Long Range Interactions

The Secondary Structure for Synthetic Polymers Long-Range Interactions

Boltzman Probability For a Thermally Equilibrated System

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

Gaussian Probability For a Chain of End to End Distance R

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

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

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

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

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

So,

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

Flory-Krigbaum Theory Result is called a Self-Avoiding Walk $R^* \sim l_K n^{3/5}$

 $W_0(R)$ is the Gaussian probability $P(R,N)4\pi R^2 dR$ times the total number of chain conformations possible for chains of N steps, Z^N ,

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

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

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

where the second equality uses the fact that for small x, $\ln(1-x) = -x$, and that for large N, (N-1)=>N. W(R)dR for the excluded volume chain can be estimated by $W_0(R)p(R)dR$ and since both are expressed as exponentials the powers sum leading to,

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

The derivative of $W_0(R)$ will equal 0 at $R_0^* = (2Nb^2/3)^{1/2}$. This is proportional to $N^{1/2}b$ as expected. Setting the derivative of W(R) to 0 yields,

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

Rearranging and substituting R^{*}₀ yields,

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

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

$$R^* \simeq R_0^* \left(\frac{N^{\frac{1}{2}}V_C}{b^3}\right)^{\frac{1}{2}} = kN^{\frac{3}{2}}$$

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

The Secondary Structure for Synthetic Polymers

Linear Polymer Chains have Two Possible Secondary Structure States:

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

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

The Secondary Structure for Synthetic Polymers

Linear Polymer Chains have Two Possible Secondary Structure States:

Self-Avoiding Walk
Good Solvent
Expanded Coil
(The Normal Condition in Solution)

Gaussian Chain Random Walk Theta-Condition Brownian Chain (The Normal Condition in the Melt/Solid)

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

$$d_f = \frac{5}{3} \approx 1.67 \qquad \qquad d_f = 2$$

Consider going from dilute conditions, $c < c^*$, to the melt by increasing concentration.

The transition in chain size is gradual not discrete. Synthetic polymers at thermal equilibrium accommodate concentration changes through a scaling transition. Primary, Secondary, Tertiary Structures.



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

We have considered an athermal hard core potential

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

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

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

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

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

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

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

The volume fraction of monomers in the polymer coil is nV_c/R^3 And there are n monomers in the chain with a conformational state of end-to-end distance

R so,

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

We can then write the energy of the chain as,

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

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



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

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







Fig. 1.6 The coil-globule transition in a solution of polystyrene in cyclohexane. The radius of gyration R_g and the hydrodynamic radius R_h of the polymer show a dramatic change as temperature passes through the θ temperature. The hydrodynamic radius R_h is defined by $R_h = k_B T/6\pi\eta D$, where D is the diffusion constant of the polymer and η is the viscosity of the solvent. (Sun, S.T., Nishio, I., Swislow, G., and Tanaka, T. (1980). J. *Chem. Phys.*, 73, 5971, Fig.2.)

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



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



http://rkt.chem.ox.ac.uk/lectures/liqsolns/regular_solutions.html

Wilding, Müller, and Binder: Polymer-solvent critical point parameters

J. Chem. Phys., Vol. 105, No. 2, 8 July 1996



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

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

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

Wilding, Müller, and Binder: Polymer-solvent critical point parameters

J. Chem. Phys., Vol. 105, No. 2, 8 July 1996



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

J. Chem. Phys., Vol. 105, No. 2, 8 July 1996



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

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

Overlap Composition

Consider also Φ^* which is the coil composition, generally below the critical composition for normal n or N

$$\phi^* = \frac{n}{V} = \frac{n}{R^3}$$

~ $n^{-\frac{4}{5}}$ (for good solvents)
or ~ $n^{-\frac{1}{2}}$ (for theta solvents)

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

J. Chem. Phys., Vol. 105, No. 2, 8 July 1996



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

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

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

Overlap Composition

Both Φ^* and Φ_c depend on I/\sqrt{N}

Below Φ^* the composition is fixed since the coil can not be diluted!





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

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

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

Overlap Composition

Both Φ^* and Φ_c depend on I/\sqrt{N}

Below Φ^* the composition is fixed since the coil can not be diluted!

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



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

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

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

Overlap Composition

Both Φ^* and Φ_c depend on I/\sqrt{N}

Below Φ^* the composition is fixed since the coil can not be diluted!

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

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



The polymer concentration is Mass/Volume, within a chain

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

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



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



J.R. Fried Introduction to Polymer Science

$$\eta \sim c^{P}$$
$$P = 1 \text{ for } c < c^{*}$$

$$E(R) = kT \left(\frac{3R^2}{2nl^2} + \frac{n^2 V_c \left(\frac{1}{2} - \chi\right)}{R^3} \right)$$
$$\frac{\Delta G}{kTN_{cells}} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \phi_A \phi_B \chi$$

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

Lower-Critical Solution Temperature (LCST)



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

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

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

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

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

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

Lower-Critical Solution Temperature (LCST)



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



Poly vinyl methyl ether/Water PVME/PS

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

What Happens to the left of the theta temperature?



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

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

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

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

$$\alpha^2 = \frac{R^2}{R_\theta^2} = \frac{R^2}{zl^2} \tag{2}$$

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

where B is the second virial coefficient,

$$B = V_0 \left(1 - 2\chi \right) \tag{4}$$

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

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

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

The virial expansion of the enthalpic interactions is given by,

$$U(\alpha) = V_{Coil}kT \left[n^2 B + n^3 C + ... \right] \approx V_{Coil}kTn^2 B \sim \frac{kTR^3 Bz^2}{R^6} = \frac{z^{1/2} BkT}{2\alpha^3 l^3}$$
(6)

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

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



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

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

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

Small size g^* units have a lower T_c compared to large size g^* units.

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

Blob model for coil collapse



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

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

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

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

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

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

and a sum of these terms (approximation),

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

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

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

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

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

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

and a sum of these terms (approximation),

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

α is >1 for expansion <1 for contraction

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

(10).

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

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

where x is related to B and is given by,

$$x = K_1 B z^{1/2} / l^3 \tag{12}$$

and y is related to C and is given by,

 $y = K_2 C/l^6$ (13). If α is small you can neglect the terms on the left hand side of equation (11) and solve for R,

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

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

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

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

Chapter 8 Coils and Globules 134 FIGURE 8.3 1.4 The dependence $\alpha(x)$ given by equation (8.7) 1.2 for different values of y; from top to bottom, Q 0.8 the curves correspond to the following values 0.6 of v: 10, 1, 0.1, 1/60, 0.01, 0.001, 0.0001. 0.4 0.2 0 -0.8 -0.6 -0.4 -0.2 0 0.2 0.4 x 27

(11)



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

FIGURE 8.5 The curves $\alpha(x)$ in Figure 8.3 are multivalued at some x; in this figure, one solution is selected for each x such that the values of $\alpha(x)$ correspond to the absolute minimum free energy for every x. The values of y are the same as in Figure 8.3.

136



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





Figure 4. Temperature dependence of average radius of gyration ($\langle R_g \rangle$) and hydrodynamic radius ($\langle R_h \rangle$) of poly(*N*,*N*-diethylacrylamide) (PDEAM) chains in water in one heating-and-cooling cycle.



I.5 Theta
I.6 Expanded
0.774 Sphere
0.92 Draining Sphere
(We will Look at this further)

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*-diethylacry-lamide) (PDEAM) chains in water in one heating-and-cooling cycle.

Macromolecules 2008, 41, 8927-8931

The Coil-to-Globule-to-Coil Transition of Linear Polymer Chains in Dilute Aqueous Solutions: Effect of Intrachain Hydrogen Bonding

Kejin Zhou, † Yijie Lu, ‡ Junfang Li, ‡ Lei Shen, ‡ Guangzhao Zhang, $^{\bullet,\ddagger}$ Zuowei Xie, $^{\dagger,\$}$ and Chi Wu**^{\ddagger}

ABSTRACT: Our previous studies of the captioned transition have shown that thermally sensitive poly(Nisopropilary)amide) (PNIPAM) in water can form stable individual single-chain globales, but not for polystyree (PS) in cyclobe-ane. In the current study, using poly(N-A-disthylary)tamide) (PDEAM) ($M_{\rm e}=1.7\times10^{2}$ fm) and $M_{\rm e}M_{\rm A}=1.06$) with no hydrogen donator site, we intend to find whether the intrachain hydrogen bonding plays a role in shiftizing individual collapsed PNIPAM single-chain globales. We found the PDEAM can also from stable single-chain globules in water even though the transition is less sharp. The resultant individual PDEAM single-chain globules are less compact, reflecting in a lower chain density and a higher ratio of the radius of gyration to hydrodynamic radius, presumably due to the lack of intrachain hydrogen bonding. Our result also shows that, unlike PNIPAM, there is no hysteresis in the transition, indicedly supporting our previous assumption that the hysteresis observed for PNIPAM is due to the formation of some intrachain additional hydrogen bonds



FIG. 2. Temperature dependence of the average radius of gyration $\langle R_g \rangle$ and the average hydrodynamic radius $\langle R_h \rangle$, respectively, in the coil-to-globule (heating) and the globule-to-coil (cooling) processes, where each point was obtained at least 2 h after the solution reached the thermal equilibrium to ensure that the polymer chains were thermodynamically stable. The inset shows the temperature dependence of $\langle R_g \rangle / \langle R_h \rangle$ in the heating and the cooling processes.



4 May 1998

Globule-to-Coil Transition of a Single Homopolymer Chain in Solution

Chi Wu^{1,2,*} and Xiaohui Wang

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

Radius of Gyration, R_g

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

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

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

$$Z = N - 1$$

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

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

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

Radius of Gyration, R_g

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

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

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

2.45
$$R_g = R_{eted}$$

R_g is a direct measure of the end-to-end distance for a Gaussian Chain

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter I.pdf
Static Light Scattering for R_g

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

Guinier Plot linearizes this function

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

The exponential can be expanded at low-q and linearized to make a Zimm Plot

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

Guinier's Law



Zimm Plot



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

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

Concentration part will be described later

$$\frac{\phi}{S(qR_g <<1)} = \left(\frac{1}{N} + (1-2\chi)\phi\right) \left(1 + \frac{q^2R_g^2}{3}\right)$$
(6)



n_e Reflects the density of a Point generating waves

N is total number of points

The Scattering Event



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





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

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

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



-For high θ , *r* is small



-For small θ , *r* is large













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



That follows a Gaussian Distribution.

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

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



Whose Fourier Transform is Guinier's Law.

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

Static Light Scattering for Radius of Gyration

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



 $I(0) = N n_e^2$ $I(1/r) \sim N(r)n(r)^2$

Scattered Intensity is the Fourier Transform of The Binary Autocorrelation Function

$$\gamma_0(r) = 1 - \frac{S}{4V}r + \dots \qquad \text{ex}$$

$$\exp\left(\frac{-3r^2}{4R_g^2}\right) \approx 1 - \frac{3r^2}{4R_g^2} + \dots$$

$$r \Rightarrow 0$$
 then $\frac{d(\gamma_{Gaussian}(r))}{dr} \Rightarrow 0$

A particle with no surface

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

density $\rho(r)$.



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

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

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



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

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

Table 3.1. Radii of Gyration of Some	Homogeneous Bodies	
Sphere of radius R	$R_g^2 = \frac{3}{5} R^2$	
Spherical shell with radii $R_1 > R_2$	$R_g^2 = \frac{3}{5} \frac{R_1^5 - R_2^5}{R_1^3 - R_2^3}$	
Ellipse with semiaxes a and b	$R_g^2 = \frac{a^2 + b^2}{4}$	
Ellipsoid with semiaxes a, b , and c	$R_{\rm g}^2 = \frac{a^2 + b^2 + c^2}{5}$	
Prism with edges A , B , and C	$R_{\rm g}^2 = \frac{A^2 + B^2 + C^2}{12}$	
Elliptical cylinder with semiaxes a and b and height h	$R_{\rm g}^2 = \frac{a^2 + b^2}{4} + \frac{h^2}{12}$	semi akil
Hollow circular cylinder with radii $R_1 > R_2$ and height h	$R_{\rm g}^2 = \frac{R_1^2 + R_2^2}{2} + \frac{h^2}{12}$	- Junior
	- LIUN STAN	



Two possibilities for an arrow with both ends in a particle (A) Different Particles => Guinier's Law (B) Same Particle => Surface Scattering (Only near the surface is there constructive interference with no intermediate destructive vector at ½ the distance r) There is a transition between (A) and (B) near r = R_g

Debye Scattering Function for Gaussian Polymer Coil

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

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

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

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

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

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

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

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

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

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

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

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

Low-q and High-q Limits of Debye Function

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

where Q = q²Nb²/6 = q²R_g²

At high q the last term => 0
Q-1 => Q

$$g(q) => 2/Q \sim q^{-2}$$

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

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

Bracketed term $=> Q^2/2-Q^3/6+...$

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

Which is Guinier's Law

Ornstein-Zernike Function, Limits and Related Functions

The Zimm equation involves a truncated form of the Guinier Expression intended For use at extremely low- qR_g :

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

If this expression is generalized for a fixed composition and all q, R_g is no longer the size parameter and the equation is empirical (no theoretical basis) but has a form similar to the Debye Function for polymer coils:

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

This function is called the Ornstein-Zernike function and ξ is called a correlation length.

The inverse Fourier transform of this function can be solved and is given by (Benoit-Higgins *Polymers and Neutron Scattering* p. 233 1994):

$$p(r) = \frac{K}{r} \exp\left(-\frac{r}{\xi}\right)$$

This function is empirical and displays the odd (impossible) feature that the correlation function for a "random" system is not symmetric about 0, that is + and – values for r are not equivalent even though the system is random. (Compare with the normal behavior of the Guinier correlation function.)

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

Ornstein-Zernike Function, Limits and Related Functions

Debye (Exact)

Ornstein-Zernike (Empirical)

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

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

$$g(q)_{Gaussian} = \frac{2}{Q^{2}} [Q-1+\exp(-Q)]$$
where $Q = q^{2}Nb^{2}/6 = q^{2}R_{g}^{2}$

$$I(q) = \frac{G}{q^{2}\xi^{2}}$$

$$2\xi^{2} = R_{g}^{2}$$

$$I(q) = \frac{2G}{q^{2}R_{g}^{2}}$$
Low-q limit
$$I(q) \sim G\exp(-q^{2}\xi^{2})$$

$$3\xi^{2} = R_{g}^{2}$$

$$I(q) \sim G\left(1-\frac{q^{2}R_{g}^{2}}{3}\right) \sim G\exp\left(-\frac{q^{2}R_{g}^{2}}{3}\right)$$

Ornstein-Zernike Function, Limits and Related Functions

Empirical Correlation Function

Transformed Empirical Scattering Function

$$p(r) = \frac{K}{r} \exp\left(-\frac{r}{\xi}\right)$$
 Ornstein-Zernike Function $I(q) = \frac{G}{1+q^2\xi^2}$

$$p(r) = K \exp\left(-\frac{r}{\xi}\right)$$
 Debye-Bueche Function I

$$I(q) = \frac{G}{1 + q^4 \xi^4}$$

$$p(r) = \frac{K}{r} \exp\left(-\frac{r}{\xi}\right) \sin\left(\frac{2\pi r}{d}\right)$$
 Teubner-Strey Function

$$I(q) = \frac{G}{1 + q^2 c_2 + q^4 c_3}$$

 c_2 is negative to create a peak

$$p(r) = \frac{K}{r^{3-d_f}} \exp\left(-\frac{r}{\xi}\right)$$
 Sinha Fe

Sinha Function

$$I(q) = \frac{G \sin \left[(d_f - 1) \arctan (q\xi) \right]}{q\xi (1 + q^2 \xi^2)^{(d_f - 1)/2}}$$

Correlation function in all of these cases is not symmetric about 0 which is physically impossible for a random system. The resulting scattering functions can be shown to be non-physical, that is they do not follow fundamental rules of scattering. Fitting parameters have no physical meaning.

Measurement of the Hydrodynamic Radius, R_h



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

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

Kirkwood, J. Polym. Sci. 12 1 (1953).

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

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



Viscosity





Native state has the smallest volume

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

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

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

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

We can approximate (1) as:

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

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

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

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

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



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

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

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

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



Concentration Effect, c*

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

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

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

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

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



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

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

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

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



Molecular Weight Effect

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

$$[\eta] = KM^a$$

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



Viscosity

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



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

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

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

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

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



Viscosity

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

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

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

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

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

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

$$[\eta] \sim M_{Molecule}^{\frac{3}{d_f}-1}$$
Intrinsic, specific & reduced "viscosity"

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

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

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



Temperature Effect

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

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



Intrinsic, specific & reduced "viscosity"

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

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

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

We can approximate (1) as:

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

 $\frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c$

Huggins Equation

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

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

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

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

$$[\eta] = \frac{v N_A V_H}{M}$$

For a solid object with a surface v is a constant in molecular weight, depending only on shape For a symmetric object (sphere) v = 2.5 (Einstein) $[\eta] = \frac{2.5}{\rho} ml/g$

For ellipsoids v is larger than for a sphere,

$$v = \frac{J^2}{15(\ln(2J) - 3/2)}$$
 prolate
a, b, b :: a>b
$$J = a/b$$
$$v = \frac{16J}{15\tan^{-1}(J)}$$
 oblate
a, a, b :: a



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

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

Hydrodynamic volume for "bound" solvent

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

 $\begin{array}{ll} \mbox{Partial Specific Volume} & \overline{v}_2 \\ \mbox{Bound Solvent (g solvent/g polymer)} & \mathcal{\delta}_S \\ \mbox{Molar Volume of Solvent} & v_1^0 \end{array}$

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_{η} End Effect term ~ 2 ln 2 – 25/12 Yamakawa 1975

Shear Rate Dependence for Polymers



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 γ 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

$$\frac{Volume}{time} = \frac{\pi R^4 \Delta p}{8\eta l}$$
$$\Delta p = \rho g h$$
$$\dot{\gamma}_{Max} = \frac{4Volume}{\pi R^3 time}$$



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{y} and the shear stress r have a maximum at the capillary wall and are zero in the middle of the capillary

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

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 ρ_{equ} in solution than linear polymers and therefore





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

Branching and Intrinsic Viscosity

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



TIGURE 1.7 Plots of viscometric branching parameter, g_{η} , versus branch functionality, p, for the chains on a simple cubic lattice (unfilled circles), together with experimental data for star programmers in theta solvents: •, polystyrene in cyclohexane; \blacktriangle , polyisoprene in dioxane. Solid **dashed** lines represent calculated values via Eqs. (1.70) and (1.71), respectively. (Adapted **Time Shi**da et al. [2004].)

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

Polyelectrolytes and Intrinsic Viscosity



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



Fig. 5.15. Reduced viscosity η_{red} as a function of the concentration *c* for the polyelectrolyte sodium poly(styrene sulfonate) in nearly salt free aqueous solution ($c_{\text{NaCl}}=4\times10^{-6} \text{ mol } \text{l}^{-1}$) and for different molar masses. The concentration is plotted on a logarithmic scale to show the maximum behavior of the viscosity at very low concentrations of the polyelectrolyte. Data from [83, 97]

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



Polyelectrolytes and Intrinsic Viscosity

RE1.16 Determination of the chain overlap concentration c^* , the entanglement concentration c_* , the electrostatic blob overlap concentration c^{**} from the concentration dependence **concentration** is a 17%-quaternized P2VP copolymer (17PMVP-Cl) in solution in ethy**concentration** at 25°C. Symbols are experimental data and solid lines represent the power laws **concentration** from scaling theory. (Adapted from Dou and Colby [2006].)

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

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/ HydrodyamicRadius.pdf

Consider motion of molecules or nanoparticles in solution

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

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

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 l(q,t)

This fluctuation is related to the diffusion of the particles

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



 $a = R_H = Hydrodynamic Radius$

The radius of an equivalent sphere following Stokes' Law

Dynamic Light Scattering

my DLS web page

http://www.eng.uc.edu/~gbeaucag/Classes/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

Wiki Einstein Stokes

http://webcache.googleusercontent.com/search?q=cache:yZDPRbgZ1BIJ:en.wikipedia.org/wiki/Einstein relation (kinetic theory)+&cd=1&hl=en&ct=clnk&gl=us

Diffusing Wave Spectroscopy (DWS)

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

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

Static Scattering for Fractal Scaling



At intermediate sizes the chain is "self-similar"



At intermediate sizes the chain is "self-similar"

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

N = Number of Intermediate Spheres in the Aggregate



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

 n_e = Mass of inter. sphere $Nn_e^2 \sim \left(\frac{r_{int}}{R_1}\right)$

$$\frac{d}{d_1} \int_{-1}^{d_f} \left(\frac{R_2}{R_1}\right)^{d_f} \quad \Rightarrow \quad I(q) \sim \left(\frac{R_2}{R_1^2}\right)^{d_f} q^{-d_f}$$

The Debye Scattering Function for a Polymer Coil



The Debye Scattering Function for a Polymer Coil



Ornstein-Zernike Equation

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

 \sim

Has the correct functionality at high q Debye Scattering Function =>

$$I(q) = \frac{2}{q^2 R_g^2} \left(q^2 R_g^2 - 1 + \exp(-q^2 R_g^2) \right) \qquad \qquad I(q \Longrightarrow) = \frac{2G}{q^2 R_g^2}$$

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

Ornstein-Zernike Equation

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

Has the correct functionality at low q Debye =>

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

$$R_g^2 = 3\zeta^2$$

The relatoinship 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





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

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 ξ

anchor-distance

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

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 $c^* \sim 1/[\eta]$

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

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

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

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

What is the value of ξ ?

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

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

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

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

Coil Size in terms of the concentration

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

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

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, ξ_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, $d_f = 2$.



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

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

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





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

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

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

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

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

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

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

By equating these:

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





Fig. 4: Transmission electron micrographs of silica nanoparticles at production rates of 150 (top row) and 300 g/h (bottom row) using 12.5 Umin air (a,b) or O₂ as dispersion gas without (c,d) and with (e,f) additional 25 Umin of O₂ sheath flow using 1.26 M HMDSO in EtOH.

Fractal Aggregates and Agglomerates



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.



Polymer Chains are Mass-Fractals

$R_{RMS} = n^{1/2} I$ Mass	~ Size ²	
----------------------------	---------------------	--

- 3-d object Mass ~ Size³
- 2-d object Mass ~ Size²
- I-d object Mass ~ Size¹

d_f-object

Mass ~ Size^{df}

~. d.

This leads to odd properties:

density
$$\rho = \frac{Mass}{Volume} = \frac{Mass}{Size^3} = \frac{Size^{a_f}}{Size^3} \sim Size^{d_f - 3}$$

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



Disk



$$d_f = 2$$

 $d_{\min} = 1$
 $c = 2$

Extended β-sheet (misfolded protein)

Random Coil



Unfolded Gaussian chain





Primary Size for Fractal Aggregates

Primary Size for Fractal Aggregates

- -Particle counting from TEM
- -Gas adsorption V/S => d_p
- -Static Scattering Rg, dp
- -Dynamic Light Scattering



Figure 2. TEM picture of titania (TiO₂) 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

Primary Size for Fractal Aggregates

- -Particle counting from TEM
- -Gas adsorption V/S => d_p
- -Static Scattering Rg, dp
- -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 $g_1(q, \tau)$

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



 $a = R_H = Hydrodynamic Radius$

Dynamic Light Scattering

my DLS web page

http://www.eng.uc.edu/~gbeaucag/Classes/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

Wiki Einstein Stokes

http://webcache.googleusercontent.com/search?q=cache:yZDPRbgZ1BIJ:en.wikipedia.org/wiki/Einstein relation (kinetic theory)+&cd=1&hl=en&ct=clnk&gl=us

Gas Adsorption

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

 $A + S \leq AS$



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





http://www.chem.ufl.edu/~itl/4411L_f00/ads/ads_1.html

Gas Adsorption

Multilayer adsorption



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



http://www.chem.ufl.edu/~itl/4411L_f00/ads/ads_1.html







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



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

http://www.eng.uc.edu/~gbeaucag/Classes/Nanopowders/GasAdsorptionReviews/ReviewofGasAdsorptionGOodOne.pdf

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 π R², V = 4/3 π R³

So $d_p = 6V/S$

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

Log-Normal Distribution

$$f(R) = \frac{1}{R\sigma(2\pi)^{1/2}} \exp\left\{-\frac{\left[\log(R/m)\right]^2}{2\sigma^2}\right\},\$$
$$\left\langle R^r \right\rangle = m^r \exp\left(r^2\sigma^2/2\right) = \exp\left(r\mu + r^2\sigma^2/2\right),\$$
$$\left\langle R \right\rangle = m \exp\left(\sigma^2/2\right),\$$
Mean
$$\sigma_g = \exp(\sigma) \qquad \mathbf{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%20JappIcryst%20Beaucage%20PSD.pdf

Log-Normal Distribution

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

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

Geometric standard deviation and geometric mean (median)

Static Scattering Determination of Log Normal Parameters

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

and

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

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



Primary Size for Fractal Aggregates

- -Particle counting from TEM
- -Gas adsorption V/S => 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. $d_{V/S} = 16.7$ nm (corrected to 18.0 nm), PDI = 3.01 ($\sigma_g = 1.35$), $R_g = 11.2$ nm, $d_t = 1.99$, $z_{2:1} = 175$, $z_{R_g} = 226$, $R_{g2} = 171$ nm. From gas adsorption, $d_p = 16.2$ 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. $d_{V/S} = 20.3$ nm, PDI = 10.8 ($\sigma_g = 1.56$), $R_g = 26.5$ nm, $d_t = 2.90$. From gas adsorption, $d_p = 19.7$ nm.

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

Primary Size for Fractal Aggregates



Particle counting from TEM Gas adsorption V/S => d_p Static Scattering R_g, d_p



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 m² 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, singlegrain 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 exp m, with m defined by equation (18), and the median particle size calculated from an analysis of TEM data on TiO₂. (b) Mean particle size, (R) 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).

(a)

0

0

10

20

30

d_{1.0} (TEM), nm (b)

(0)

40

50





Figure 5

3.1 g h⁻¹ 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. $d_{VS} = 34.9$ nm, PDI = 14.4 ($\sigma_g = 1.60$), $R_g = 44.2$ nm.



Fractal Aggregate Primary Particles



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

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

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

Aggregate growth

Colloids with Strongly attractive forces





NEAR EQUILIBRIUM: Ostwald Ripening

Kinetic Growth: DIFFUSION LIMITED





Kinetic Growth: CHEMICALLY LIMITED



Reaction Limited, Short persistence of velocity



Precipitated Silica

Aggregate growth

Sticking Law

Particle-Cluster Growth



Cluster-Cluster Growth



Aggregate growth

Transport



Diffusion-Limited

Ballistic

Reaction-Limited (Independent of transport)

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)

2

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



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

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



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 octoamers etc. This is a stepgrowth process except that all reactions occur synchronously (monodisperse system).

In DLCA the "sticking probability is I. Clusters follow random walk.

Aggregate growth

Analysis of Fractals

Log(N) = D Log(R)



Aggregate growth

Self Similarity









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%20Japplcryst%20Beaucage%20PSD.pdf

Hierarchy of Polymer Chain Dynamics

Dilute Solution Chain Dynamics of the chain

5.1 Response Functions



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)

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

The exponential term is the "response function" response to a pulse perturbation

Dilute Solution Chain

Dynamics of the chain



Damped Harmonic Oscillator

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



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

$$\langle x(t)x(0)\rangle = \int_{-\infty}^{t} dt_1 \int_{-\infty}^{0} dt_2 \exp\left[-k_{spr}\left(t-t_1-t_2\right)/\xi\right] \langle g(t_1)g(t_2)\rangle$$
$$\langle g(t_1)g(t_2)\rangle = \frac{2kT}{\xi} \partial(t_1-t_2)$$

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

au is a relaxation time.

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



$$E = \frac{k_{spr}}{2} \sum_{i=1}^{N} (R_i - R_{i-1})^2$$
$$\frac{dR_i}{dt} = \frac{-(dE/dR_i)}{\xi} + g_i(t)$$

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

Beads 0 and N are special

For Beads I to N-I

$$\frac{dR_{i}}{dt} = \frac{-k_{spr}}{\xi} \left(R_{i+1} + R_{i-1} - 2R_{i} \right) + g_{i}(t)$$

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

This is called a closure relationship
Dilute Solution Chain

Dynamics of the chain



$$\frac{dR_{i}}{dt} = \frac{-k_{spr}}{\xi} \left(R_{i+1} + R_{i-1} - 2R_{i} \right) + g_{i}(t)$$

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

$$\frac{dR}{dt} = \frac{-k_{spr}}{\xi} \frac{d^2 R}{di^2} + g_i(t) \qquad \text{With } dR/dt = 0 \text{ at } i = 0 \text{ and } N$$

$$\frac{d^2 R}{di^2} \qquad \text{Reflects the curvature of R in i,}$$
it describes modes of vibration like on a guitar string



Dilute Solution Chain Dynamics of the chain Rouse Motion

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

For the "p' th" mode (0' th mode is the whole chain (string))

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

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



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 N² (actually follows N³/df) Diffusion constant follows I/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



FIGURE 3.6-4. Plots of constant + log η_c vs constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proparticular to concentration, which is constant for a given undiluted polymer. For each polymer the dopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. For, Adz. Polym. Sci., 5, 261–357 (1968).]

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 paramters"

Tube Diameter d⊤ Kuhn Length I_K Packing Length p



http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/SukumaranScience.pdf



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 $u = q^2(12kTa_R^2t/\zeta_R)^{1/2}$ (*bottom*). From Richter et al.[67]



entanglements by a 'tube'. The average over the rapid wriggling motion within the tube defines the 'primitive path' (continuous dark line)

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

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

Each curve is for a different q = 1/size

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

At large sizes there is substantial constraint (the tube)

By extrapolation to high times a size for the tube can be obtained d_{T}



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 $N^{3.4}$)



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



Reptation predicts that the diffusion coefficient will follow N² (Experimentally it follows N²) Reptation has some experimental verification Where it is not verified we understand that tube renewal is the main issue.

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

Reptation of DNA in a concentrated solution



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

Simulation of the tube



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



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

Simulation of the tube

Plateau Modulus





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]

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

Packing Length- length were polymers interpenetrate $p = 1/(\rho_{chain} < R^2 >)$ where ρ_{chain} is the number density of monomers Fig. 2. Dimensionless plateau moduli Gl $k/k_{\rm p}T$ as a function of the dimensionless ratio I_{κ}/p of Kuhn length l_{κ} and packing length p. The figure contains (i) experimentally measured plateau moduli for polymer melts (25) (+; colors mark different groups of polymers as indicated) and semidilute solutions (26-28) (×); (ii) plateau moduli inferred from the normal tensions measured in computer simulation of bead-spring melts (35, 36) (1) and a semi-



atomistic polycarbonate melt (37) (\diamond) under an elongational strain; and (iii) predictions of the tube model Eq. 1 based on the results of our primitive-path analysis for bead-spring melts (**■**), 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 $d_T \sim p$



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.



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

Block Copolymers

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

Block Copolymers

SBR Rubber













Figure I. 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 $(N_A >> N_B)$ and the small core case $(N_A << N_B)$, respectively.

http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/BCP%20Modeling.pdf

Hierarchy in BCP's and Micellar Systems

$$HO - \left(CH_2 CH_2 O \right)_{n/2} \left(CH_2 CH_0 \right)_m \left(CH_2 CH_2 O \right)_{n/2} H$$

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 σ

so larger D means less surface and a lower Free Energy F. $F_{surface} \cong 2\sigma \frac{L}{D}L^2$

-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

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

b is the step length per N unit, ν c is the excluded volume for a unit step So the stretching free energy, F, increases with D².

-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.

So < R > = 0

<R²> has a value:

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

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

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