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

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

Force

Force

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

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

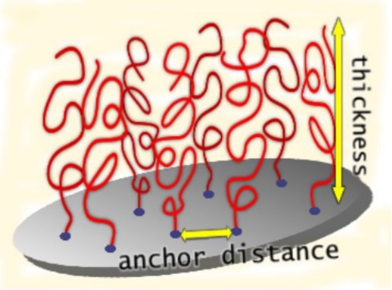
Tensile Blob

For **Larger *External* 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



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

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

Force * Distance = Energy = 3kT = F ξ_{Tensile}

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

For large perturbations of the chain $\xi_{Tensile} = \frac{3kT}{F}$

Application of an external stress to the ends of a chain create a transition size where the coil goes from Gaussian to Linear called the Tensile Blob.

Because the mechanical response of a polymer chain depends on its size or mass, n

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

$$k_{spr} = \frac{3kT}{nl_K^2}$$

Mechanical deformation leads to a transition size scale, ζ

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

For sizes smaller than ζ the structure is not perturbed.

External Force

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

For sizes smaller than ζ the structure is not perturbed.

Both lead to a size scale for transition

Internal Force

Similar to the Bjerrum Length, l_B

$$\frac{e^2}{4\pi\varepsilon l_B} = k_B T \Rightarrow l_B = \frac{e^2}{4\pi\varepsilon k_B T}$$

For sizes larger you find mean field behavior => SAW (not directional Mean Field)
Below you find charges impact structure => Rod (directional)

Or the Debye Screening Length, r_D

$$r_D = \left(\frac{\varepsilon kT}{4\pi n e^2}\right)^{1/2}$$

$$r_D^2 = \frac{V_{per\ charge} kT}{4\pi r U(r)_{with\ r_D = \infty}}$$

$$U(r) = \frac{e^2}{\varepsilon r}\exp\left(-\frac{r}{r_D}\right)$$

For sizes larger there is no charge => Gaussian (not directional)
Below you find charges impact structure => SAW (Mean Field or Rod (directional)

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

Thermal (thermic) blob (de Gennes),
Concentration blob (Edwards), and
Tensile (tension) blob (Pincus)

Mechanical deformation leads to a transition size scale, ζ

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

For sizes smaller than ξ the structure is not perturbed.

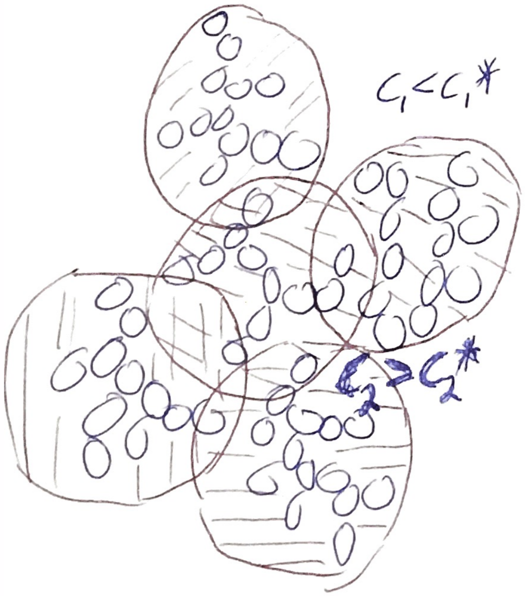
Hierarchical Symmetry of Blob Structures

Blob Type	Mass Fractal	Dimension	
	Large Scale	Small Scale	
Tensile	1	2	External Force
Thermal	5/3	2	Internal Collapse
Concentration	2	5/3	External Collapse
Kuhn	2	1	Internal Force
Collapsed Coil	2	3	Internal Collapse

Particle Models

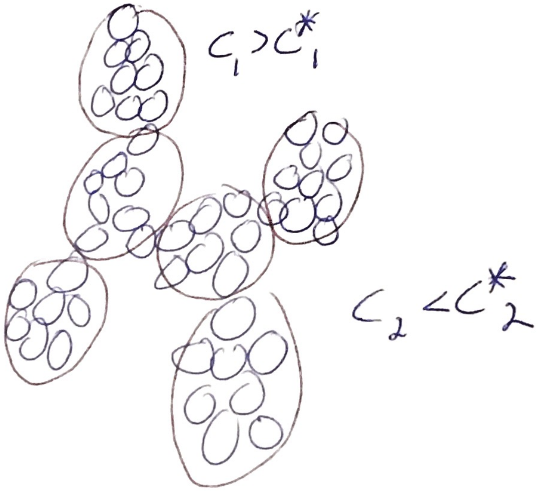
Concentration Blob
(Expanded substructure)

Consider miscible particles
above c^*



Thermal Blob
(Clustering)

Consider immiscible particles



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A “*scaling argument*” for chain size as a function of F, n and T

A tensile blob is Gaussian so,
$l_{ten}^2 = (n/n_{ten})\, l^2$ where n_{ten} is the number of tensile blobs

So, $n_{ten} = n\, l^2/l_{ten}^2$

The Chain is a rod so,
$R = n_{ten}\, l_{ten}$

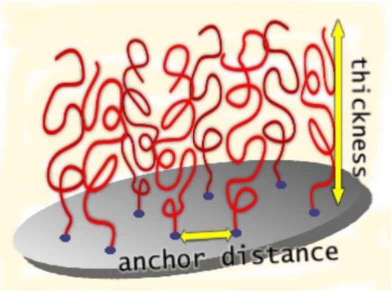
From an energy balance we have,
And $l_{ten} = 3kT/F$

So, $R = n\, l^2/l_{ten} = n\, l^2\, F/(3kT)$

R is proportional to n and F and decreases with kT

Thermal energy and entropy opposes the applied force

What is the thickness of the layer for chains of n, and temperature T?



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Mechanical deformation leads to a transition size scale, ξ

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

For sizes smaller than ζ the structure is not perturbed.

Concentration Blob

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

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

What happens when c is larger than c*?

We can't "see" an individual coil, no "n" dependence

Below the screening length (concentration blob size) we can see the same thing as in dilute

Above that size we see uniform structure like a fleece cloth

Interactions are screened, the **structure is Gaussian above the blob size** and **expanded coil (dilute) below**

As concentration c/c* increases the coil becomes more Gaussian and smaller

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

The Flory-Krigbaum Equation Describes the situation above c*

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

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(Expanded substructure)

Consider miscible particles
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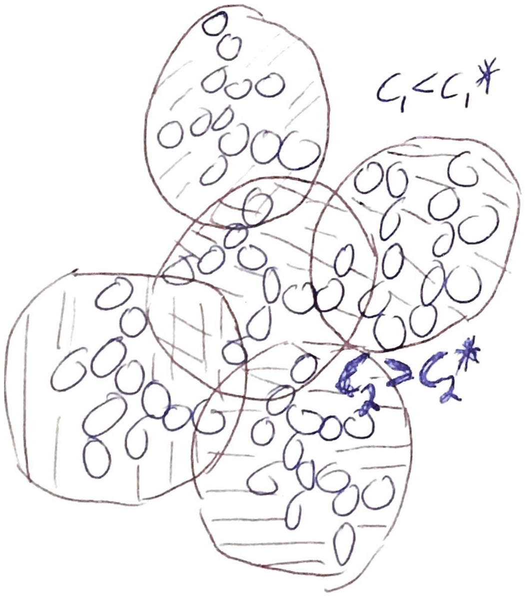
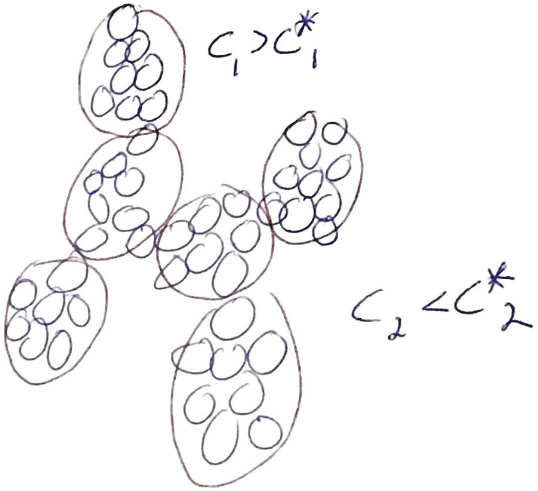


Thermal Blob
(Clustering)

Consider immiscible particles



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?

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^*

$$c^* = k\,n/R^3 = k\,n^{-4/5}$$

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

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

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

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

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

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

This is called the "**Concentration Blob**"

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Blob Type	Mass Fractal	Dimension	
	Large Scale	Small Scale	
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J. Physique **43** (1982)531 - 538

Star shaped polymers :
a model for the conformation and its concentration dependence

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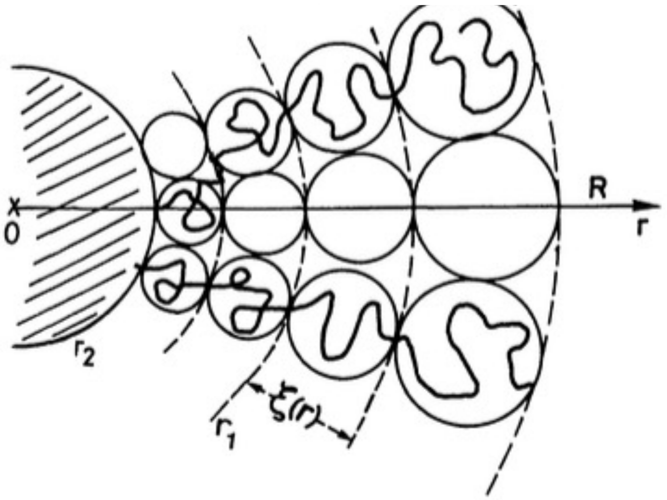


Fig. 1. — A representation of our model : every branch is made of a succession of blobs with a size ξ increasing from the centre of the star to the outside.

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

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

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

For all these regimes the variation of the size of a star is predicted as a function of N, f, v and c.

Thermal Blob

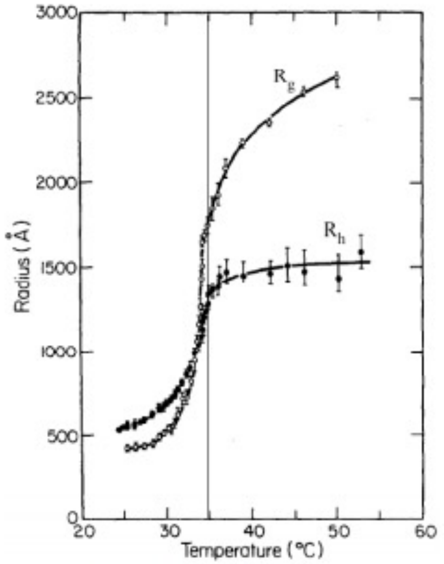


Figure 3. *Radius of gyration, R_g, and hydrodyamic radius R_h versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].*

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

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

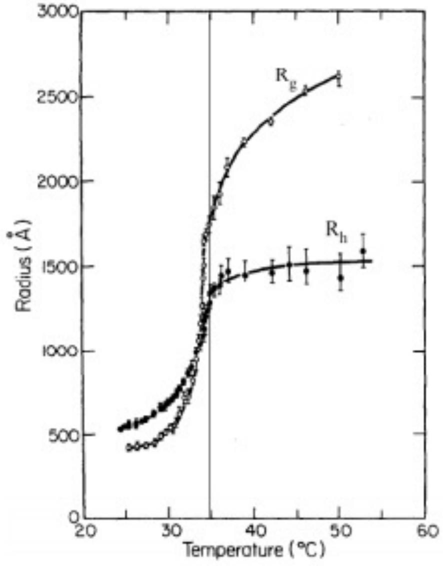
Flory-Krigbaum equation describes this
What occurs structurally, is the chain RW or SAW?
(Or both?)

Thermal Blob

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

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

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



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

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

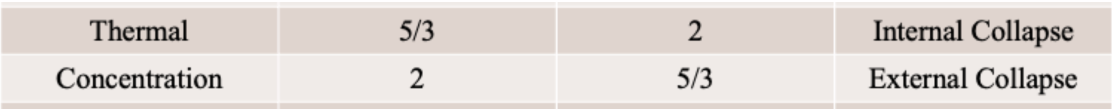
Thermal Blob

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

Energy Depends on *n*, a chain with a mer unit of length 1 and *n* = 10,000 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 (worse solvation) **on small scales first**.
This is the opposite of the concentration blob.



Thermal	5/3	2	Internal Collapse
Concentration	2	5/3	External Collapse

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

N_T is number of blobs, n_T number in a blob

At Large Scale, a SAW

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

At Small Scale, a RW

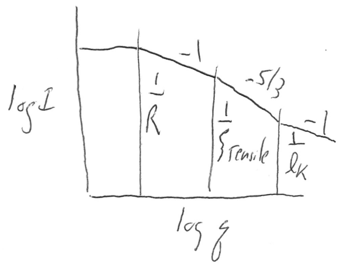
Flory-Krigbaum Theory yields: $R = V_c^{1/5}\left(1-2\chi\right)^{1/5}N^{3/5}l^{2/5}$

By equating these:

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

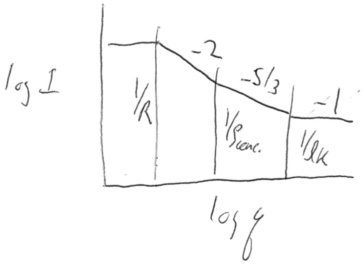
Tensile Blob

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



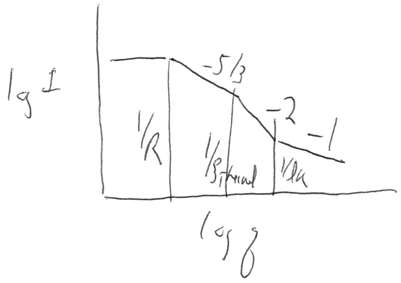
Concentration Blob

$$\xi_{Concentration} \sim R_{\text{Good Solvent}} \left(\frac{c}{c^*}\right)^{-3/4} \sim bN^{3/5} \left(\frac{c}{c^*}\right)^{-3/4}$$



Thermal Blob

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



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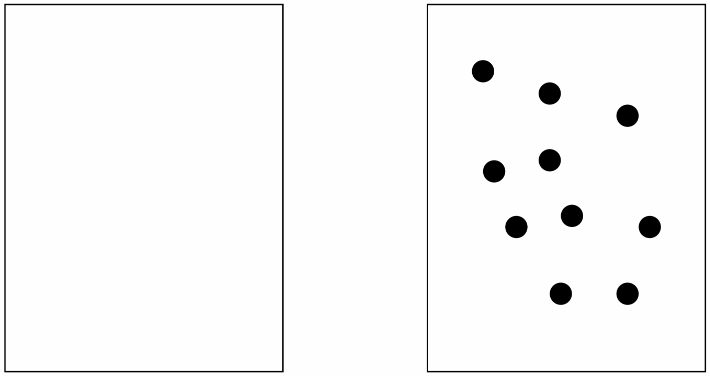
Osmotic Pressure



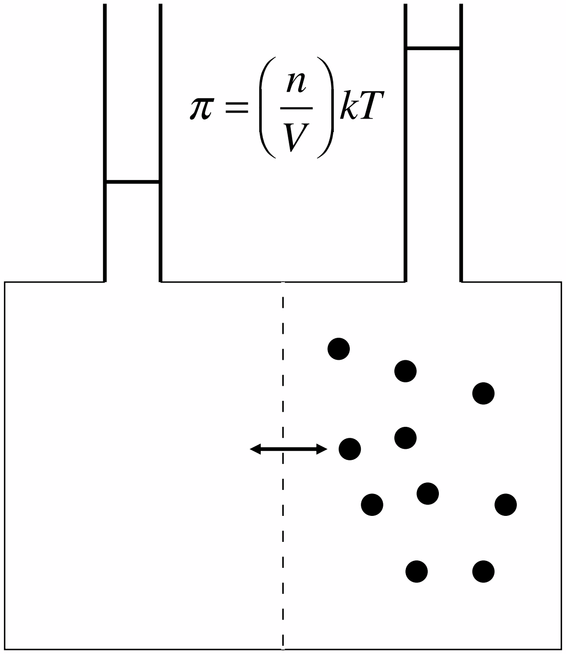
$$\pi = \left(\frac{n}{V}\right)kT$$

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

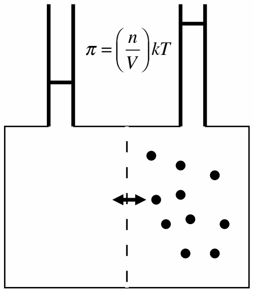
We can use this to count the number of solute molecules, *n* (π is a **colligative** property). For a known mass used to make the solution we can obtain the number average molecular weight.

Osmotic Pressure

Ideal Conditions



$$\pi = \left(\frac{n}{V}\right)kT$$



Osmotic Pressure

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

$$\frac{\pi}{kT} = B_1\rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + \ldots$$

$$\rho = \frac{n}{V} = \frac{Mass}{V}\frac{1}{(MW)_n} = \frac{\phi}{N}$$

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

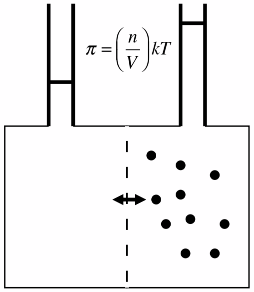
For Polymers:

$$\frac{\pi}{kT} = \frac{\rho}{N} + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + \cdots$$

$$B_2 = \left(\frac{1}{2} - \chi\right)$$

Colligative => M_n

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



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$$\rho = \frac{n}{V} = \frac{Mass}{V}\frac{1}{(MW)_n} = \frac{\phi}{N}$$

Heimez's *B* is usually called A_2

$B_2 = A_2/M^2$

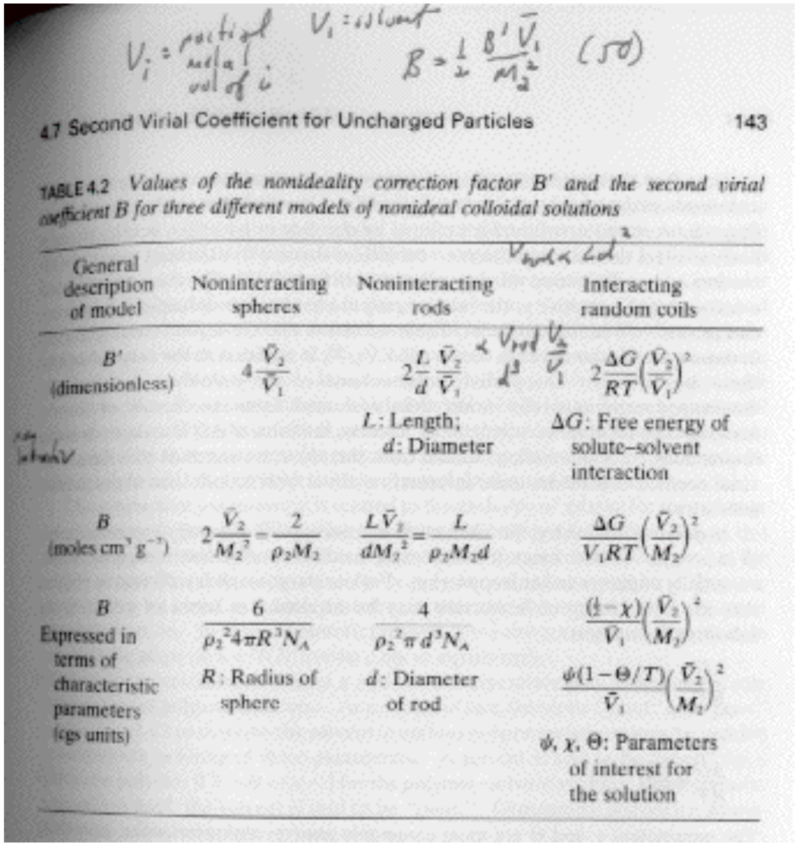
B_2 has units of effective excluded volume per mole

By comparison with van der Waals equation

$B_2 = b - a/\mathrm{k}T$

b is the hard-core excluded volume per mole

a is the attractive potential between particles per mole



V_i = partial molal vol of i V_1 = solvent

$B = \frac{1}{2}\frac{B'\bar{V}_1}{M_2^2}$ (50)

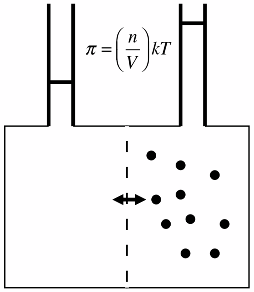
4.7 Second Virial Coefficient for Uncharged Particles 143

TABLE 4.2 *Values of the nonideality correction factor B' and the second virial coefficient B for three different models of nonideal colloidal solutions*

$V_{rod} \propto Ld^2$

General description of model	Noninteracting spheres	Noninteracting rods	Interacting random coils
B' (dimensionless)	$4\frac{\bar{V}_2}{\bar{V}_1}$	$2\frac{L}{d}\frac{\bar{V}_2}{\bar{V}_1} \propto \frac{V_{rod}}{d^3}\frac{V_2}{\bar{V}_1}$	$2\frac{\Delta G}{RT}\left(\frac{\bar{V}_2}{\bar{V}_1}\right)^2$
		L: Length; d: Diameter	ΔG: Free energy of solute–solvent interaction
B (moles cm^3 g^{-2})	$2\frac{\bar{V}_2}{M_2^2} = \frac{2}{\rho_2 M_2}$	$\frac{L\bar{V}_2}{dM_2^2} = \frac{L}{\rho_2 M_2 d}$	$\frac{\Delta G}{V_1 RT}\left(\frac{\bar{V}_2}{M_2}\right)^2$
B Expressed in terms of characteristic parameters (cgs units)	$\frac{6}{\rho_2^2 4\pi R^3 N_A}$ R: Radius of sphere	$\frac{4}{\rho_2^2 \pi d^3 N_A}$ d: Diameter of rod	$\frac{(\frac{1}{2}-\chi)}{\bar{V}_1}\left(\frac{\bar{V}_2}{M_2}\right)^2$ $\frac{\psi(1-\Theta/T)}{\bar{V}_1}\left(\frac{\bar{V}_2}{M_2}\right)^2$ ψ, χ, Θ: Parameters of interest for the solution

Heimez
"*Colloidal Chemistry*"



Osmotic Pressure

$$\frac{\pi}{kT} = \frac{\rho}{N} + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + \cdots$$

$$B_2 = \left(\frac{1}{2} - \chi\right)$$

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

Flory's consideration of polymer mixing

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

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

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

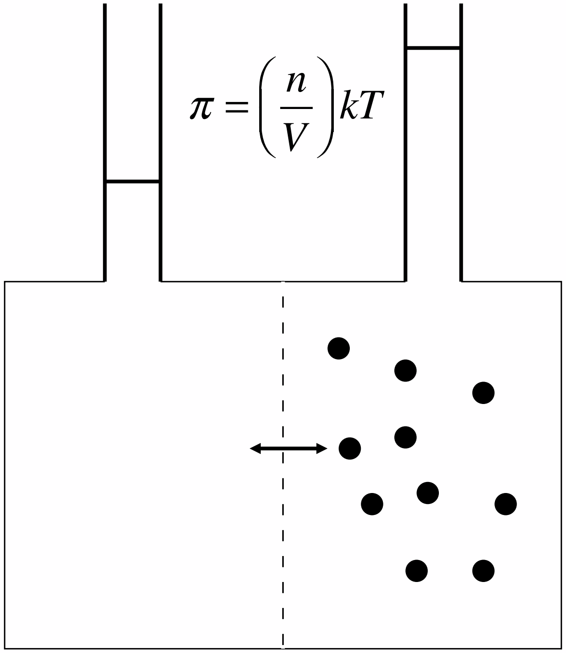
$$\Delta S_{mixing} = \frac{\phi}{N}\ln \phi + (1-\phi)\ln(1-\phi)$$

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

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

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

Osmotic Pressure

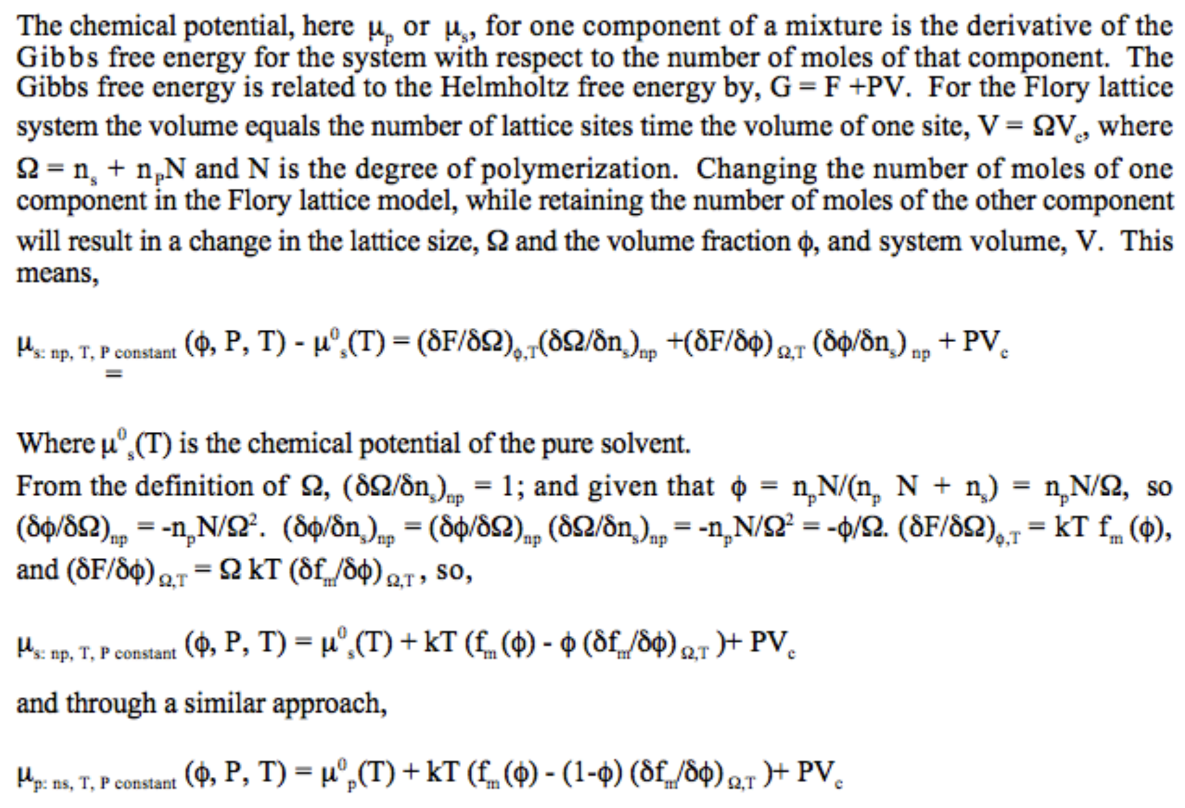


$$\pi = \left(\frac{n}{V}\right)kT$$

At equilibrium, the ***chemical potentials*** of the solvent (and the polymer) in the two solutions are identical.

Chemical potential is the change in free energy with respect to concentration for a given **component** in a given **phase** ***(you need to specify the component and the phase when you say chemical potential)***

-S U V
 H   A   G = A + VP
-P G T



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

$$\mu_{\underset{=}{s:\ np,\ T,\ P\ \mathrm{constant}}}(\phi, P, T) - \mu^0_s(T) = (\delta F/\delta\Omega)_{\phi,T}(\delta\Omega/\delta n_s)_{np} + (\delta F/\delta\phi)_{\Omega,T}\,(\delta\phi/\delta n_s)_{np} + PV_c$$

Where $\mu^0_s(T)$ is the chemical potential of the pure solvent.

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

$$\mu_{s:\ np,\ T,\ P\ \mathrm{constant}}(\phi, P, T) = \mu^0_s(T) + kT\,(f_m(\phi) - \phi\,(\delta f_m/\delta\phi)_{\Omega,T}) + PV_c$$

and through a similar approach,

$$\mu_{p:\ ns,\ T,\ P\ \mathrm{constant}}(\phi, P, T) = \mu^0_p(T) + kT\,(f_m(\phi) - (1-\phi)\,(\delta f_m/\delta\phi)_{\Omega,T}) + PV_c$$

$$\phi = \rho/d\,ensity$$

Osmotic Pressure:

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

$$\mu_{s:}\ (\phi, P+\Pi, T) = \mu_s(\phi{=}0, P, T)$$

At $\phi = 0$ $f_m = 0$ so $\mu_s(\phi{=}0, P, T) = \mu^0_s(T) + PV_c$, and using the above expression,

$$\mu_s(\phi, P+\Pi, T) = \mu^0_s(T) + kT\ (f_m(\phi) - \phi\ (\delta f_m/\delta\phi)_{\Omega,T}) + (P+\Pi)V_c,$$

so,

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

and

$$\Pi = (kT/V_c)\ (\phi\ (\delta f_m/\delta\phi)_{\Omega,T} - f_m(\phi))$$

$$f_m(\phi) = \phi \ln\phi / N + (1-\phi)\ln(1-\phi) + \chi\ \phi\ (1-\phi)$$

$$(\delta f_m/\delta\phi)_{\Omega,T} = \ln\phi/N + 1/N - (1+\phi)/(1-\phi) - \ln(1-\phi) + \chi(1 - 2\phi)$$

so,

$$\begin{aligned}\phi\ (\delta f_m/\delta\phi)_{\Omega,T} - f_m(\phi) &= \phi/N - \ln(1-\phi) - \phi\ (1-\phi)/(1-\phi) + \chi\ \{\phi(1 - 2\phi) - \phi\ (1-\phi)\}\\ &= \phi/N - \ln(1-\phi) - \phi - \chi\ \phi^2\end{aligned}$$

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

$$\Pi = (kT/V_c)\ [\phi/N + (1/2 - \chi)\ \phi^2 + \phi^3/3 + \phi^4/4 + \ldots]$$

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

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

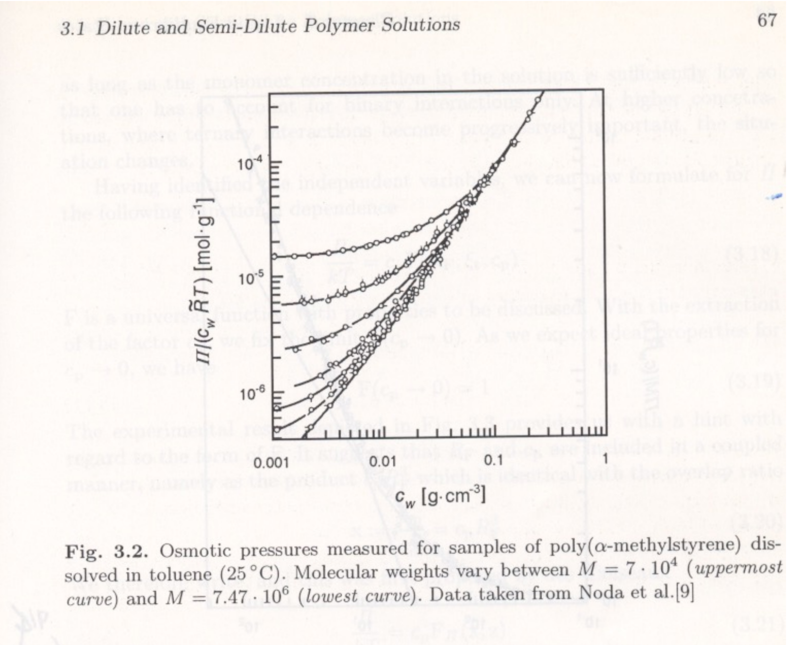

3.1 Dilute and Semi-Dilute Polymer Solutions 67

Fig. 3.2. Osmotic pressures measured for samples of poly(α-methylstyrene) dissolved in toluene (25 °C). Molecular weights vary between $M = 7 \cdot 10^4$ (*uppermost curve*) and $M = 7.47 \cdot 10^6$ (*lowest curve*). Data taken from Noda et al.[9]

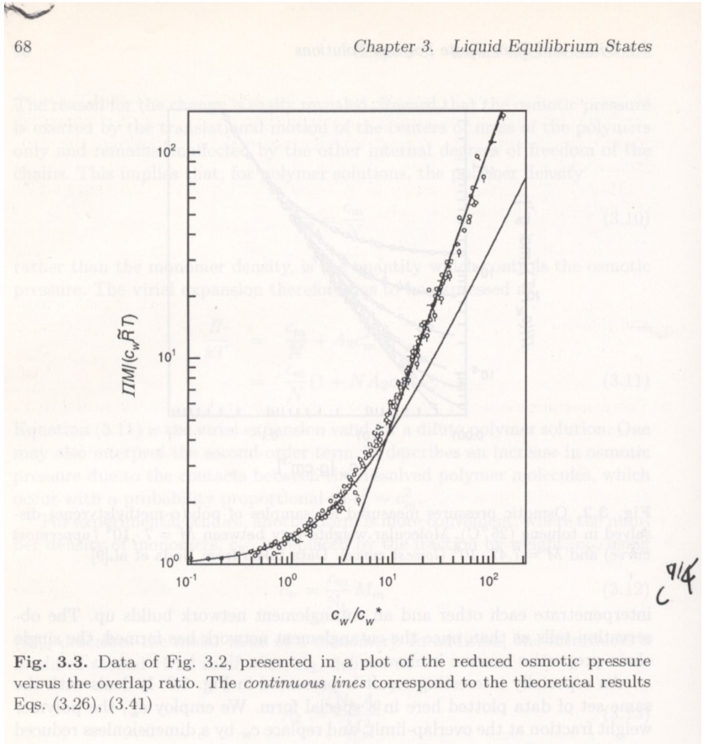

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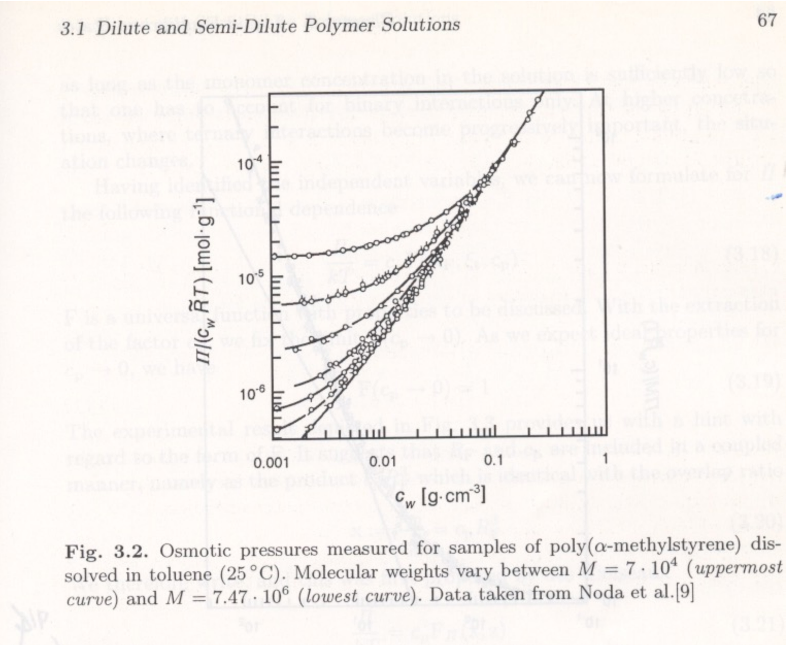
Fig. 3.3. Data of Fig. 3.2, presented in a plot of the reduced osmotic pressure versus the overlap ratio. The *continuous lines* correspond to the theoretical results Eqs. (3.26), (3.41)

From Gert Strobl, Polymer Physics

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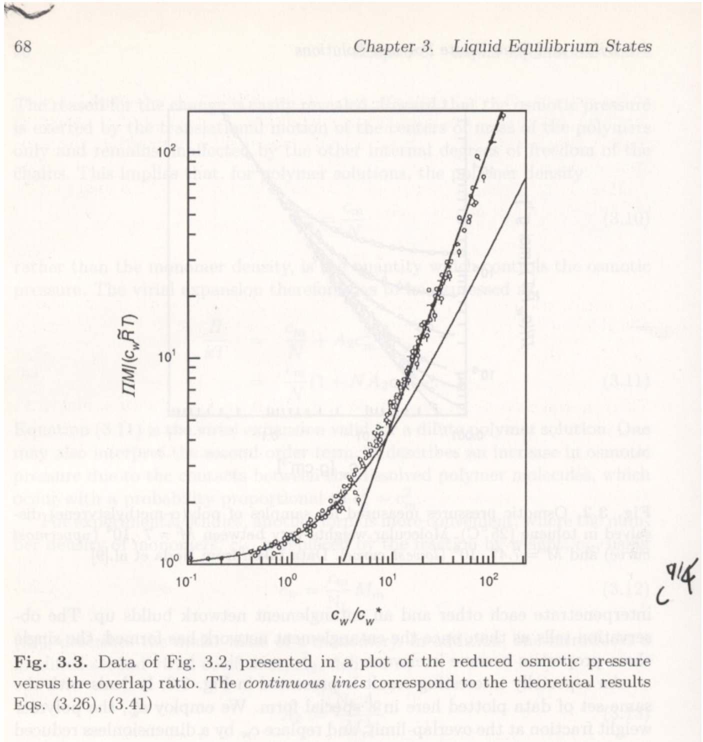
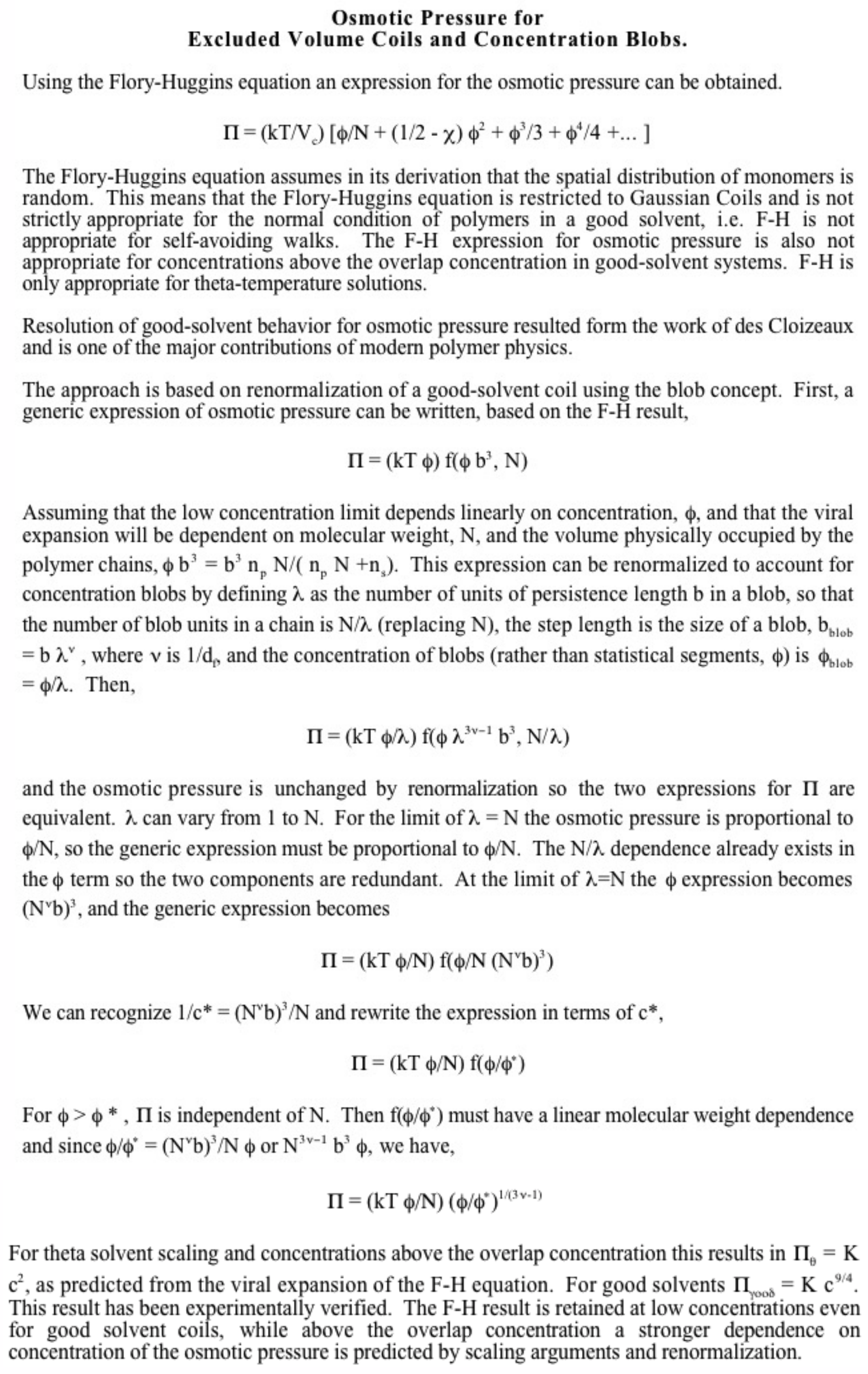

68 Chapter 3. Liquid Equilibrium States

$c^{9/4}$

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

Right graph shows that:

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



Osmotic Pressure for Excluded Volume Coils and Concentration Blobs.

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

$$\Pi = (kT/V_c)\,[\phi/N + (1/2 - \chi)\,\phi^2 + \phi^3/3 + \phi^4/4 + \ldots]$$

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

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

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

$$\Pi = (kT\,\phi)\, f(\phi\, b^3, N)$$

Assuming that the low concentration limit depends linearly on concentration, ϕ, and that the viral expansion will be dependent on molecular weight, N, and the volume physically occupied by the polymer chains, $\phi\, b^3 = b^3\, n_p\, N/(\, n_p\, N + n_s)$. This expression can be renormalized to account for concentration blobs by defining λ as the number of units of persistence length b in a blob, so that the number of blob units in a chain is N/λ (replacing N), the step length is the size of a blob, $b_{blob} = b\, \lambda^{\nu}$, where ν is $1/d_p$, and the concentration of blobs (rather than statistical segments, ϕ) is $\phi_{blob} = \phi/\lambda$. Then,

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

and the osmotic pressure is unchanged by renormalization so the two expressions for Π are equivalent. λ can vary from 1 to N. For the limit of $\lambda = N$ the osmotic pressure is proportional to ϕ/N, so the generic expression must be proportional to ϕ/N. The N/λ dependence already exists in the ϕ term so the two components are redundant. At the limit of λ=N the ϕ expression becomes $(N^{\nu}b)^3$, and the generic expression becomes

$$\Pi = (kT\,\phi/N)\, f(\phi/N\, (N^{\nu}b)^3)$$

We can recognize $1/c^* = (N^{\nu}b)^3/N$ and rewrite the expression in terms of c*,

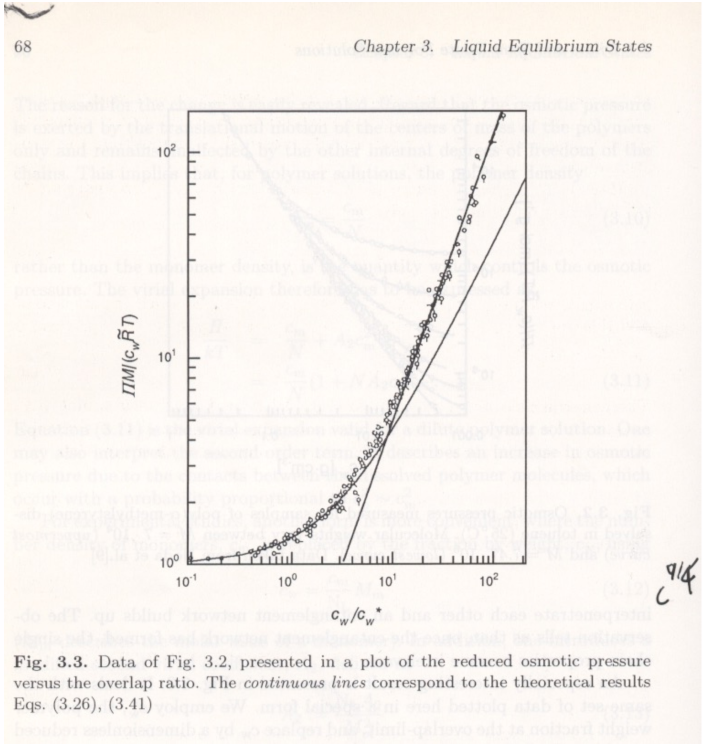
$$\Pi = (kT\,\phi/N)\, f(\phi/\phi^*)$$

For $\phi > \phi^*$, Π is independent of N. Then $f(\phi/\phi^*)$ must have a linear molecular weight dependence and since $\phi/\phi^* = (N^{\nu}b)^3/N\, \phi$ or $N^{3\nu-1}\, b^3\, \phi$, we have,

$$\Pi = (kT\,\phi/N)\, (\phi/\phi^*)^{1/(3\nu-1)}$$

For theta solvent scaling and concentrations above the overlap concentration this results in $\Pi_\theta = K\, c^2$, as predicted from the viral expansion of the F-H equation. For good solvents $\Pi_{\gamma o o \delta} = K\, c^{9/4}$. This result has been experimentally verified. The F-H result is retained at low concentrations even for good solvent coils, while above the overlap concentration a stronger dependence on concentration of the osmotic pressure is predicted by scaling arguments and renormalization.

Concentration Blob Prediction



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$c^{9/4}$

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

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

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

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

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

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

Flory-Huggins Equation for a Polymer Blend

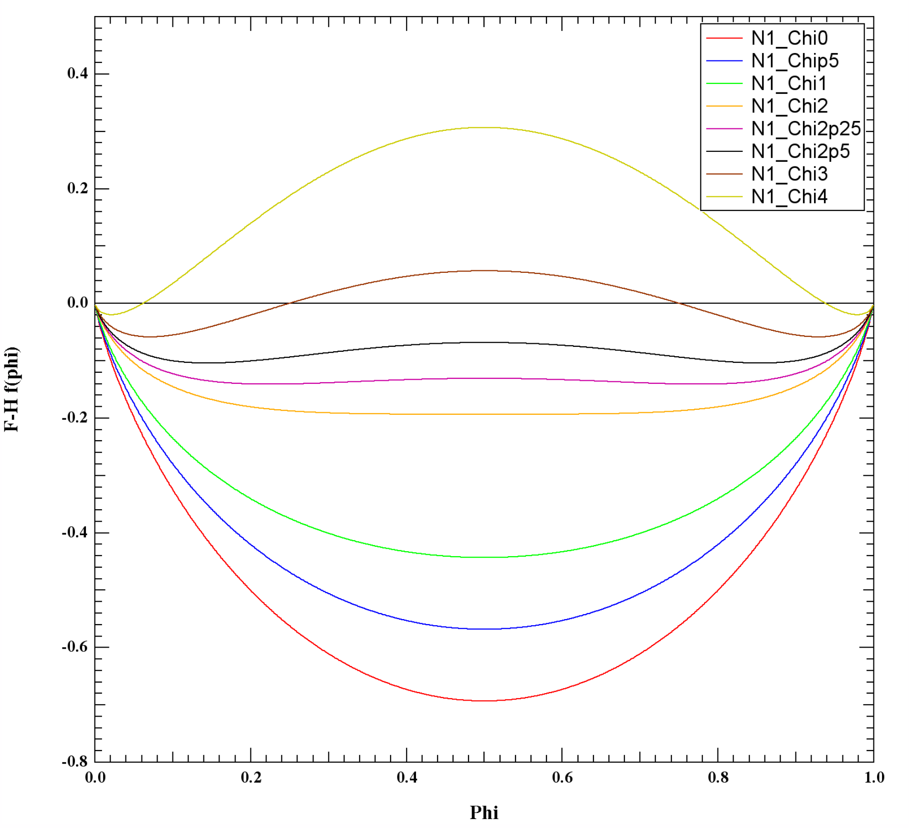
$$\Delta f_{mixing} = \frac{\phi_A}{N_A}\ln\phi + \frac{(1-\phi_A)}{N_B}\ln(1-\phi_A) + \chi\phi_A(1-\phi_A)$$

$$\text{if } N_A = N_B = N$$

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

Spinodal Curve

$$2\chi_{spinodal\,AB} = \frac{1}{\phi_A N_A} + \frac{1}{\phi_B N_B}$$

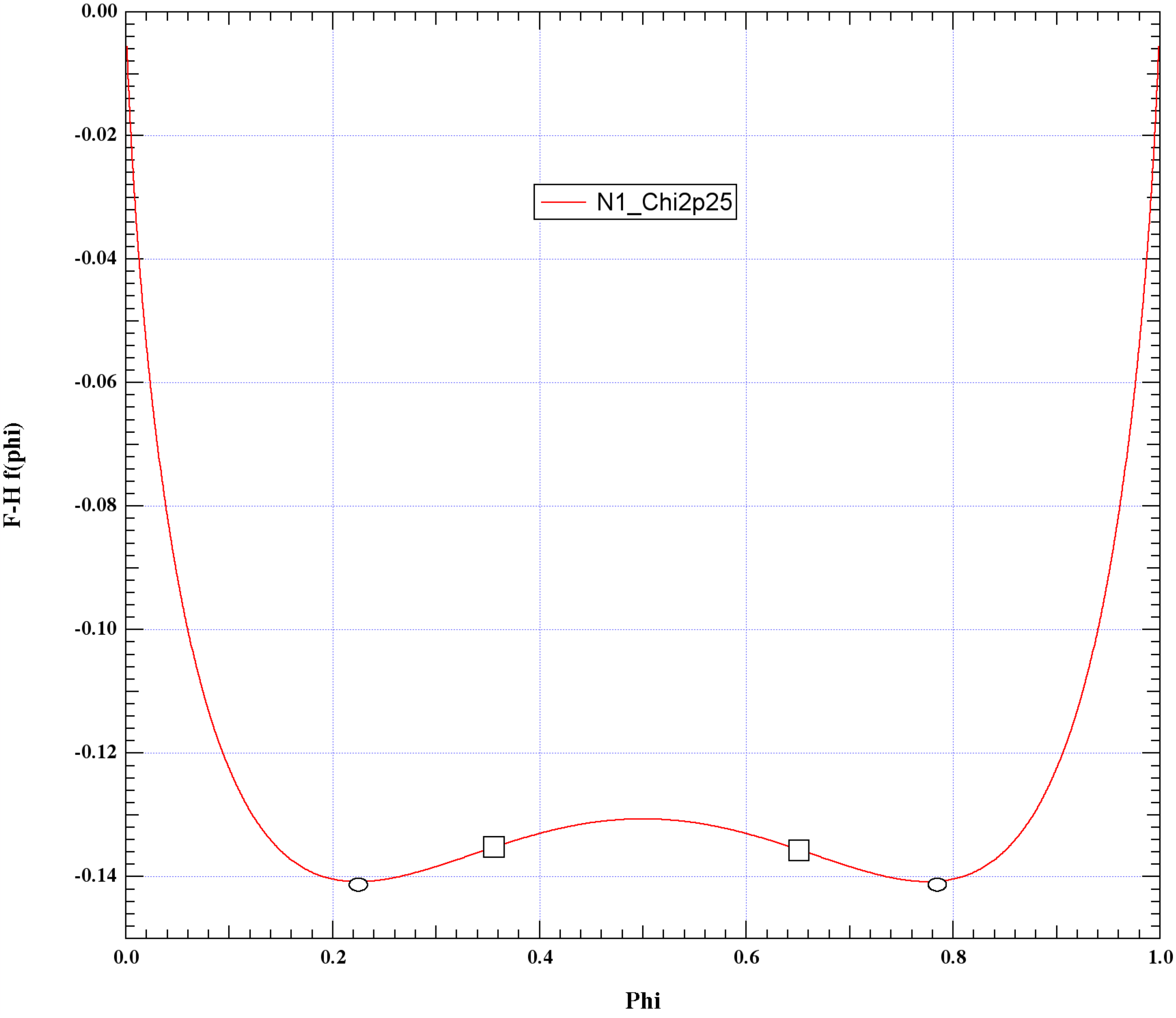


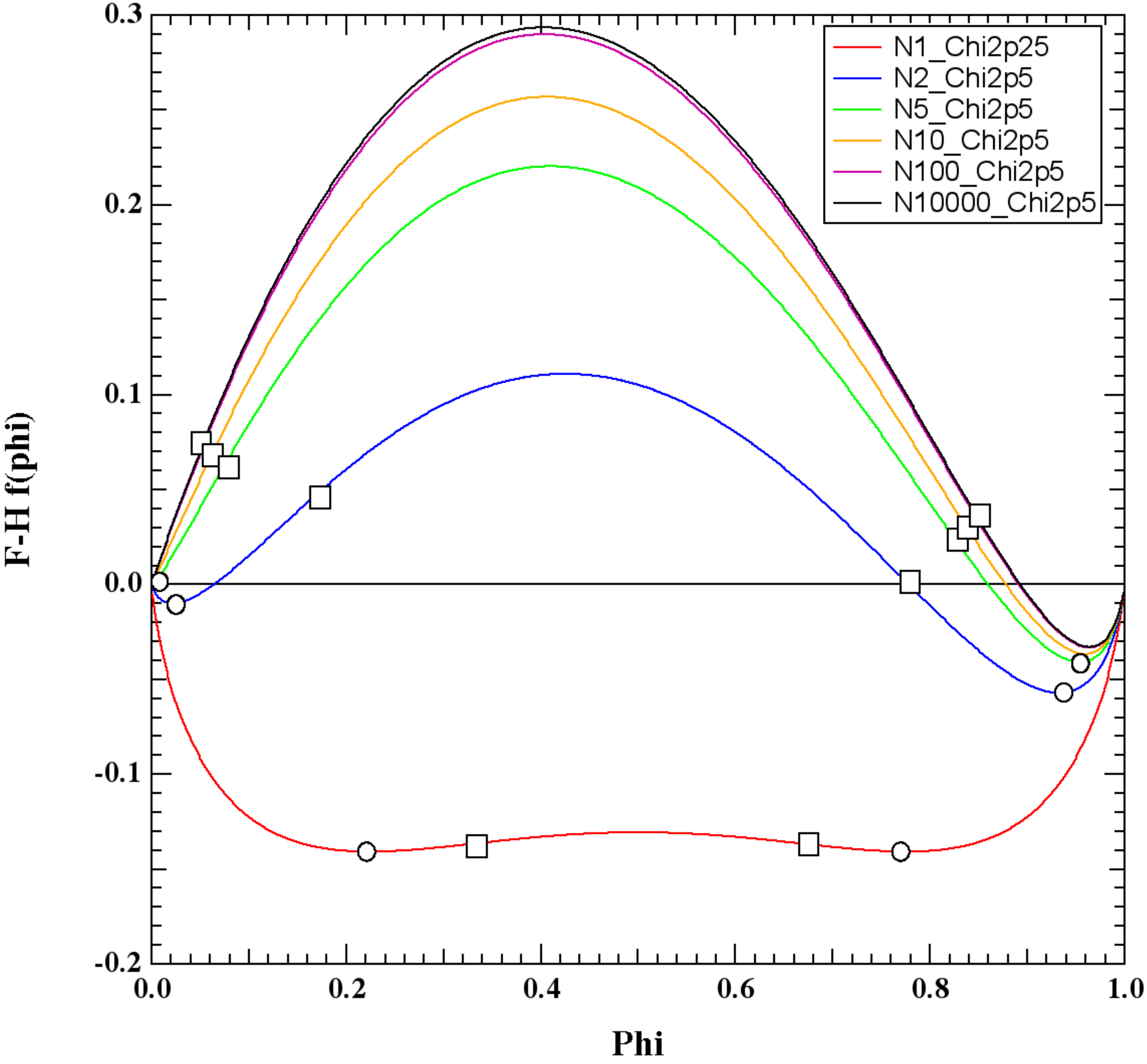
The critical point is where (χN) = 2

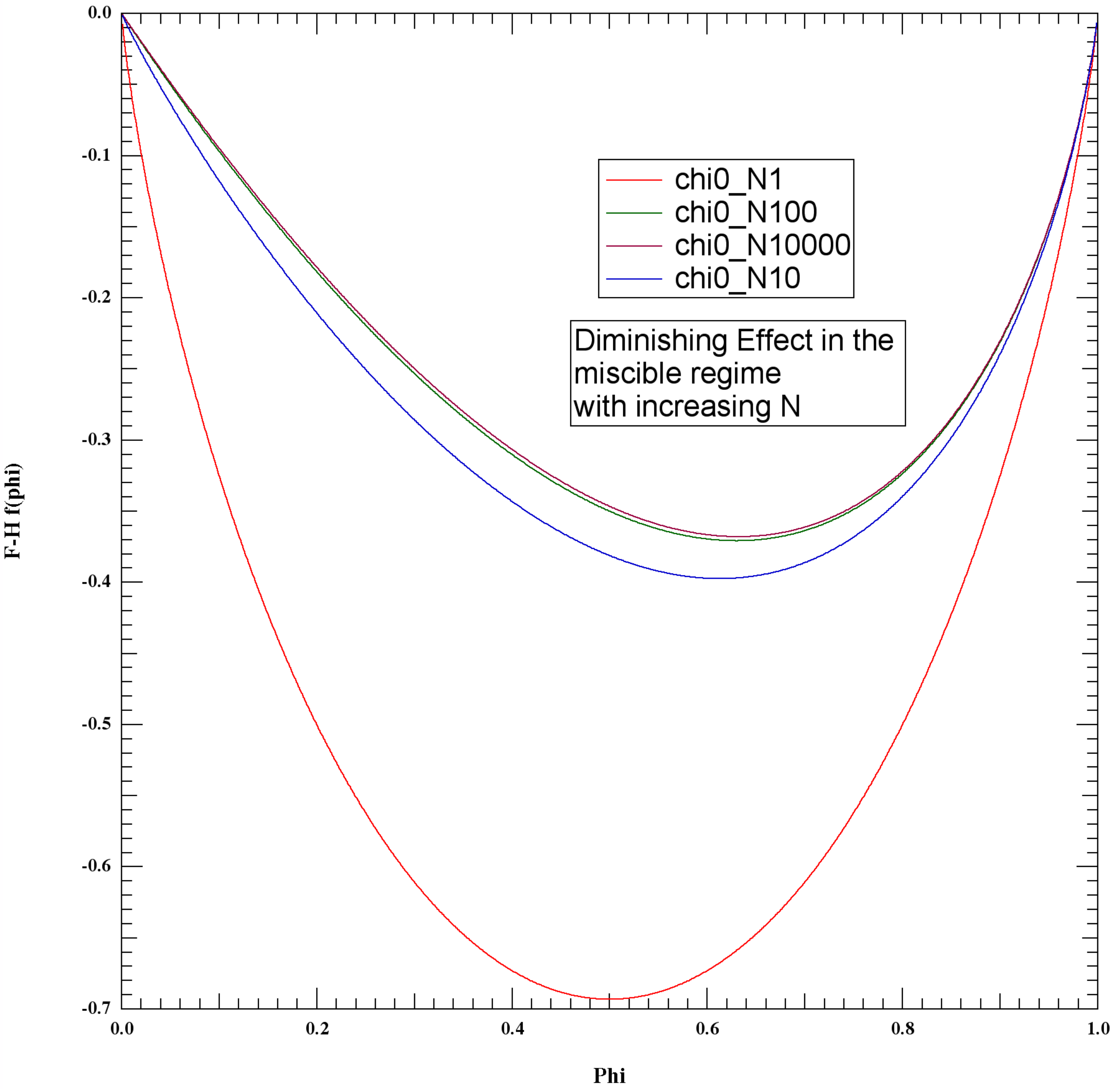
$$\text{if } N_A \neq N_B$$

$$\phi_{cA} = \frac{N_A^{1/2}}{N_A^{1/2} + N_B^{1/2}}$$

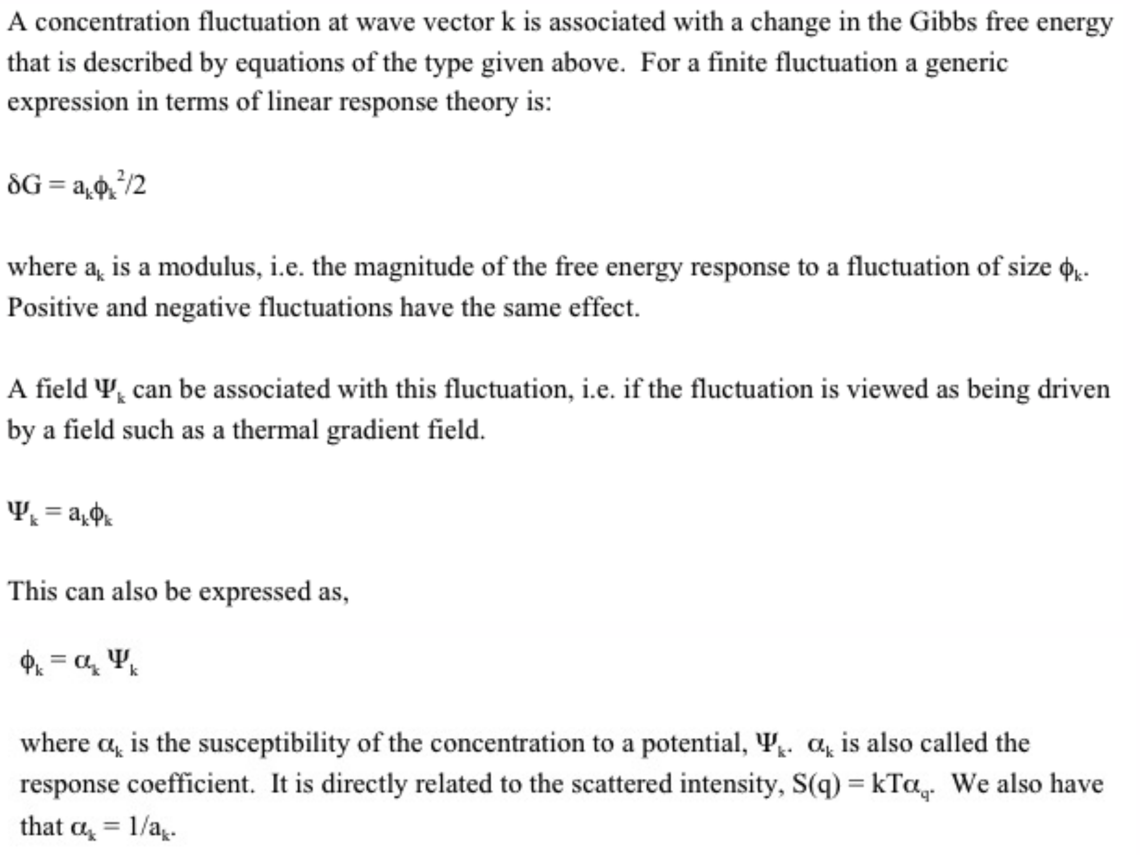
$$\chi_{cAB} = \frac{\left(N_A^{1/2} + N_B^{1/2}\right)^2}{2N_A N_B}$$


0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
F-H f(phi)
N1_Chi2p25
0.0
0.2
0.4
0.6
0.8
1.0
Phi


0.3
0.2
0.1
0.0
-0.1
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
F-H f(phi)
Phi
N1_Chi2p25
N2_Chi2p5
N5_Chi2p5
N10_Chi2p5
N100_Chi2p5
N10000_Chi2p5


0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
F-H f(phi)
0.0
0.2
0.4
0.6
0.8
1.0
Phi
chi0_N1
chi0_N100
chi0_N10000
chi0_N10
Diminishing Effect in the miscible regime with increasing N

Concentration Fluctuations and Linear Response Theory (Nomenclature)



A concentration fluctuation at wave vector k is associated with a change in the Gibbs free energy that is described by equations of the type given above. For a finite fluctuation a generic expression in terms of linear response theory is:

$\delta G = a_k \phi_k^2/2$

where a_k is a modulus, i.e. the magnitude of the free energy response to a fluctuation of size ϕ_k. Positive and negative fluctuations have the same effect.

A field Ψ_k can be associated with this fluctuation, i.e. if the fluctuation is viewed as being driven by a field such as a thermal gradient field.

$\Psi_k = a_k \phi_k$

This can also be expressed as,

$\phi_k = \alpha_k \Psi_k$

where α_k is the susceptibility of the concentration to a potential, Ψ_k. α_k is also called the response coefficient. It is directly related to the scattered intensity, $S(q) = kT\alpha_q$. We also have that $\alpha_k = 1/a_k$.

The differential expression for the change in free energy is given by,

$$dG = \Psi_k \, d\phi_k = a_k \phi_k d\phi_k$$

Fluctuations are driven by thermal energy and the distribution in space is random and follows Boltzmann statistics,

$$p(\phi_k) \sim \exp(- a_k \phi_k^2 / 2kT)$$

so the mean square fluctuations are given by the variance of the distribution,

$$<\phi_k^2> = kT/a_k = \alpha_k kT$$

The scattered intensity from a homogeneous system is governed by the mean square fluctuations,

$$v_c \, S_c(q = k) = <\phi_k^2> = \alpha_k kT$$

$$\phi_k = \alpha_k \Psi_k; \quad dG = \Psi_k d\phi_k = \frac{\phi_k d\phi_k}{\alpha_k}; \quad G = \frac{\phi_k^2}{2\alpha_k} = \frac{a_k \phi_k^2}{2}$$

$$S(k) = \left\langle \phi_k^2 \right\rangle$$

$$p(\phi_k) = \exp\left(-\frac{G}{kT}\right) = \exp\left(-\frac{a_k \phi_k^2}{2kT}\right)$$

$$\left\langle \phi_k^2 \right\rangle = \alpha_k kT$$

$$S(k) = \left\langle \phi_k^2 \right\rangle = \alpha_k kT$$

$$dG = \Psi_k d\phi_k = \frac{\phi_k d\phi_k}{\alpha_k}$$

$$\alpha_k = \phi_k / \left(dG_k / d\phi_k\right) \approx \phi\left(d\pi/d\phi\right)^{-1} \quad \text{Inverse Osmotic Compressibility}$$

$$\left(\Delta G = -\pi V_{sp}\right)$$

2) Consider scattering from a dilute solution of polymer in solvent. For a one phase system such as a polymer in solution the deviation in concentration is caused by thermal fluctuations of the concentration that are dampened by the increase in reduced osmotic pressure π with increasing concentration. The fluctuations are constantly changing in space and time. Then we consider the scattered intensity as proportional to the integral of the derivative or the average change in ϕ^2, $2\phi\langle d\phi/d(\pi/kT)\rangle$

$$S(q \Rightarrow 0) = 2kT\phi\left\langle \frac{d\phi}{d\pi} \right\rangle \qquad (1)$$

3) We have a simple expression for $d\pi/d\phi$ from the Flory-Huggins equation,

$$\frac{\pi}{kT} = \frac{\phi}{N} + \frac{(1-2\chi)}{2}\phi^2 \qquad (2)$$

so,

$$\frac{\phi}{S(q \Rightarrow 0)} = \left(\frac{1}{N} + (1-2\chi)\phi\right) \qquad (3)$$

4) Zimm used the approximation that equation (1) could be generalized to all q by simply multiplying the contrast factor of equation (1) by the Debye scattering function,

$$S_D(Q) = \frac{2}{Q^2}\left(Q - 1 + \exp(-Q)\right) \text{ where } Q = q^2R_g^2 \qquad (4)$$

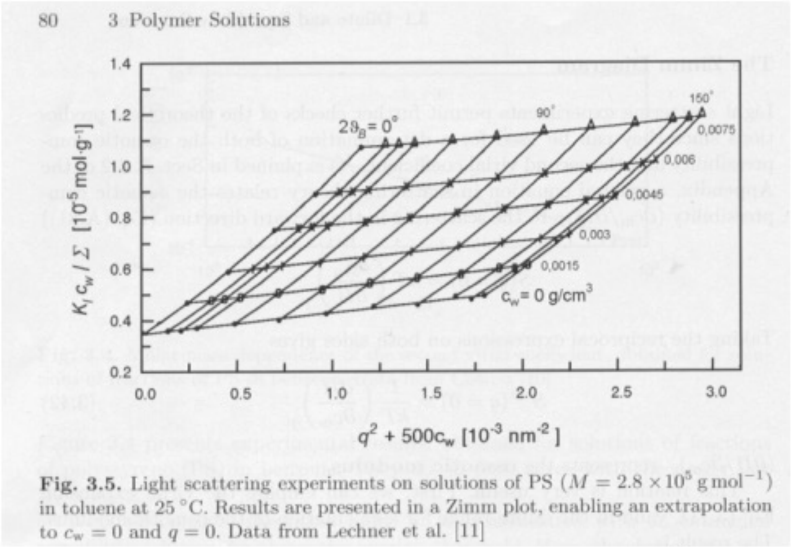
We previously found that equation (4) can be reduced to Guinier's law at low-q,

$$S_D(q \Rightarrow 0) = \exp\left(\frac{-q^2R_g^2}{3}\right) \text{ and } \frac{1}{S_D(q \Rightarrow 0)} = \exp\left(\frac{q^2R_g^2}{3}\right) \cong \left(1 + \frac{q^2R_g^2}{3}\right) \qquad (5)$$

Zimm arrived at the following equation,

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

Equation (6) is based on the assumption that the chain scattering function (equation (5)) is independent of the thermodynamics causing concentration fluctuatoins (equation(3)) so that the two components contribute to the scattering intensity independently. This is, of course, absurd since the chain structure is determined by thermodynamics. However, the assumption becomes plausible in the limit of $\phi \Rightarrow 0$ and $q \Rightarrow 0$. For this reason Zimm suggested a plot involving a double extrapolation as shown below.



80 3 Polymer Solutions

Fig. 3.5. Light scattering experiments on solutions of PS ($M = 2.8 \times 10^5\ \mathrm{g\,mol^{-1}}$) in toluene at 25 °C. Results are presented in a Zimm plot, enabling an extrapolation to $c_w = 0$ and $q = 0$. Data from Lechner et al. [11]

From Gert Strobl, The Physics of Polymers 3'rd Edition. $K_I = \dfrac{4\pi^2 n^2 \left(\dfrac{dn}{dc}\right)^2}{N_0 \lambda^4}$ *and Σ is the scattering intensity.*

At c => 0 (bottom line) the slope is proportional to $\frac{R_g^2}{3N}$, while at q => 0 (left curve) the slope is proportional to $(1 - 2\chi)$ or A_2. The intercept on the y-axis is proportional to 1/N, the weight average molecular weight for the polymer.

The Zimm plot is widely used to determine the weight average molecular weight, the coil radius of gyration and the second virial coefficient despite the approximation involved because it is only used in extrapolation.

A rigorous and general description of the scattering from polymer blends and solutions at all values of q was arrived at by de Gennes using the random phase approximation (RPA). The RPA is discussed in a separate section, the function for scattered intenstity is,

$$\frac{1}{S(q)} = \frac{1}{\phi_1 N_1 S_D(q, R_{g1})} + \frac{1}{\phi_2 N_2 S_D(q, R_{g2})} - 2\chi \qquad \text{(7) (RPA Blend)}$$

where Ni is the weight average molecular weight and the equation is written for a polymer blend. For a polymer solution $N_1 = 1$, $\phi_1 \sim 1$ and $S_D(q,R_{g1}) \sim 1$ so equation (7) can be rewritten,

$$\frac{\phi_2}{S(q)} = \frac{1}{N_2 S_D(q, R_{g2})} + \phi_2(1 - 2\chi) \qquad \text{(8) (RPA Solution)}$$

Equation (8) bears resemblance to equation (6). The difference is that the inverse Debye function modifies only the first virial term in (8) while it modifies both the first and second virial coefficients in equation (6).

The RPA equation can be generalized to include scaling transitions in the polymer coils if more sophisticated scattering functions are used rather than the Debye function such as the unified scattering function which can accommodate scaling changes including good solvent scaling and blob scaling transitions,

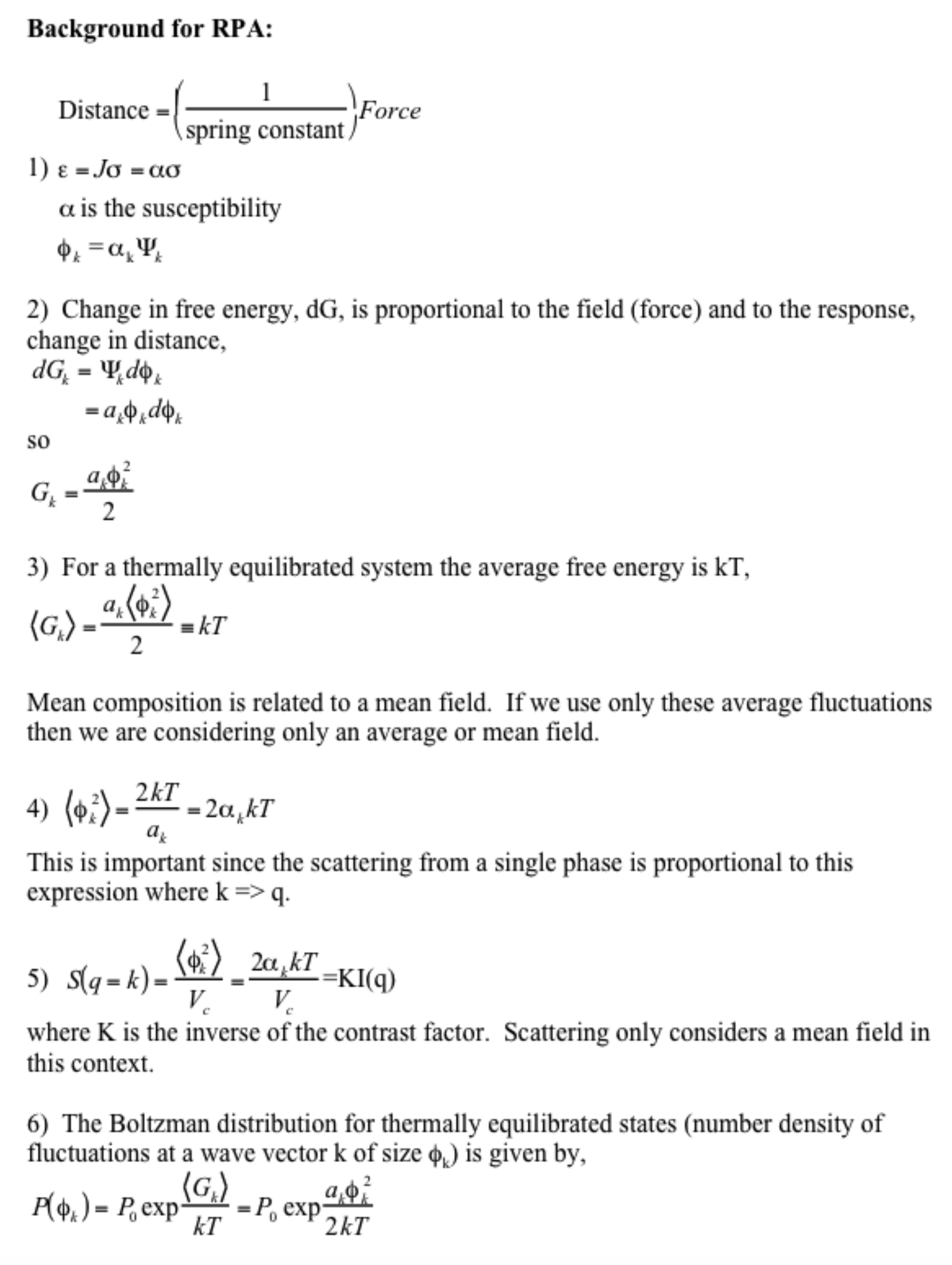
$$\frac{1}{S(q)} = \frac{1}{\phi_1 N_1 S_U\left(q,R_{g1}\right)} + \frac{1}{\phi_2 N_2 S_U\left(q,R_{g2}\right)} - 2\chi \qquad \text{(9) (RPA for Scaling Changes)}$$

where $S_U(q,R_g,d_f)$ for a chain of arbitrary fractal scaling and in the absence of blobs (simple case) is given by,

$$S_U\left(q,R_g,d_f,d_{\min}\right) = \exp\left(\frac{-q^2R_g^2}{3}\right) + \left(\frac{d_{\min}}{R_g^{d_f}}\Gamma\left({d_f}/{2}\right)\right)q^{*-d_f} \qquad (10)$$

where $d_{\min} = d_f$ for a linear chain and $1 \le d_{\min} < d_f$ for a branched chain (PRE **70**, 031401 (2004)) and $q^* = q/\left[erf\left(qR_g/6^{1/2}\right)\right]^3$.

Random Phase Approximation



Background for RPA:

$$\text{Distance} = \left(\frac{1}{\text{spring constant}}\right) Force$$

1) $\varepsilon = J\sigma = \alpha\sigma$

α is the susceptibility

$\phi_k = \alpha_k \Psi_k$

2) Change in free energy, dG, is proportional to the field (force) and to the response, change in distance,

$$dG_k = \Psi_k d\phi_k$$
$$= a_k \phi_k d\phi_k$$

so

$$G_k = \frac{a_k \phi_k^2}{2}$$

3) For a thermally equilibrated system the average free energy is kT,

$$\langle G_k \rangle = \frac{a_k \langle \phi_k^2 \rangle}{2} \equiv kT$$

Mean composition is related to a mean field. If we use only these average fluctuations then we are considering only an average or mean field.

4) $\langle \phi_k^2 \rangle = \dfrac{2kT}{a_k} = 2\alpha_k kT$

This is important since the scattering from a single phase is proportional to this expression where k => q.

5) $S(q = k) = \dfrac{\langle \phi_k^2 \rangle}{V_c} = \dfrac{2\alpha_k kT}{V_c} = \mathrm{KI(q)}$

where K is the inverse of the contrast factor. Scattering only considers a mean field in this context.

6) The Boltzman distribution for thermally equilibrated states (number density of fluctuations at a wave vector k of size ϕ_k) is given by,

$$P(\phi_k) = P_0 \exp\frac{\langle G_k \rangle}{kT} = P_0 \exp\frac{a_k \phi_k^2}{2kT}$$

Two Component, Athermal System:

1) Consider a simplified 2 component system where the field only affects component A, and the component B can not be seen, i.e. it has no scattering contrast for instance. We write (1) above in terms of component A,

$$\phi_{k,A} = \alpha_k^0 \Psi_k$$

where α_k^0 is **the collective response coefficient** for A units under athermal conditions (0) in a mixture with B units. This corresponds to the scattering from a polymer blend for example. We what to solve for this function of k or q.

2) We understand that the system is incompressible and that there is conservation of mass so that a fluctuation in A leads to an equal and opposite fluctuation in B,

$$\phi_{k,A} = -\phi_{k,B} = \phi_k$$

3) The field only effects A units, yet there must be a response to fluctuations in A by the B units according to (2). Then we can consider an effective field that acts on B units. This field is called the **internal field**.

$$\phi_{k,B} = -\phi_k = \alpha_k^{BB} \underline{\Psi}_k$$

where α_k^{BB} is the response coefficient for isolated B units, i.e. the scattering from isolated B units. For polymers this is the Debye function for a single B chain.

4) Similarly we can write the flux of A units in terms of the response coefficient for isolated A chains (these isolated coefficients are usually know and correspond to dilute conditions of a single component.

$$\phi_{k,A} = \phi_k = \alpha_k^{AA} \left(\Psi_k + \underline{\Psi}_k \right)$$

5) We need an expression for the **internal field** in terms of known functions. This can be obtained since expression 3) and 4) are related to each other, summing the two expressions we get 0,

$$\phi_k = \alpha_k^{AA}\left(\Psi_k + \underline{\Psi}_k\right) = -\alpha_k^{BB}\left(\underline{\Psi}_k\right)$$

$$\underline{\Psi}_k = -\Psi_k \frac{\alpha_k^{AA}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

6) Then we can substitute this expression for the internal field into expression 3),

$$\phi_k = -\alpha_k^{BB}\underline{\Psi}_k = \Psi_k \frac{\alpha_k^{AA}\alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

7) And equate expression 6) and 1) to solve for the collective response coefficient (scattering from a blend of two polymers for instance).

$$\phi_k = \Psi_k \frac{\alpha_k^{AA}\alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}} = \alpha_k^0 \Psi_k$$

$$\alpha_k^0 = \frac{\alpha_k^{AA}\alpha_k^{BB}}{\alpha_k^{AA} + \alpha_k^{BB}}$$

or

$$\frac{1}{\alpha_k^0} = \frac{1}{\alpha_k^{AA}} + \frac{1}{\alpha_k^{BB}}$$

that is similar to the Zimm equatin in that the inverse of the scattering is related to the inverse of the Debye function. By comparison with the Zimm function an expression to determine the interaction parameter is directly obtained.

Two Component, Thermal System:

1) Consider units with an enthalpic interaction per average units A and B of $\chi' = 2\chi kT/V_c$. This enthalpic interaction serves to dampen, if χ is negative, or enhance, if χ is positive, the externally applied field by a factor, $\phi\chi'$.

$$\phi_{k,A} = \alpha_k^0 \left(\Psi_k + \phi_k \chi' \right)$$

2) We solve for ϕ,

$$\phi_k = \frac{\alpha_k^0 \Psi_k}{1 - \alpha_k^0 \chi'}$$

3) By comparison with expression 1) for the athermal system we have for the thermal collective response coefficient,

$$\frac{1}{\alpha_k} = \frac{1}{\alpha_k^0} - \chi' = \frac{1}{\alpha_k^{AA}} + \frac{1}{\alpha^{BB}} - \frac{2kT\chi}{V_c}$$

This can be used to obtain the interaction parameter from scattering in a polymer blend.

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

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

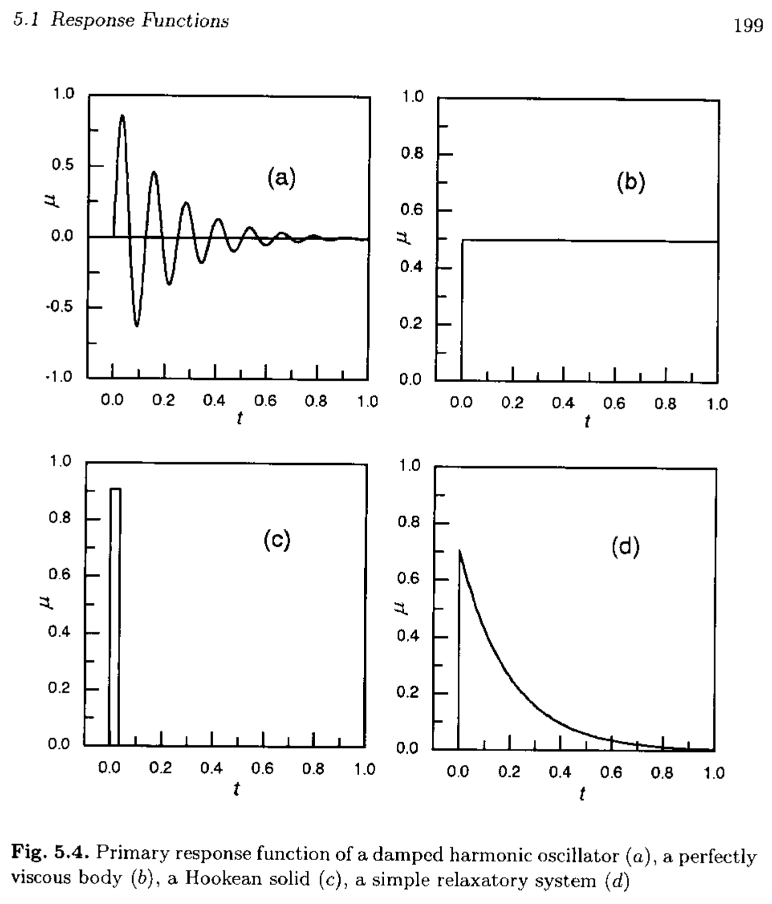


Fig. 5.4. Primary response function of a damped harmonic oscillator (*a*), a perfectly viscous body (*b*), a Hookean solid (*c*), a simple relaxatory system (*d*)

Simple exponential relaxor

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

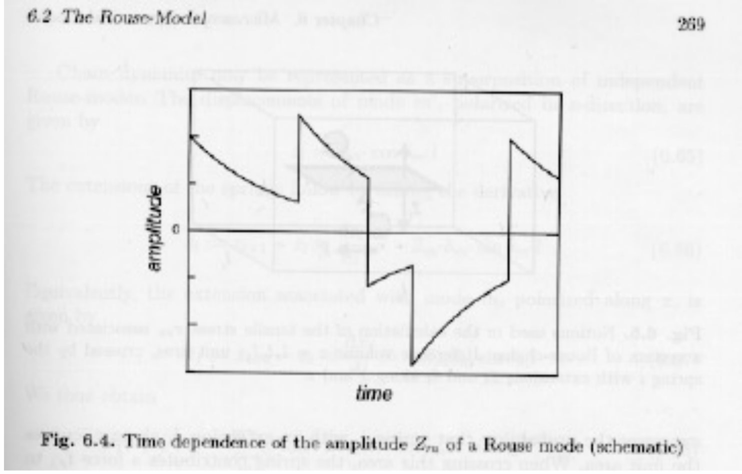


Fig. 6.4. Time dependence of the amplitude Z_{ru} of a Rouse mode (schematic)

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

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

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

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

τ is a relaxation time.

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

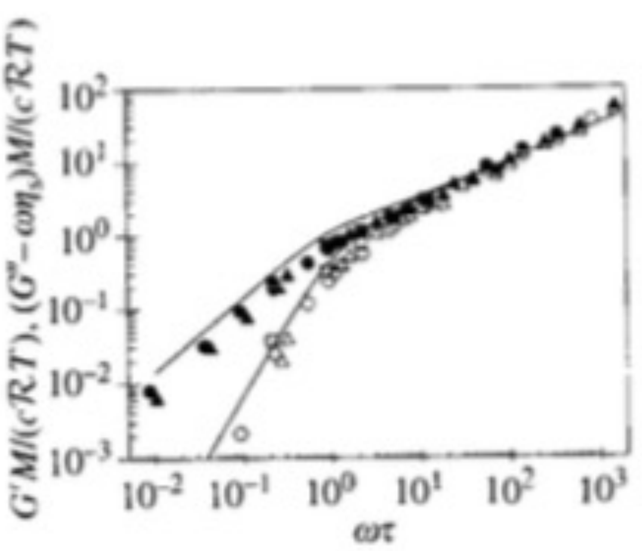


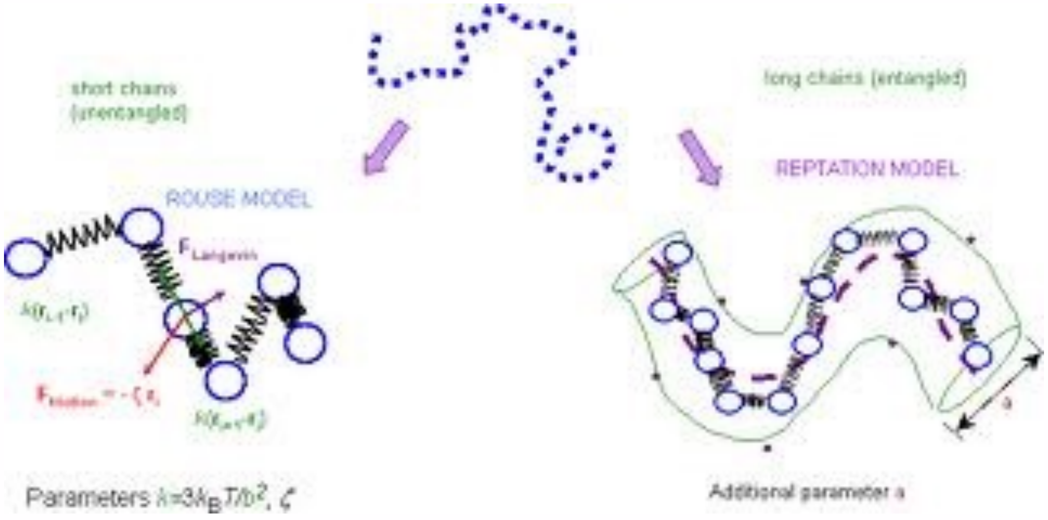
Fig. 8.5

Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus G' and filled symbols are the loss modulus G''. Squares have $c = 0.5\ \mathrm{g\ L^{-1}}$, triangles have $c = 1.0\ \mathrm{g\ L^{-1}}$, and circles have $c = 2.0\ \mathrm{g\ L^{-1}}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* **94**, 4581 (1991).

Dilute Solution Chain

Dynamics of the chain

Rouse Motion



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

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

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

Beads 0 and N are special

For Beads 1 to N-1

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

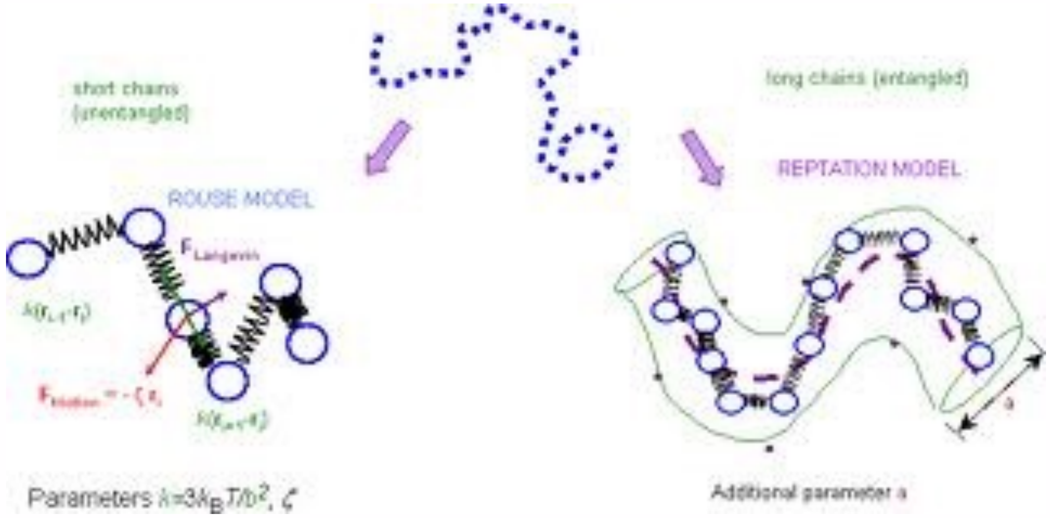
For Bead 0 use $R_{-1} = R_0$ and for bead N $R_{N+1} = R_N$

This is called a closure relationship

Dilute Solution Chain

Dynamics of the chain

Rouse Motion



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

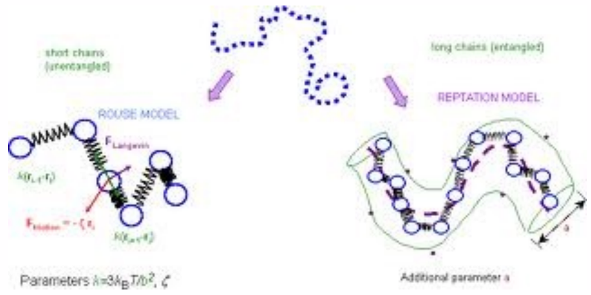
The Rouse unit size is arbitrary so we can make it very small and:

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

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

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

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

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

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

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

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

New slides to augment old talk

x, y, z decouple (are equivalent) so you can just deal with z

$$\varsigma_R \frac{dz_l}{dt} = b_R(z_{l+1} - z_l) + b_R(z_{l-1} - z_l)$$

For a chain of infinite molecular weight there are wave solutions to this series of differential equations

$$z_l \sim \exp\left(-\frac{t}{\tau}\right)\exp(il\delta)$$

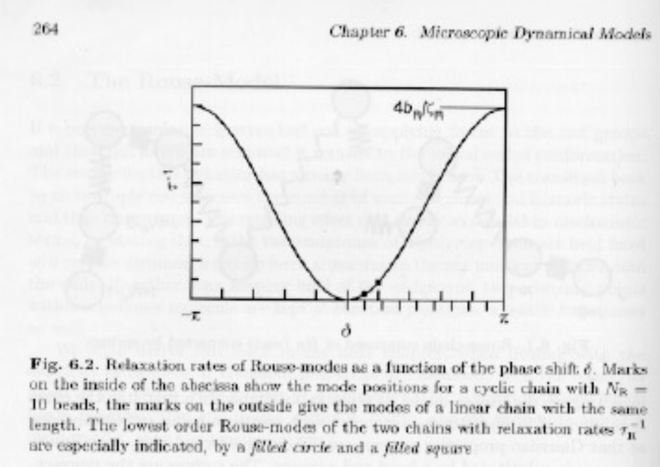


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Fig. 6.2. Relaxation rates of Rouse-modes as a function of the phase shift δ. Marks on the inside of the abscissa show the mode positions for a cyclic chain with $N_R = 10$ beads, the marks on the outside give the modes of a linear chain with the same length. The lowest order Rouse-modes of the two chains with relaxation rates τ_R^{-1} are especially indicated, by a *filled circle* and a *filled square*

$$\tau^{-1} = \frac{b_R}{\zeta_R}\left(2 - 2\cos\delta\right) = \frac{4b_R}{\zeta_R}\sin^2\frac{\delta}{2}$$

For N_R = 10

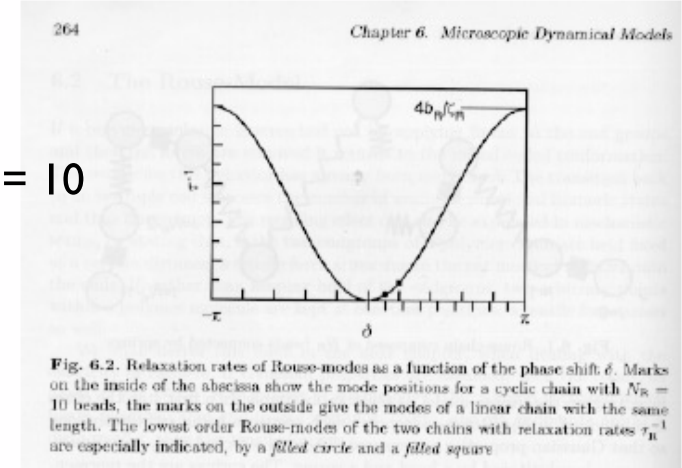
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Fig. 6.2. Relaxation rates of Rouse-modes as a function of the phase shift δ. Marks on the inside of the abscissa show the mode positions for a cyclic chain with N_R = 10 beads, the marks on the outside give the modes of a linear chain with the same length. The lowest order Rouse-modes of the two chains with relaxation rates τ_R^{-1} are especially indicated, by a *filled circle* and a *filled square*

$$\tau^{-1} = \frac{b_R}{\zeta_R}(2 - 2\cos\delta) = \frac{4b_R}{\zeta_R}\sin^2\frac{\delta}{2}$$

Cyclic Boundary Conditions:

$$z_l = z_{l+N_R}$$

$$N_R\delta = m2\pi$$

N_R values of phase shift

$$\delta_m = \frac{2\pi}{N_R}m; \quad m = -\left(\frac{N_R}{2} - 1\right),\ldots,\frac{N_R}{2}$$

For N_R = 10

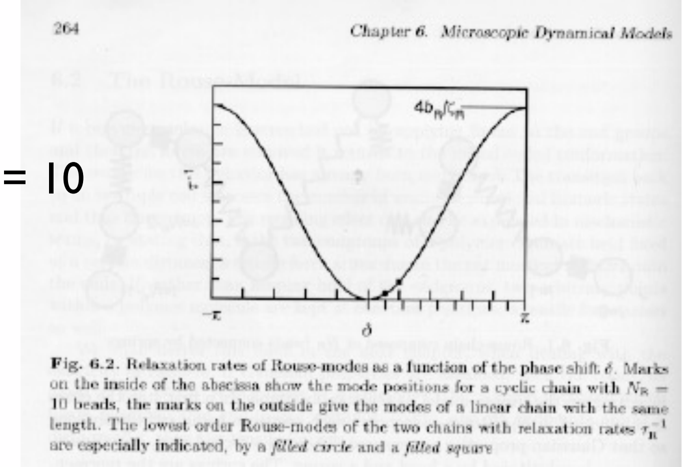

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Fig. 6.2. Relaxation rates of Rouse-modes as a function of the phase shift δ. Marks on the inside of the abscissa show the mode positions for a cyclic chain with N_R = 10 beads, the marks on the outside give the modes of a linear chain with the same length. The lowest order Rouse-modes of the two chains with relaxation rates τ_R^{-1} are especially indicated, by a *filled circle* and a *filled square*

$$\tau^{-1} = \frac{b_R}{\zeta_R}\left(2 - 2\cos\delta\right) = \frac{4b_R}{\zeta_R}\sin^2\frac{\delta}{2}$$

Free End Boundary Conditions:

$$z_l - z_0 = z_{N_R-1} - z_{N_R-2} = 0$$

$$\frac{dz}{dl}\left(l = 0\right) = \frac{dz}{dl}\left(l = N_R - 1\right) = 0$$

$$\left(N_R - 1\right)\delta = m\pi$$

N_R values of phase shift

N_R Rouse Modes of order “m”

$$\delta_m = \frac{\pi}{\left(N_R - 1\right)}m; \quad m = 0,1,2,\ldots,\left(N_R - 1\right)$$

Lowest order relaxation time dominates the response

$$\tau_R = \frac{1}{3\pi^2} \frac{\left(\frac{\zeta_R}{a_R^2}\right)}{kT} R_0^4$$

This assumes that $\left(\frac{\zeta_R}{a_R^2}\right)$

is constant, friction coefficient is proportional to number of monomer units in a Rouse segment

This is the basic assumption of the Rouse model,

$$\zeta_R \sim a_R^2 \sim \frac{N}{N_R} = n_R$$

Lowest order relaxation time dominates the response

$$\tau_R = \frac{1}{3\pi^2} \frac{\left(\frac{\zeta_R}{a_R^2}\right)}{kT} R_0^4$$

Since $R_0^2 = a_0^2 N$

$$\tau_R \sim \frac{N^2}{kT}$$

The amplitude of the Rouse modes is given by:

$$\left\langle Z_m^2 \right\rangle = \frac{2}{3\pi^2}\frac{R_0^2}{m^2}$$

The amplitude is independent of temperature because the free energy of a mode is proportional to kT and the modes are distributed by Boltzmann statistics

$$p\left(Z_m\right) = \exp\left(-\frac{\langle F\rangle}{kT}\right)$$

90% of the total mean-square end to end distance of the chain originates from the lowest order Rouse-modes so the chain can be often represented as an elastic dumbbell

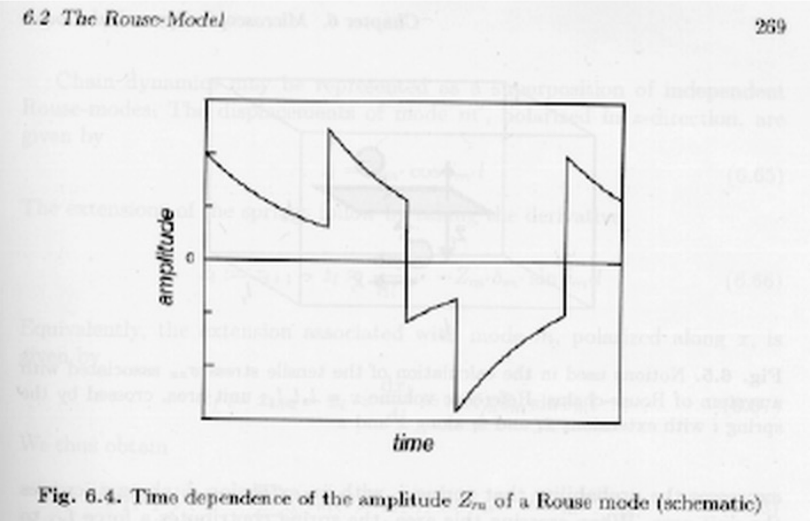

6.2 The Rouse-Model 269

Fig. 6.4. Time dependence of the amplitude Z_{rn} of a Rouse mode (schematic)

Rouse dynamics (like a dumbell response)

Dumbbell

$$\frac{dx}{dt} = -\frac{\left(\frac{dU}{dx}\right)}{\zeta} + g(t) = -\frac{k_{spr}x}{\zeta} + g(t)$$

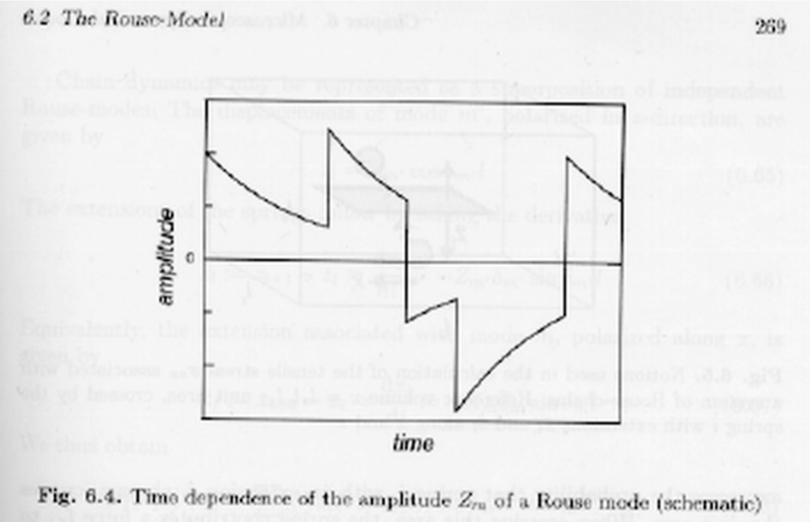
$$x(t) = \int_{-\infty}^{t} dt' \exp\left(-\frac{t-t'}{\tau}\right) g(t)$$

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

Rouse

$$\tau_R = \frac{\zeta_R}{4 b_R \sin^2 \frac{\delta}{2}}$$

$$\delta = \frac{\pi}{N_R - 1} m \; , \quad \mathrm{m=0,1,2,\ldots,N_R\text{-}1}$$



6.2 The Rouse-Model 269

Fig. 6.4. Time dependence of the amplitude Z_{ru} of a Rouse mode (schematic)

Rouse dynamics (like a dumbell response)

$$\left\langle g(t_1)g(t_2)\right\rangle = 2D\delta(t) \quad \text{where } t = t_1 - t_2 \quad \text{and } \delta(\ ) \text{ is the delta function whose integral is 1}$$

Also, $$D = \frac{kT}{\zeta}$$

$$\left\langle x(t)x(0)\right\rangle = \frac{kT\exp\left(-\frac{t}{\tau}\right)}{k_{spr}} \qquad \tau = \frac{\zeta}{k_{spr}}$$

For t => 0, $$\left\langle x^2\right\rangle = \frac{kT}{k_{spr}}$$

Predictions of Rouse Model

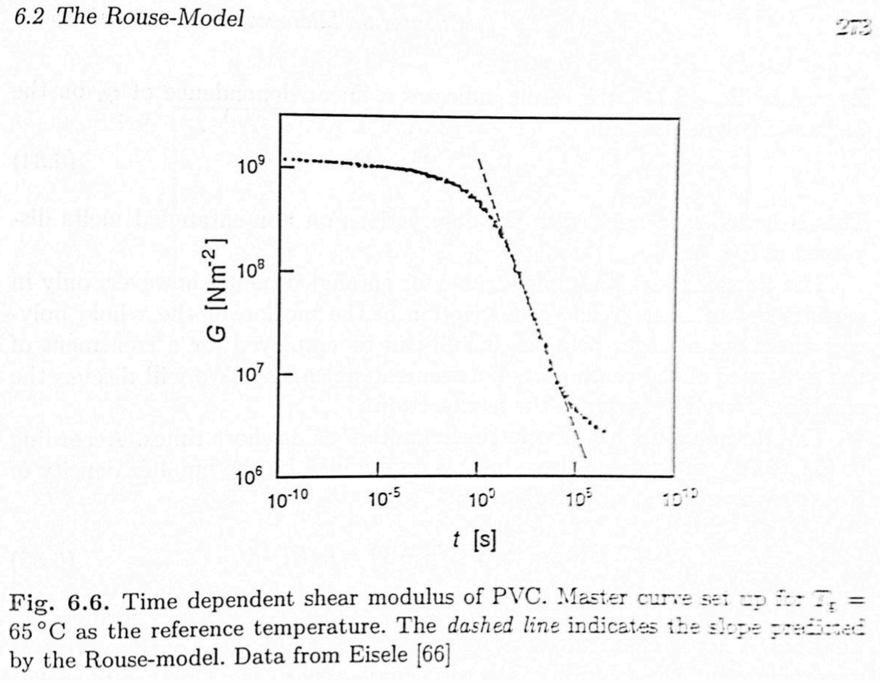


Fig. 6.6. Time dependent shear modulus of PVC. Master curve set up for T_g = 65 °C as the reference temperature. The *dashed line* indicates the slope predicted by the Rouse-model. Data from Eisele [66]

$$G(t)\sim t^{-\frac{1}{2}}$$

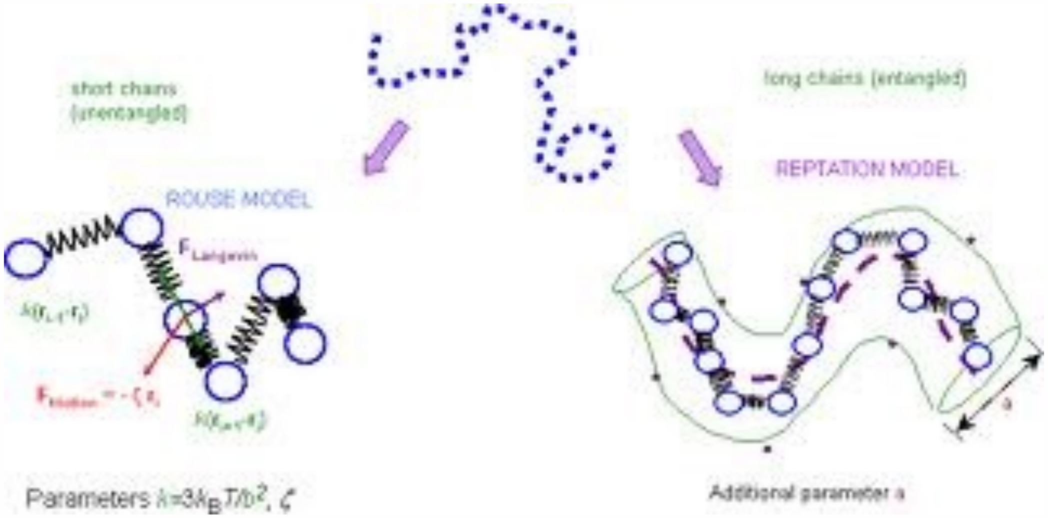
$$G'(\omega)\sim(\omega\eta_0)^{\frac{1}{2}}$$

$$\eta_0 = kT\rho_p\tau_R\frac{\pi^2}{12}\sim N$$

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

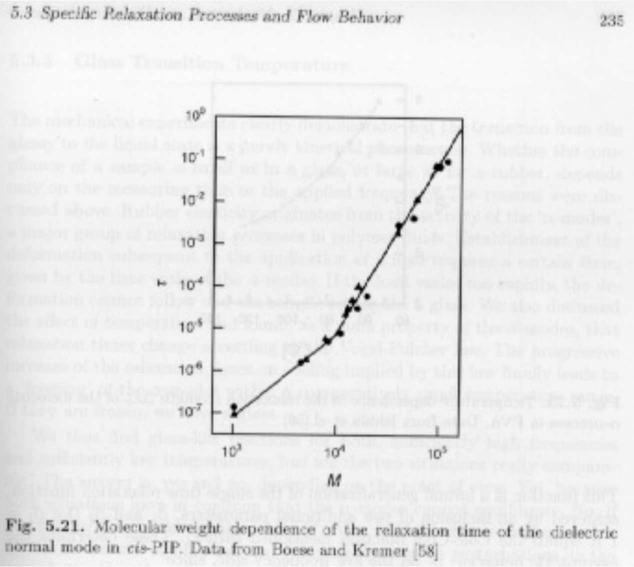

5.3 *Specific Relaxation Processes and Flow Behavior* 235

Fig. 5.21. Molecular weight dependence of the relaxation time of the dielectric normal mode in *cis*-PIP. Data from Boese and Kremer [58]

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

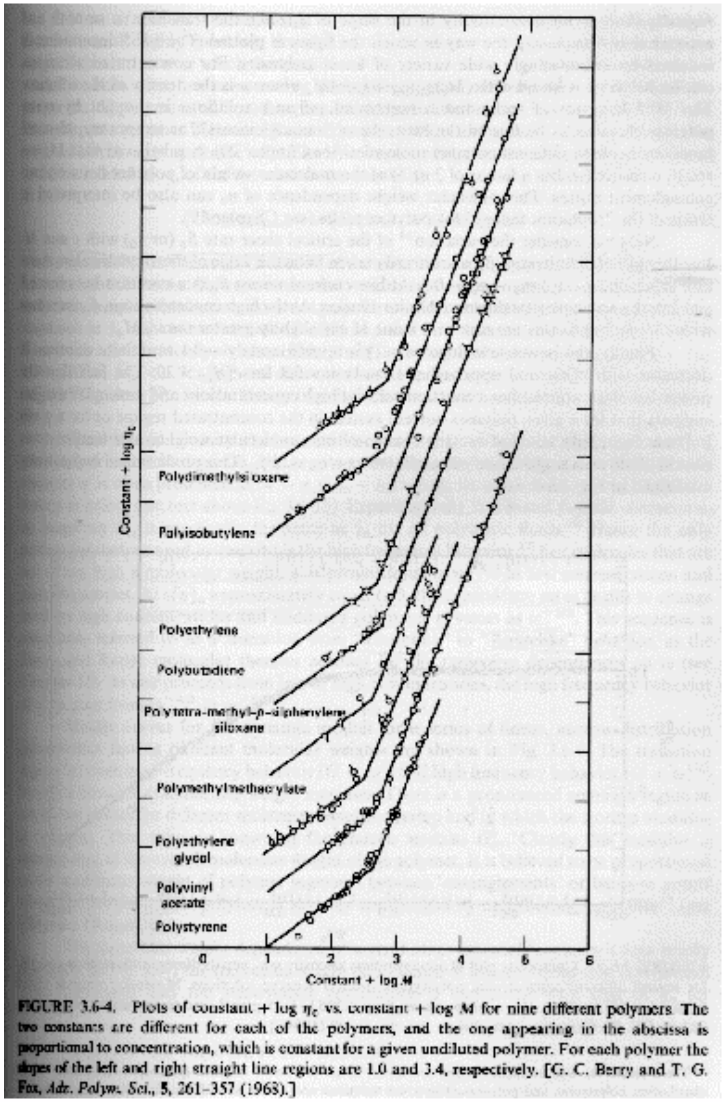


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of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

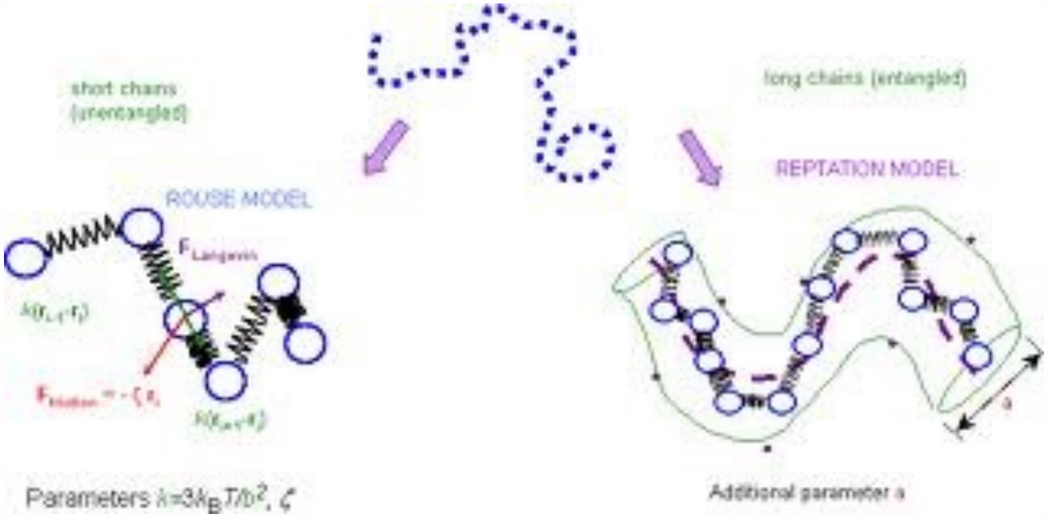
Rouse model predicts
Relaxation time follows N^2 (actually follows N^3/df)

Hierarchy of Entangled Melts

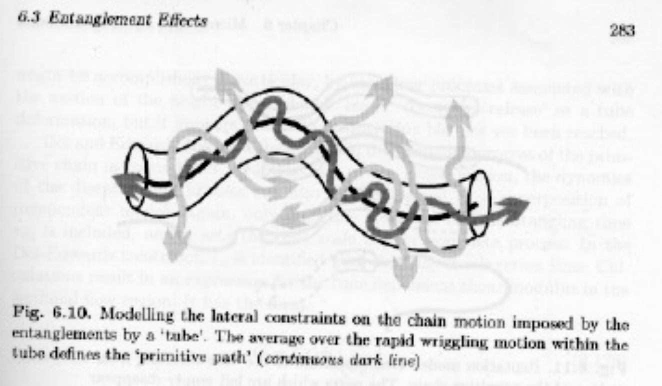
Hierarchy of Entangled Melts

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

Tube Diameter d_T
Kuhn Length l_K
Packing Length p

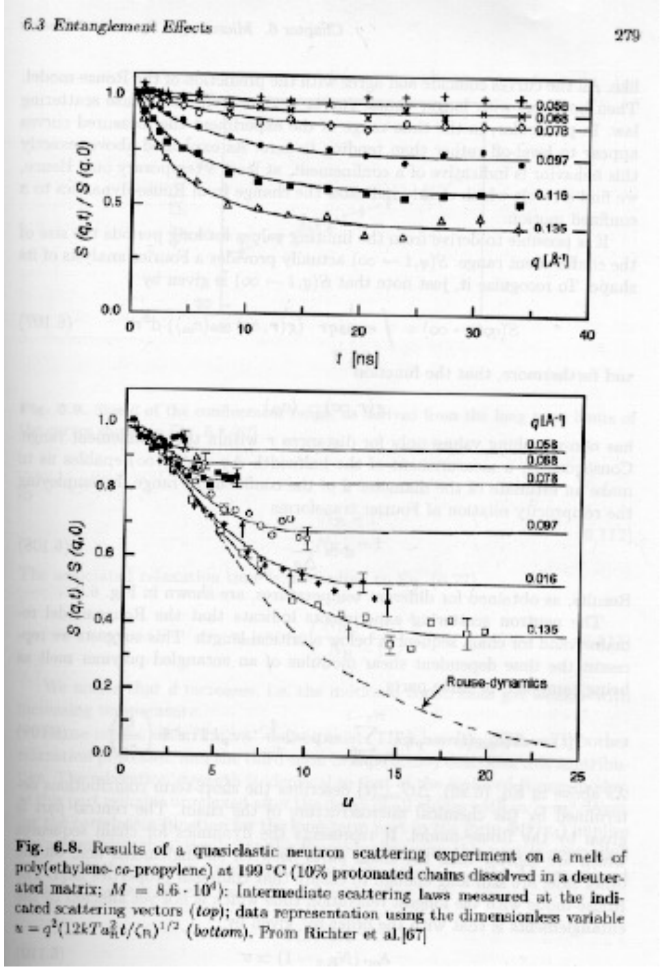


http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/SukumaranScience.pdf



6.3 Entanglement Effects 283

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*)



6.3 Entanglement Effects 279

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

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

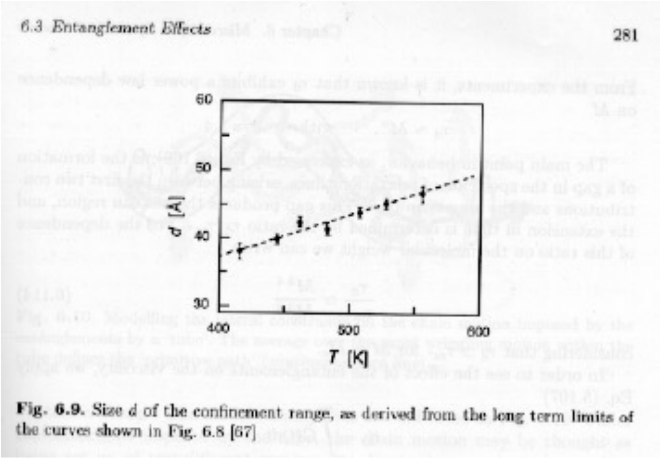
Unconstrained motion => S(q) goes to 0 at very long times

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



6.3 Entanglement Effects 281

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 $N^{3.4}$)

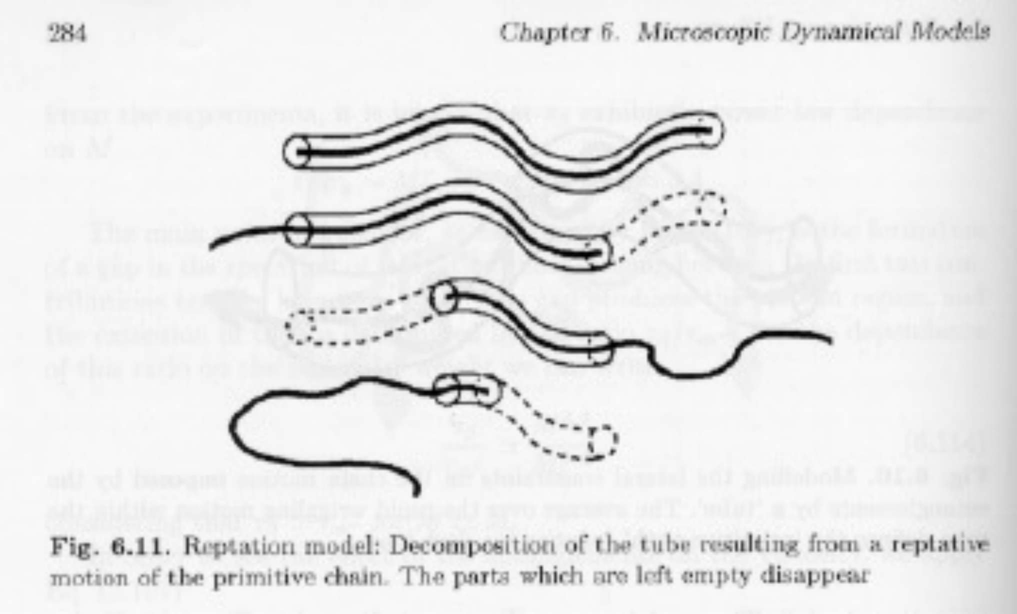


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Fig. 6.11. Reptation model: Decomposition of the tube resulting from a reptative motion of the primitive chain. The parts which are left empty disappear

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

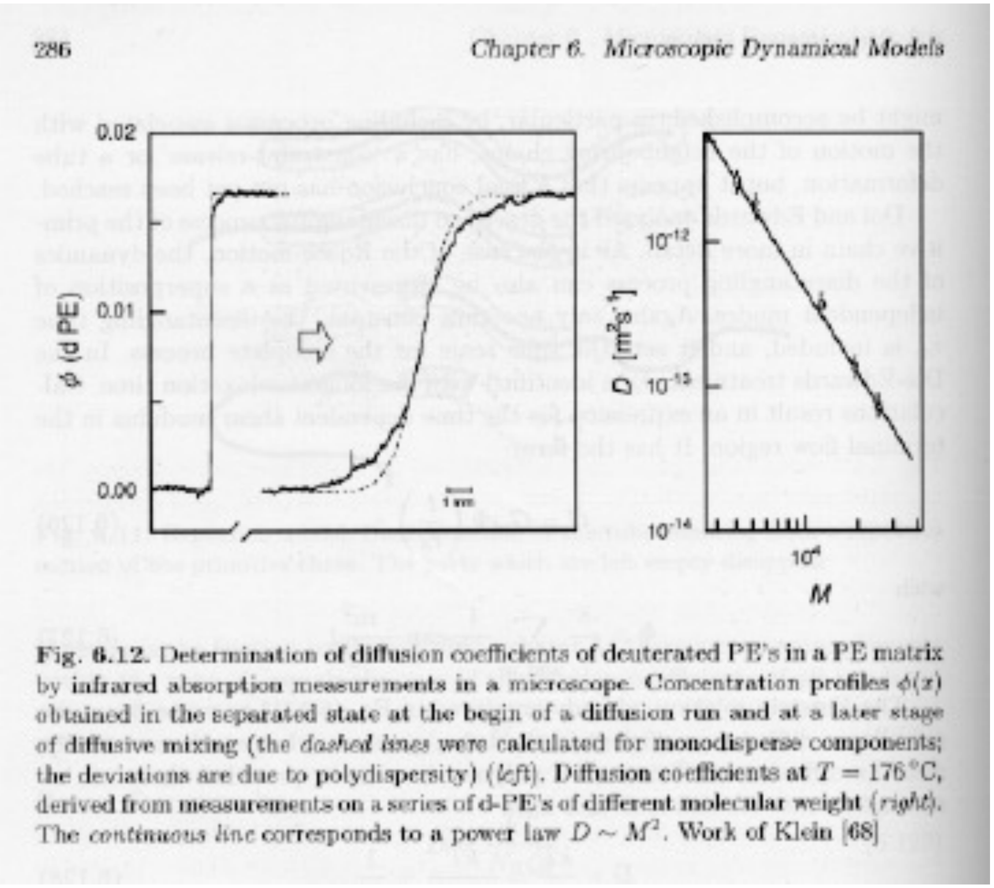

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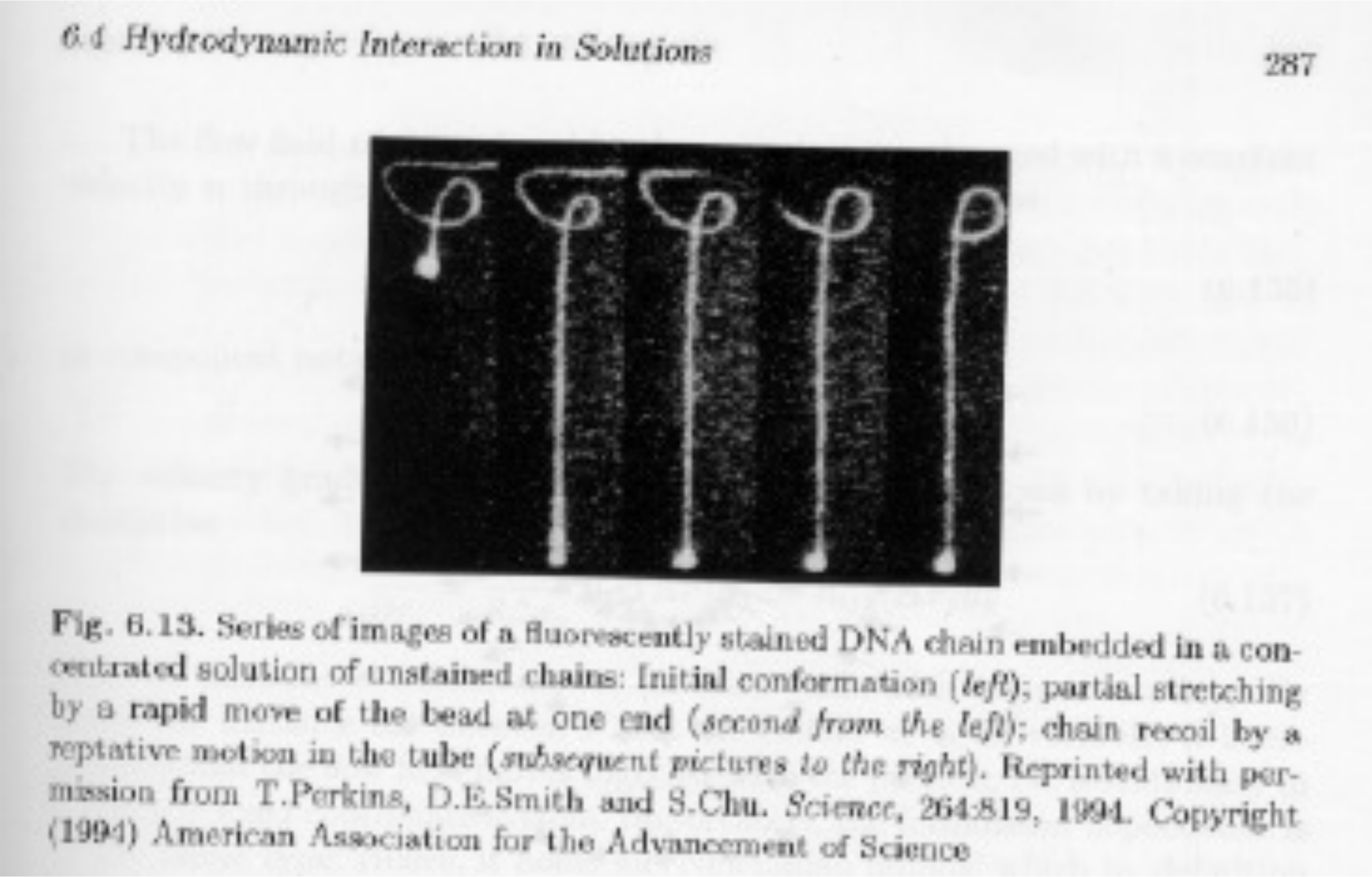
Fig. 6.12. Determination of diffusion coefficients of deuterated PE's in a PE matrix by infrared absorption measurements in a microscope. Concentration profiles $\phi(x)$ obtained in the separated state at the begin of a diffusion run and at a later stage of diffusive mixing (the *dashed lines* were calculated for monodisperse components; the deviations are due to polydispersity) (*left*). Diffusion coefficients at $T = 176\,^\circ\mathrm{C}$, 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 ~ 1/N)

Reptation of DNA in a concentrated solution



6.4 Hydrodynamic Interaction in Solutions 287

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

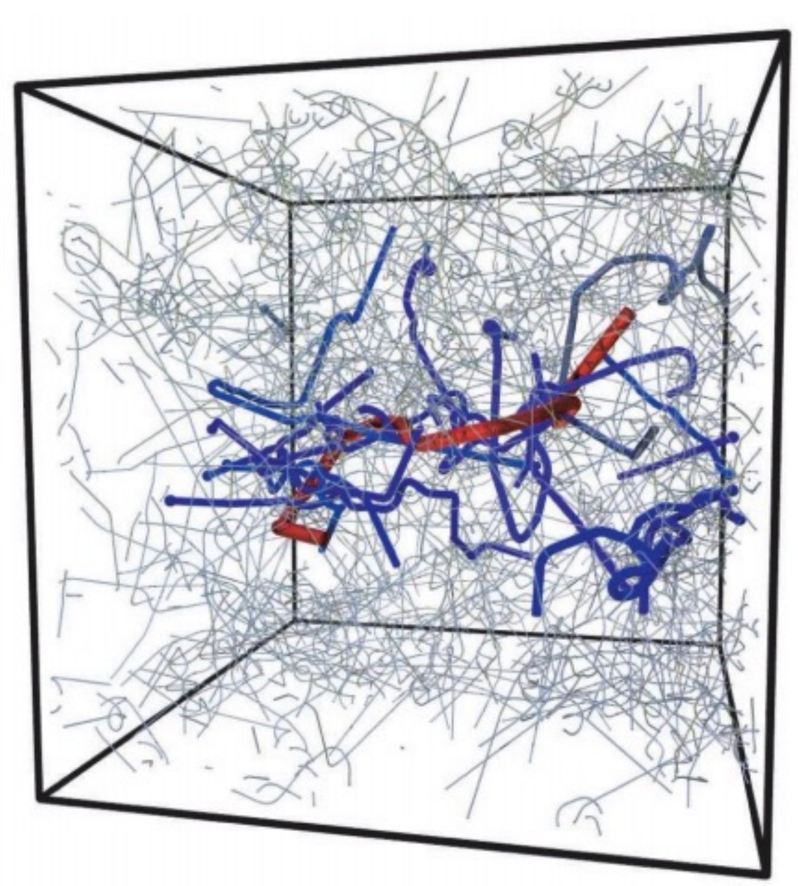


Fig. 3. Result of the primitive-path analysis of a melt of 200 chains of $N + 1 = 350$ beads. We show the primitive path of one chain (red) together with all of those it is entangled with (blue). The primitive paths of all other chains in the system are shown as thin lines.

Simulation of the tube

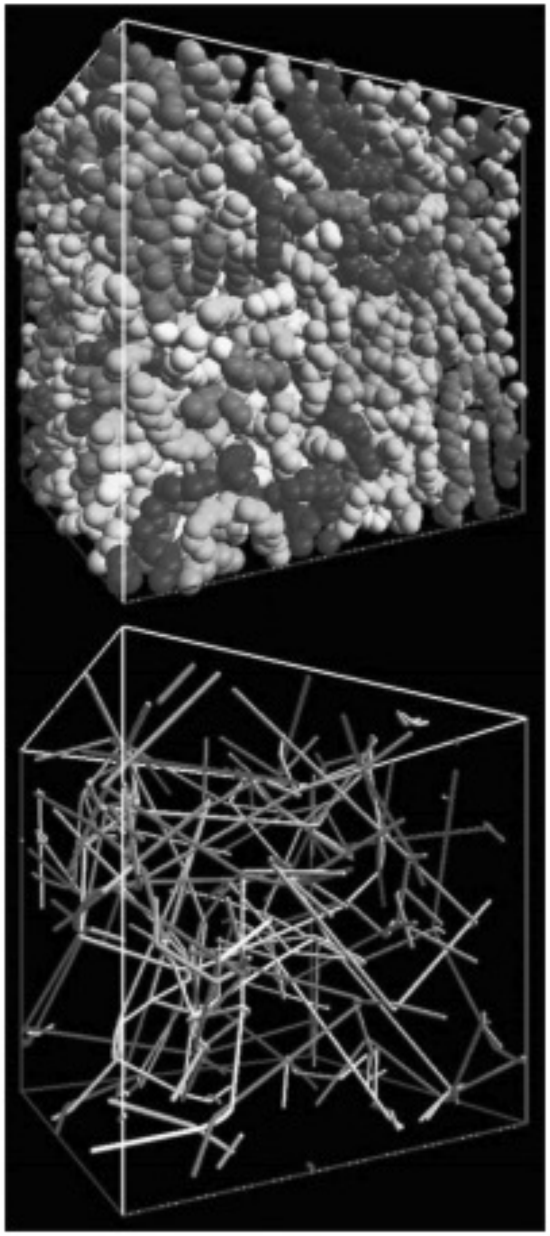


Fig. 3. A representative amorphous polymer sample and the corresponding network of primitive paths.

Plateau Modulus

Not Dependent on N, Depends on T and concentration

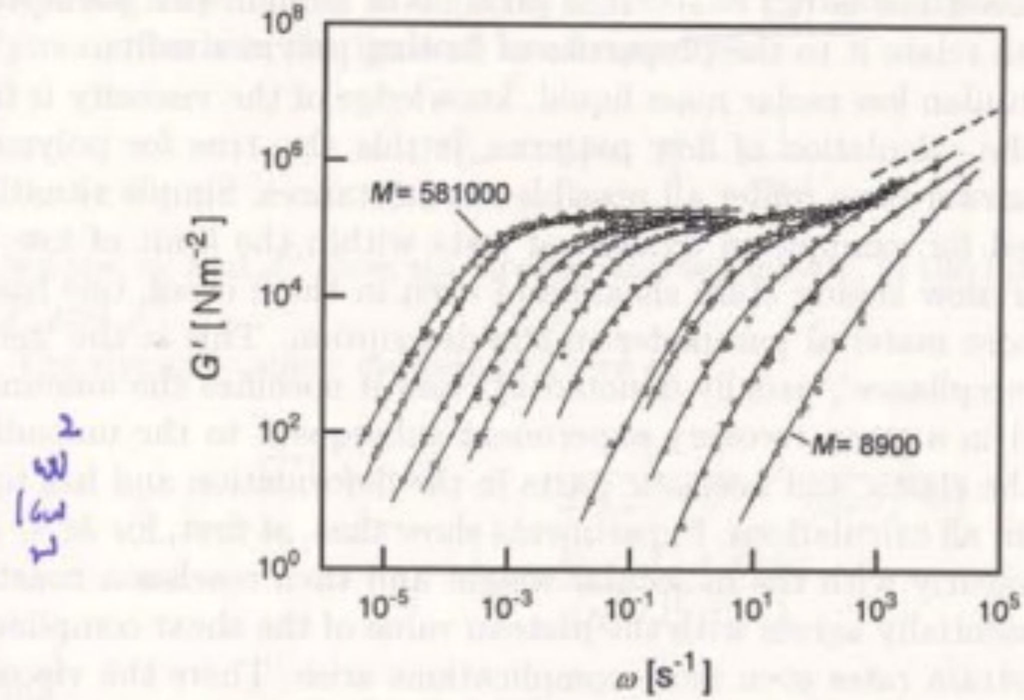


Fig. 5.15. Storage shear moduli measured for a series of fractions of PS with different molecular weights in the range $M = 8.9 \cdot 10^3$ to $M = 5.81 \cdot 10^5$. The *dashed line* in the upper right corner indicates the slope corresponding to the power law Eq. (6.81) derived for the Rouse-model of 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 $<R^2> = l_K L$

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

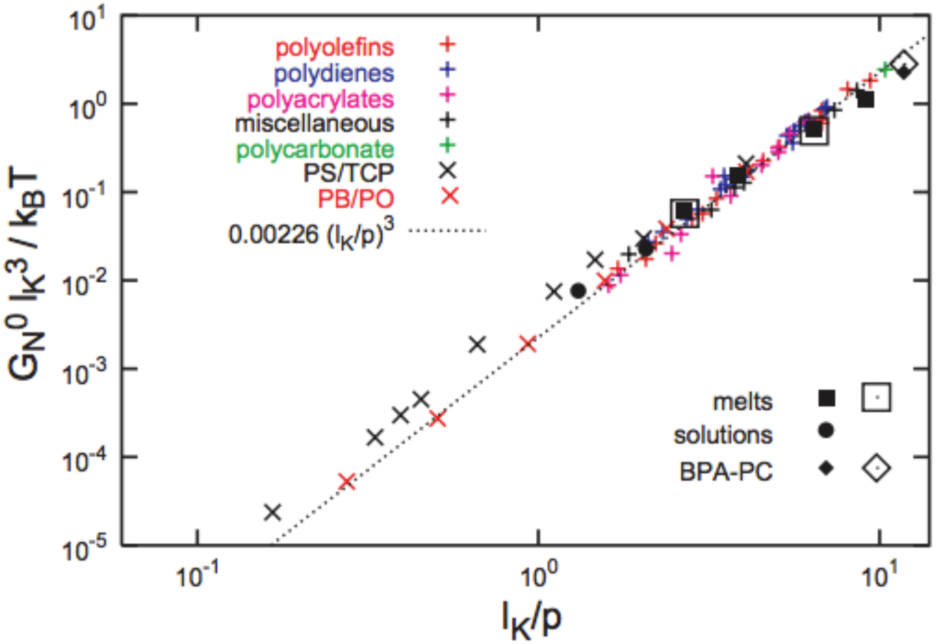


Fig. 2. Dimensionless plateau moduli Gl_K^3/k_BT as a function of the dimensionless ratio l_K/p of Kuhn length l_K and packing length p. The figure contains (i) experimentally measured plateau moduli for polymer melts (*25*) (+; colors mark different groups of polymers as indicated) and semidilute solutions (*26–28*) (×); (ii) plateau moduli inferred from the normal tensions measured in computer simulation of bead-spring melts (*35, 36*) (□) 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 $d_T \sim p$

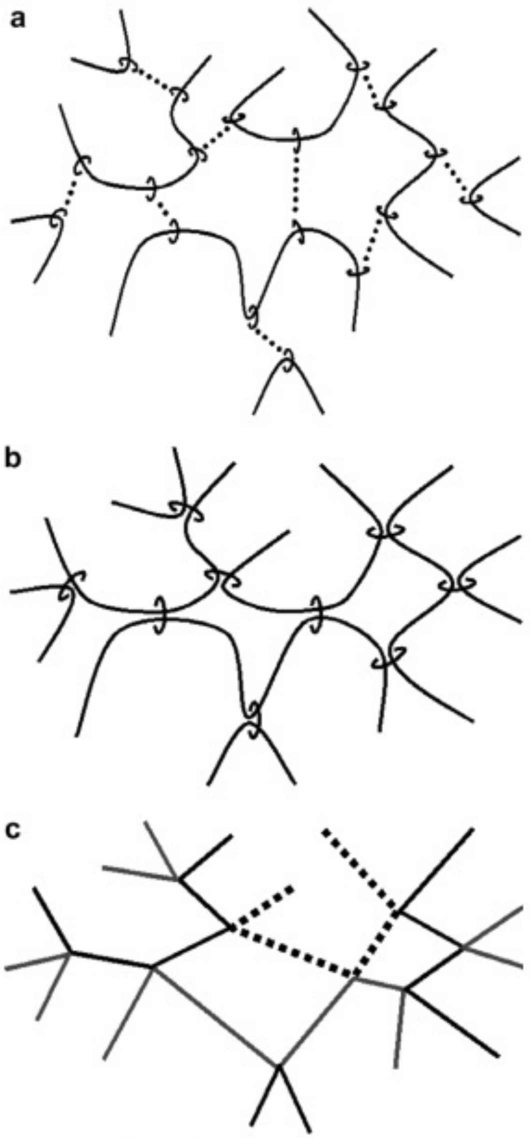
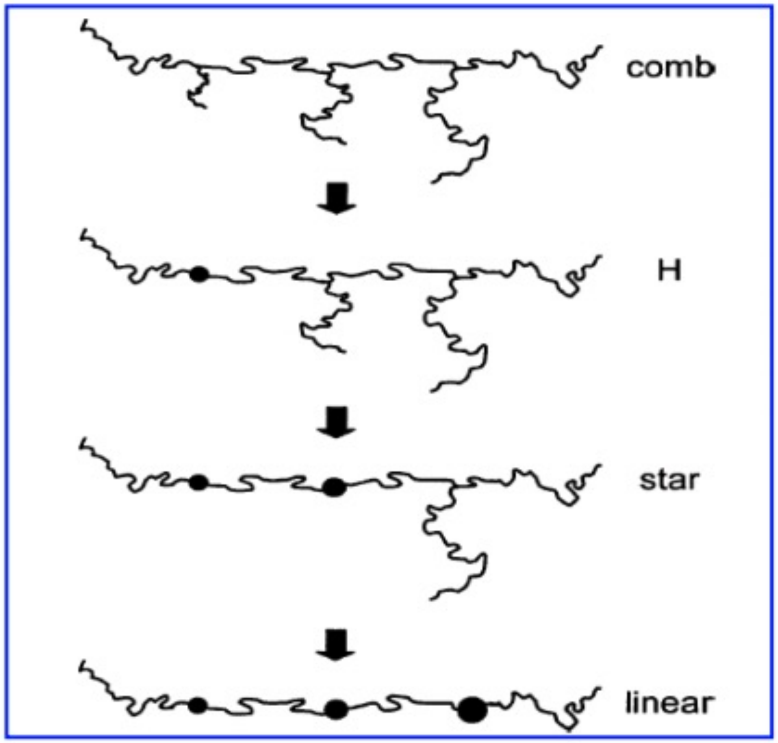


Fig. 1. Schematic representation of dual slip-links. (a) Chains coupled by virtual links. (b) Dual slip-links. (c) Real space representation of the corresponding network of primitive paths.

McLeish/Milner/Read/Larsen Hierarchical Relaxation Model

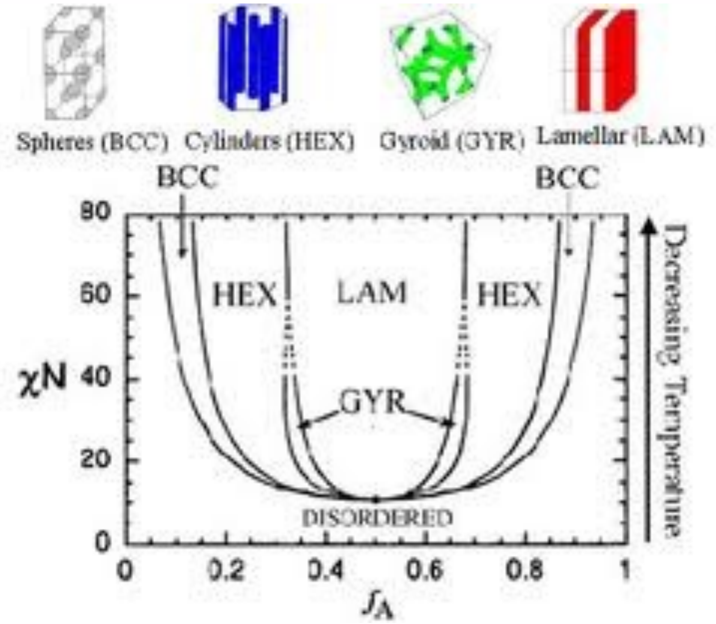


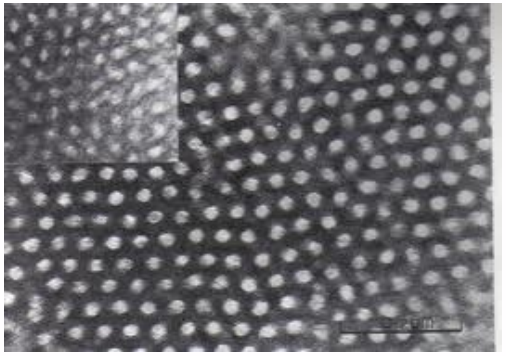
http://www.engin.umich.edu/dept/che/research/larson/downloads/Hierarchical-3.0-manual.pdf

Block Copolymers

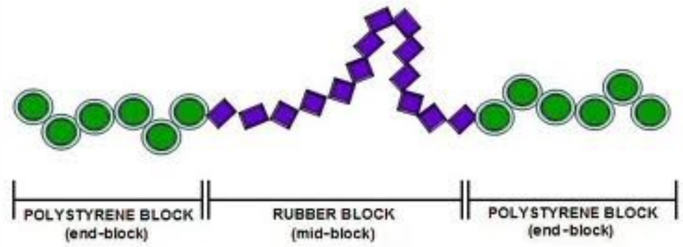
http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/BCP%20Section.pdf

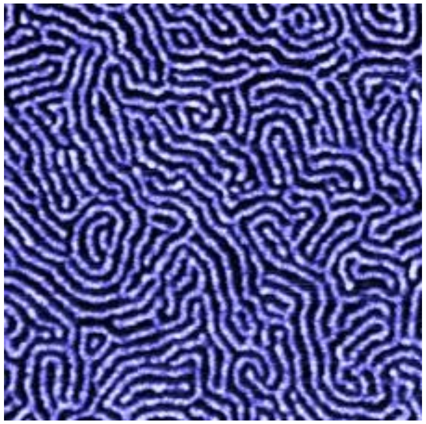
Block Copolymers





SBR Rubber





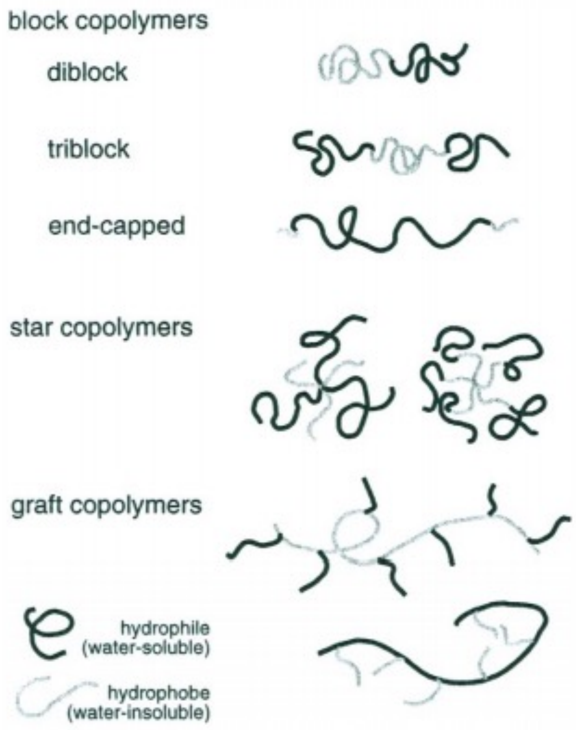


Figure 9. Schematics of block, star, and graft amphiphilic block copolymers.

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

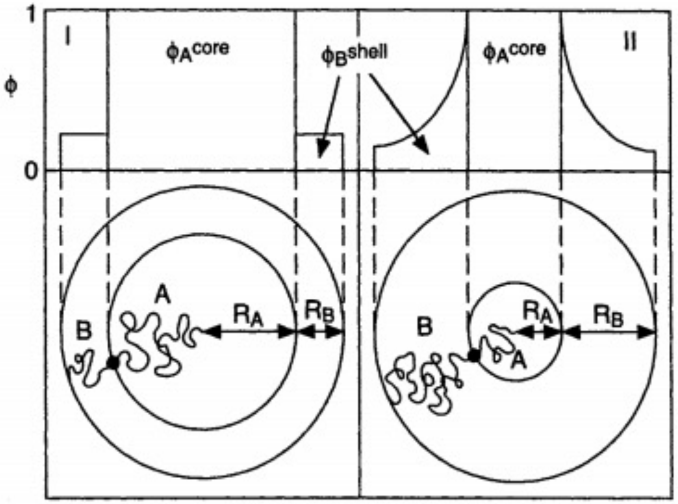
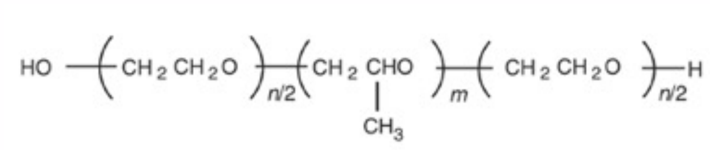


Figure 1. Illustration of model I (left) and II (right) of the AB-diblock copolymer micelle in a selective solvent (lower panel) and the volume fraction profiles of the polymer blocks (upper panel) applied for the large core case ($N_A >> N_B$) and the small core case ($N_A << N_B$), respectively.

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

Hierarchy in BCP’ s and Micellar Systems



$$HO-\left(CH_2CH_2O\right)_{n/2}\left(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO\right)_m\left(CH_2CH_2O\right)_{n/2}H$$

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 organizaiton 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 Φ = 1/2

-Layer thickness D in a cube of edge length L, surface energy σ

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

-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

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

b is the step length per N unit, νc 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 $D \cong \left(\frac{\sigma N^2 b^2 \upsilon_c}{kT} \right)^{1/3} \sim N^{2/3}$

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

<R^2> has a value:

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

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

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