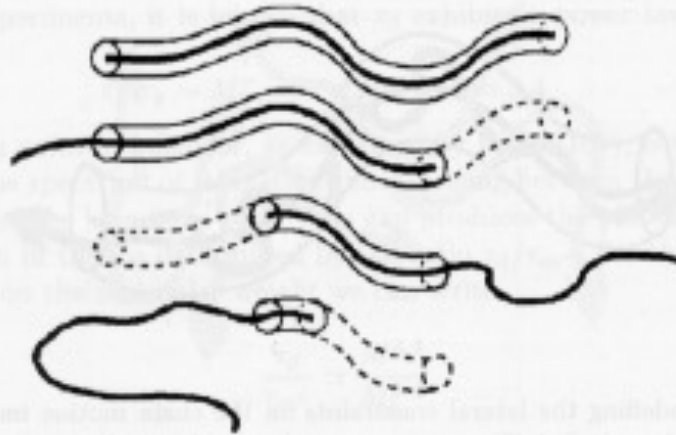
Small-scale unconstrained Rouse behavior

Large-scale tube behavior

We say that the tube follows a “primitive path”

This path can “relax” in time = Tube relaxation or Tube Renewal

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



**Fig. 6.11.** Reptation model: Decomposition of the tube resulting from a reptative motion of the primitive chain. The parts which are left empty disappear

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



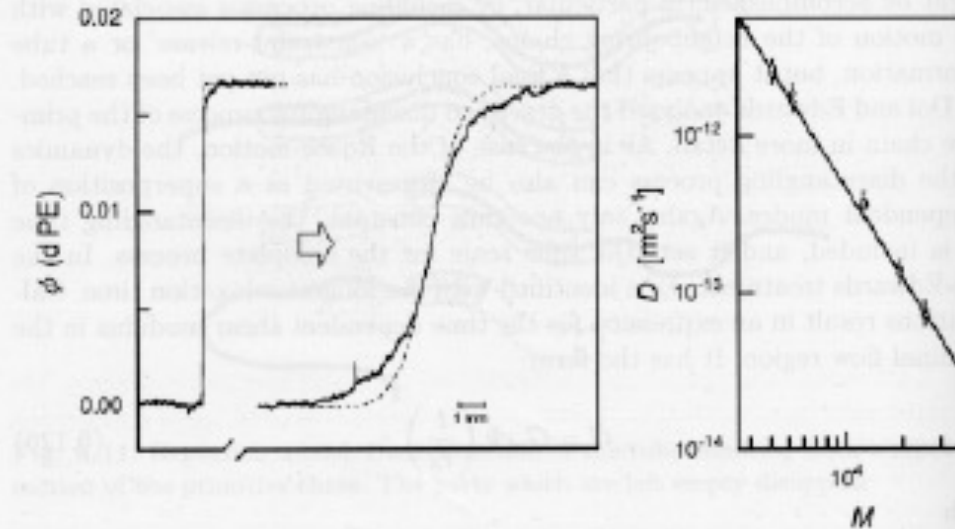


Fig. 6.12. Determination of diffusion coefficients of deuterated PE's in a PE matrix by infrared absorption measurements in a microscope. Concentration profiles  $\phi(x)$  obtained in the separated state at the begin of a diffusion run and at a later stage of diffusive mixing (the *dashed lines* were calculated for monodisperse components; the deviations are due to polydispersity) (left). Diffusion coefficients at  $T = 176^\circ\text{C}$ , derived from measurements on a series of d-PE's of different molecular weight (right). The continuous line corresponds to a power law  $D \sim M^2$ . Work of Klein [68]

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.

(Rouse Model predicts  $D \sim 1/N$ )



## Reptation of DNA in a concentrated solution

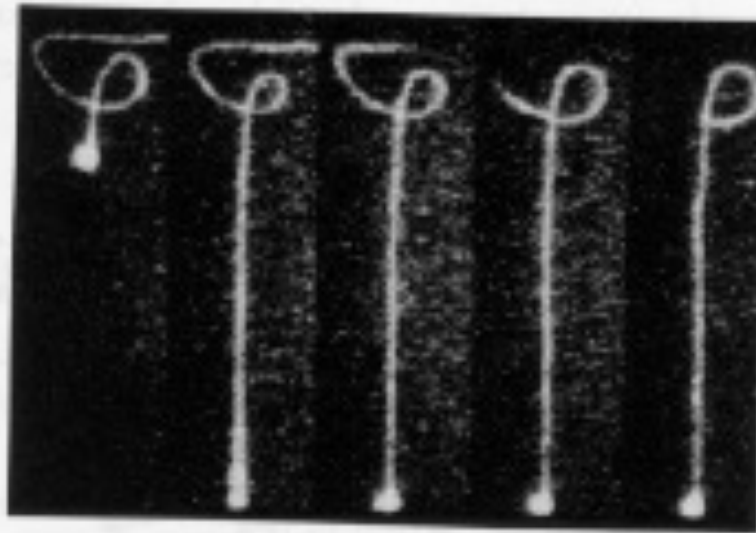
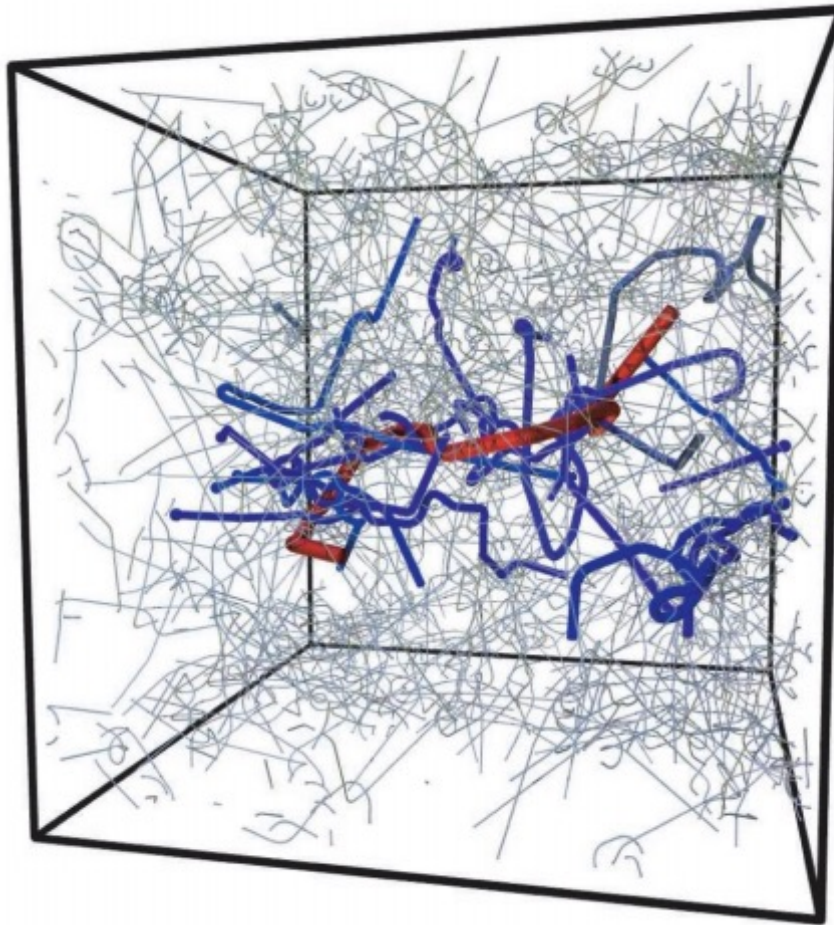


Fig. 6.13. Series of images of a fluorescently stained DNA chain embedded in a concentrated solution of unstained chains: Initial conformation (*left*); partial stretching by a rapid move of the bead at one end (*second from the left*); chain recoil by a reptative motion in the tube (*subsequent pictures 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.

Simulation of the tube

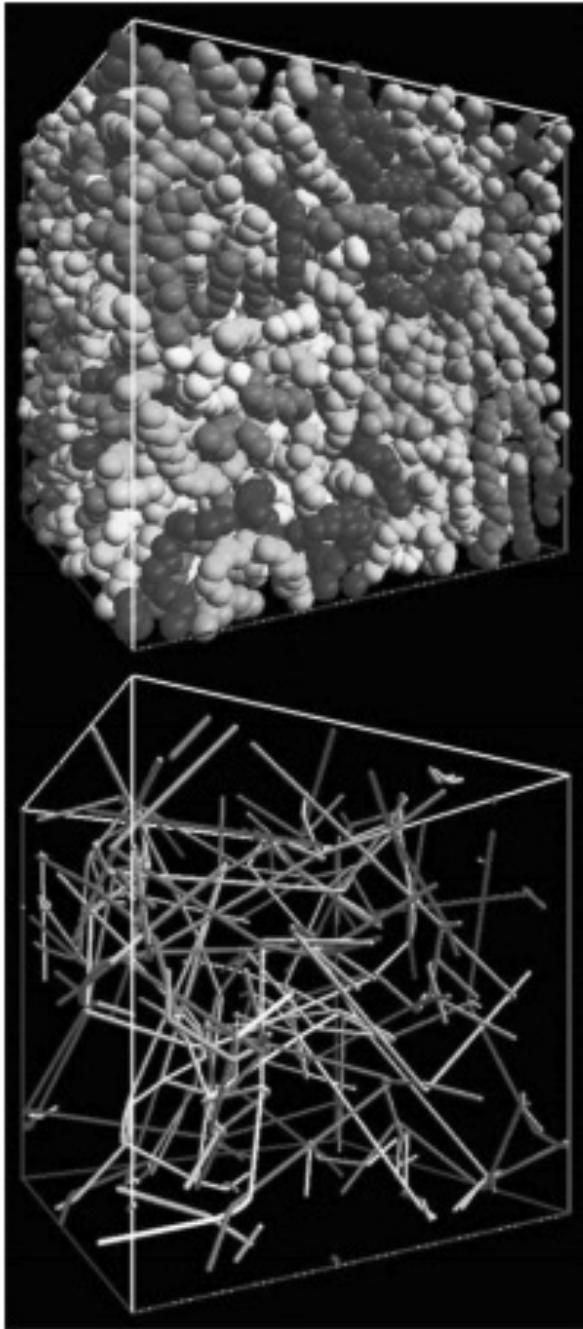
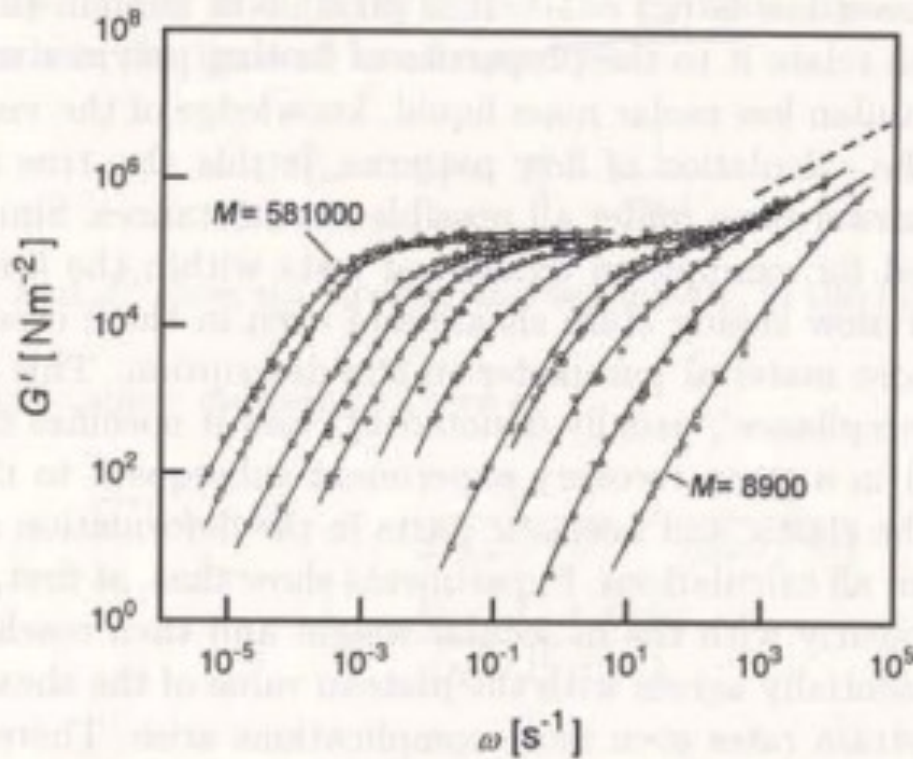


Fig. 3. A representative amorphous polymer sample and the corresponding network of primitive paths.

## Plateau Modulus

Not Dependent on N, Depends on T and concentration



**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]

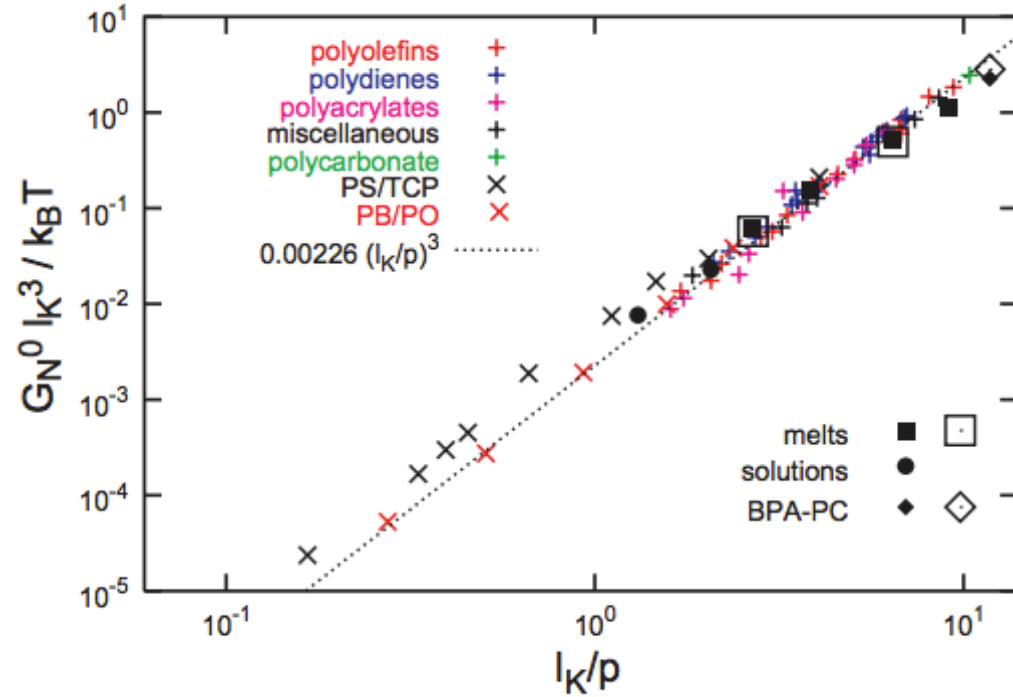
$$G_0 = \frac{4\rho RT}{5M_e} = \frac{4RT}{5p^3}$$

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

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



**Fig. 2.** Dimensionless plateau moduli  $G_N^0 l_K^3 / k_B T$  as a function of the dimensionless ratio  $l_K / \rho$  of Kuhn length  $l_K$  and packing length  $\rho$ . 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) (□) and a semi-atomistic polycarbonate melt (37) (◇) 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 (■), bead-spring semidilute solutions (●), and the semi-atomistic polycarbonate melt (◆). 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  $d\tau \sim \rho$

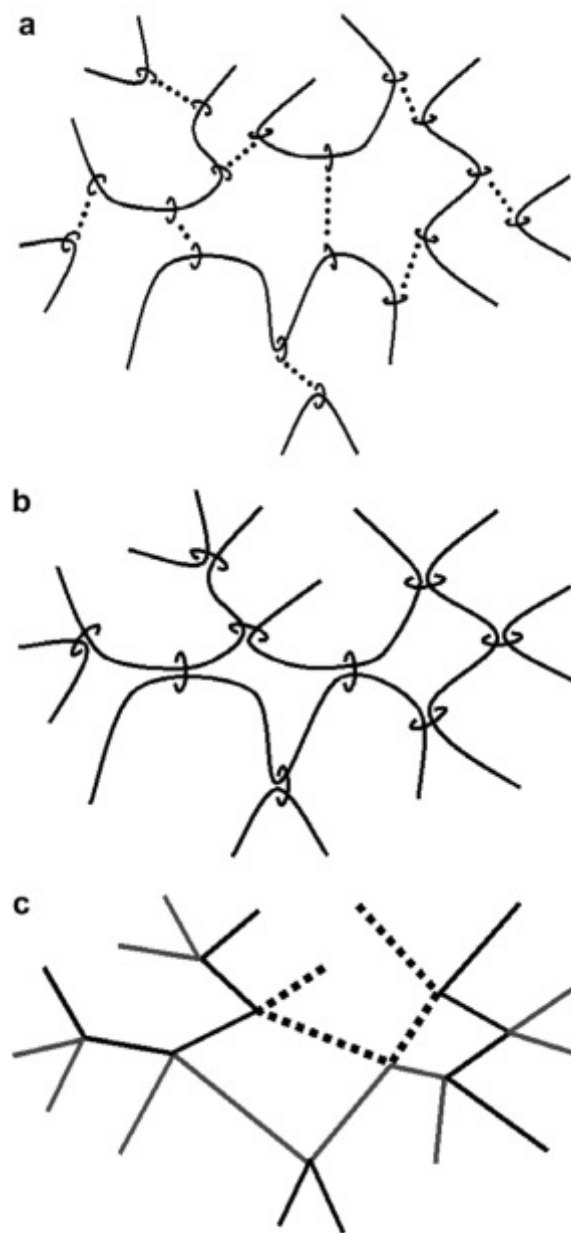


Fig. 1. Schematic representation of dual slip-links. (a) Chains coupled by virtual links. (b) Dual slip-links. (c) Real space representation of the corresponding network of primitive paths.

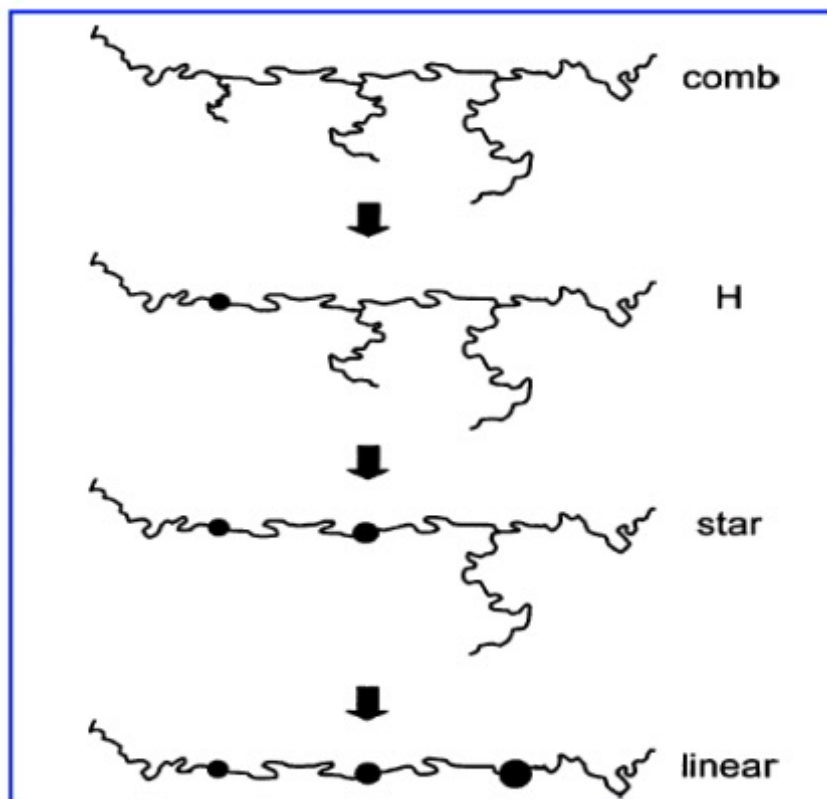








## McLeish/Milner/Read/Larsen Hierarchical Relaxation Model



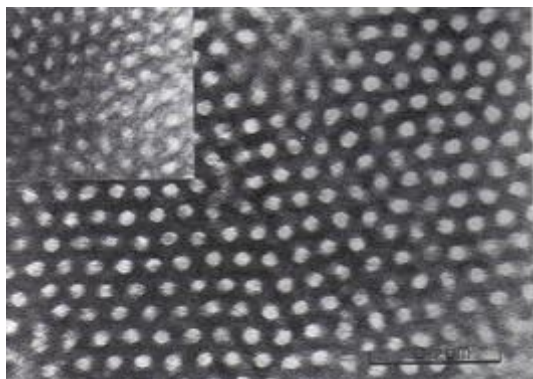
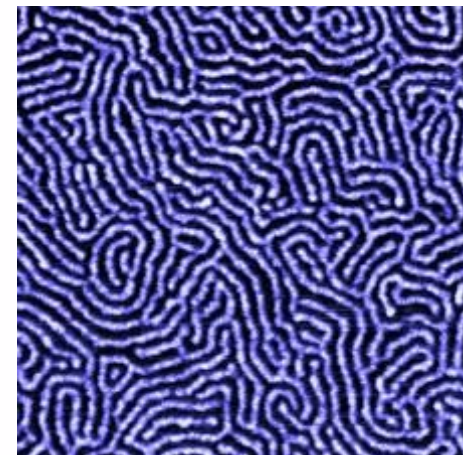
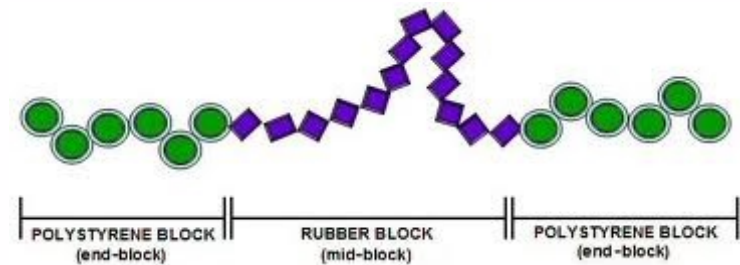
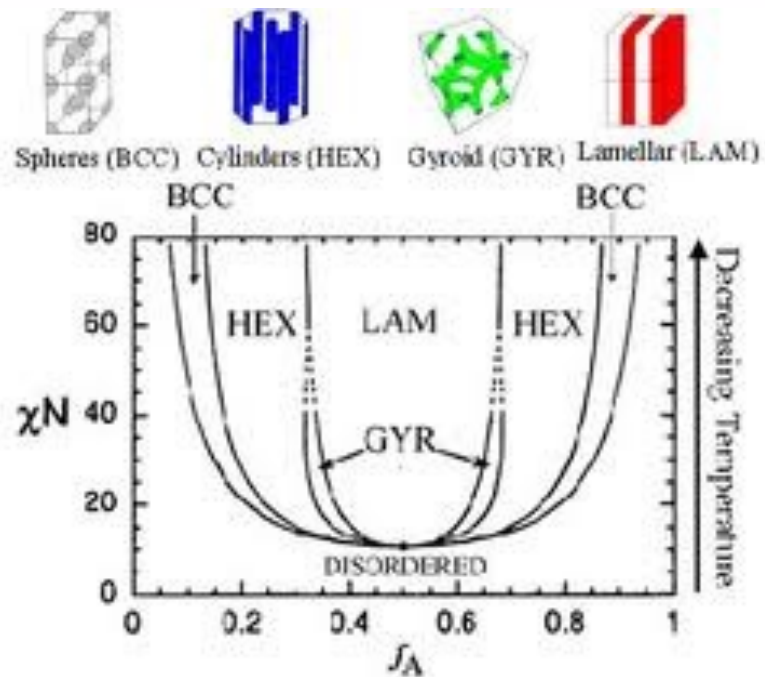
<http://www.engin.umich.edu/dept/che/research/larson/downloads/Hierarchical-3.0-manual.pdf>

## Block Copolymers

<http://www.eng.uc.edu/~gbeaucag/Courses/MorphologyofComplexMaterials/BCP%20Section.pdf>

# Block Copolymers

## SBR Rubber



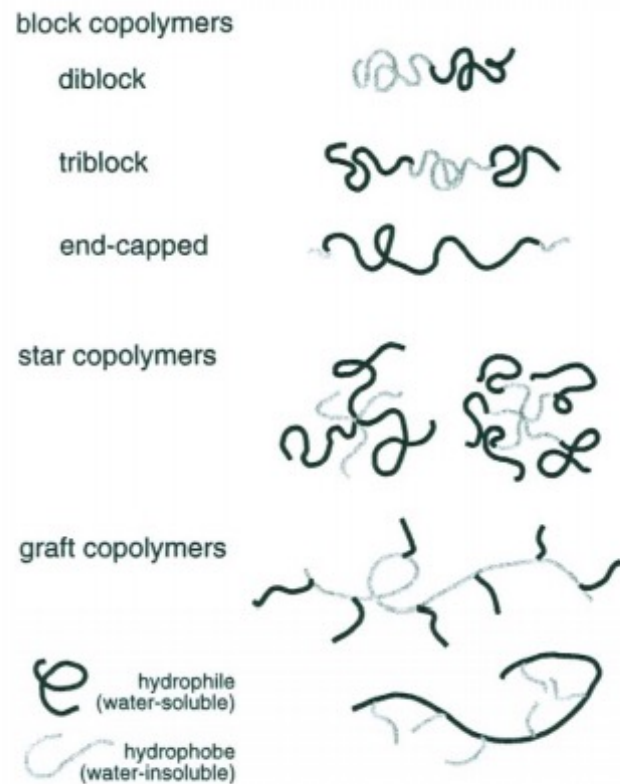
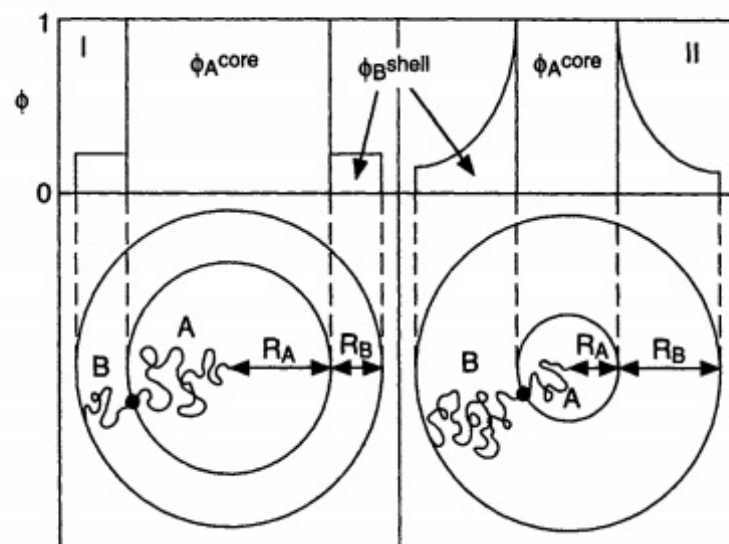
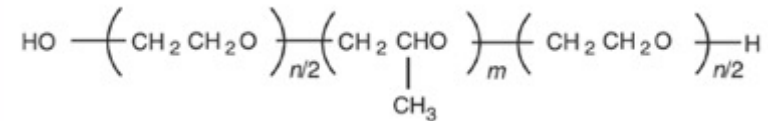


Figure 9. Schematics of block, star, and graft amphiphilic block copolymers.



*Figure 1.* Illustration of model I (left) and II (right) of the AB-diblock copolymer micelle in a selective solvent (lower panel) and the volume fraction profiles of the polymer blocks (upper panel) applied for the large core case ( $N_A \gg N_B$ ) and the small core case ( $N_A \ll N_B$ ), respectively.

## Hierarchy in BCP' s and Micellar Systems



Pluronics (PEO/PPO block copolymers)

We consider primary structure as the block nature of the polymer chain.

This is similar to hydrophobic and hydrophilic interactions in proteins.

These cause a secondary self-organization into rods/spheres/sheets.

A tertiary organization of these secondary structures occurs.

There are some similarities to proteins but BCP' s are extremely simple systems by comparison.



# What is the size of a Block Copolymer Domain?

Masao Doi, Introduction to Polymer Physics

- For and symmetric A-B block copolymer
- Consider a lamellar structure with  $\Phi = 1/2$
- Layer thickness  $D$  in a cube of edge length  $L$ , surface energy  $\sigma$
- so larger  $D$  means less surface and a lower Free Energy  $F$ .

$$F_{\text{surface}} \cong 2\sigma \frac{L}{D} L^2$$

- The polymer chain is stretched as  $D$  increases. The free energy of a stretched chain as a function of the extension length  $D$  is given by

$$- F_{\text{stretch}} \cong kT \frac{D^2}{Nb^2} \frac{L^3}{Nv_c} \text{ where } N \text{ is the degree of polymerization for A or B,}$$

$b$  is the step length per  $N$  unit,  $v_c$  is the excluded volume for a unit step  
So the stretching free energy,  $F$ , increases with  $D^2$ .

- To minimize the free energies we have 
$$D \cong \left( \frac{\sigma N^2 b^2 v_c}{kT} \right)^{1/3} \sim N^{2/3}$$



## Chain Scaling (Long-Range Interactions)

Long-range interactions are interactions of chain units separated by such a great index difference that we have no means to determine if they are from the same chain other than following the chain over great distances to determine the connectivity. That is, Orientation/continuity or polarity and other short range linking properties are completely lost.

Long-range interactions occur over short spatial distances (as do all interactions).

Consider chain scaling with no long-range interactions.

The chain is composed of a series of steps with no orientational relationship to each other.

$$\text{So } \langle R \rangle = 0$$

$\langle R^2 \rangle$  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.

$$\langle R^2 \rangle = N r^2$$