

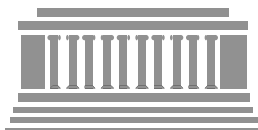
# Developments and Trends in Light Scattering on Macromolecular Solutions

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YOU CAME INTO  
THE DEN TO  
GET YOUR  
GLASSES.

The agony of getting older.

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**LIGHT  
SCATTERING**  
by small particles

by  
**H.C. van de Hulst**  
Leiden Observatory

**Dover Publications, Inc.**  
**New York**

**THE SCATTERING OF LIGHT**  

---

*AND OTHER ELECTROMAGNETIC RADIATION*

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**ACADEMIC PRESS, INC.**  
*Harcourt Brace Jovanovich, Publishers*  
San Diego New York Berkeley Boston  
London Sydney Tokyo Toronto

# STATIC LIGHT SCATTERING

**Rayleigh ratio** from a solution with solute concentration  $c$

$$\mathbf{R}_{Si}(\mathbf{q}, c) = r^2 I_{Si}(\vartheta) / V_{\text{obs}} I_{\text{INC}}$$

$S$  and  $i$  designate the polarization state of the electric vectors of the Scattered and Incident light, respectively, relative to the scattering plane.

- $\mathbf{k}_0$  vectoral wave number along the incident beam
- $\mathbf{k}$  vectoral wave number along the scattered beam
- $\mathbf{q}$  is the vector difference between the and scattered light, respectively:

$$\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$$

- $|\mathbf{k}_0| = |\mathbf{k}| = (4\pi n/\lambda)$  for static scattering, with  $\lambda$  the wavelength in vacuum
- The modulus  $|\mathbf{q}|$  of the scattering vector  $\mathbf{q}$  becomes

$$q = (4\pi/\lambda)\sin(\vartheta/2)$$

$\mathbf{R}_{Hv}(q,c)$  and  $\mathbf{R}_{Vv}(q,c)$  are given by (Using  $I_{\text{solution}} - I_{\text{solvent}}$ ):

$$\mathbf{R}_{Hv}(q,c) = \mathbf{R}_{\text{aniso}}(q,c)$$

$$\mathbf{R}_{Vv}(q,c) = \mathbf{R}_{\text{iso}}(q,c) + (4/3)\mathbf{R}_{\text{aniso}}(q,c) + \mathbf{R}_{\text{cross}}(q,c)$$

- $\mathbf{R}_{\text{iso}}(q,c)$ : Isotropic component
- $\mathbf{R}_{\text{aniso}}(q,c)$ : Anisotropic component

NOTE: When considering the scattering from a solute with isotropic scattering elements,  $\mathbf{R}_{Vv}(q,c) = \mathbf{R}_{\text{iso}}(q,c)$ , and the subscript will be suppressed

## Isotropic scatterers:

$$\mathbf{R}(q,c) = K_{op}cM \mathbf{S}(q,c) ; \quad \mathbf{S}(q,c) = P(q,c)F(q,c)$$

(Note:  $S(q,c)$  is sometimes used to denote a different function than that defined here.)

Two expressions are commonly employed to represent  $F(q,c)$ :

$$F(q,c) = 1 - cB(c)P(q,c)Q(q,c); \quad F(q,c)^{-1} = 1 + c\Gamma(c)P(q,c)H(q,c)$$

$$\Gamma(c) = B(c)/[1 - cB(c)]; \quad H(q,c) = Q(q,c) \frac{[1 - cB(c)]}{[1 - cB(c)P(q,c)Q(q,c)]}$$

$$\frac{K_{op}cM}{\mathbf{R}(q,c)} = \frac{1}{\mathbf{S}(q,c)} = \frac{1}{P(q,c)} + c\Gamma(c)H(q,c)$$

For a **monodisperse solute (*only*)**,  $F(0,c)$  is related to the equilibrium osmotic modulus  $K_{OS}$ :

$$F(0,c) = (M/cRT) K_{OS}$$

$$K_{OS} = c \partial \Pi / \partial c$$

where  $\Pi$  is the osmotic pressure.

With this expression, for a *monodisperse* solute,

$$c\Gamma(c) = \frac{M \partial \Pi}{RT \partial c} - 1$$

**Note:** This expression is often misapplied for a heterodisperse solute.

## DYNAMIC LIGHT SCATTERING

$$g^{(2)}(\tau; q, c) = 1 + f_c |g^{(1)}(\tau; q, c)|^2$$

$$g^{(1)}(\tau; q, c) \approx \sum_{\mu} r_{\mu}(q, c) \exp[-\tau \gamma_{\mu}(q, c)]; \quad \sum_{\mu} r_{\mu} = 1$$

$$\ln[g^{(2)}(\tau; q, c) - 1]^{1/2} = \ln[f_c]^{1/2} - K^{(1)}(q, c)\tau + \frac{1}{2!} K^{(2)}(q, c)\tau^2 + \dots$$

$$\lim_{q \rightarrow 0} K^{(1)}(q, c)/q^2 = D_M(c)$$

$$a_{LS}(c) = \frac{kT}{6\pi\eta D_M(c)} ; \quad \lim_{c \rightarrow 0} a_{LS}(c) = R_H; \quad \text{Hydrodynamic Radius}$$

## Static scattering extrapolated to infinite dilution:

$$[\mathbf{R}(q,c)/c]^0 = K' \hat{n}_s^2 (\partial \hat{n} / \partial c)_w^2 M_{LS} P_{LS}(q,0)$$

LS denotes an averaging over heterodispersity appropriate for scattering;  $K' = 4\pi^2 / N_A \lambda_0^4$ ,

$$M_{LS} = [\mathbf{R}(0,c)/c]^0 / K' \hat{n}_s^2 (\partial \hat{n} / \partial c)_w^2$$

In the RGD limit for a solute:

$$M_{LS} = \Psi^{-2} \sum_v^C w_v M_v^{-1} \left\{ \sum_j^{n_v} \Psi_{j,v} m_{j,v} \right\}^2$$

For identical isotropic scattering elements:

<i>Single solvent component</i>	<i>Multiple solvent components</i>
$M_{LS} = \sum_v^C w_v M_v = M_w$	$M_{LS} = \frac{(\partial \hat{n} / \partial c)_\Pi^2}{(\partial \hat{n} / \partial c)_w^2} M_w$

*Two, optically distinct scattering elements, single solvent component:*

$$M_{LS} = (1 + 2\mu_1 Y + \mu_2 Y^2)M_w$$

$$Y = \frac{\tilde{\Psi}_A - \tilde{\Psi}_B}{\tilde{\Psi}} \approx \frac{n_A - n_B}{w_A n_A + (1 - w_A)n_B}$$

$$\mu_n = \sum_v^C w_v M_v \Delta w_v^n / M_w; \quad n = 1, 2$$

$$\Delta w_v = w_{Av} - w_A = w_B - w_{Bv}$$

Special cases for which  $\Delta w_v = 0$ , so that  $\mu_1 = \mu_2 = 0$ :

- random and alternating copolymers
- regular block copolymers or stratified particles with uniform structures among the molecules

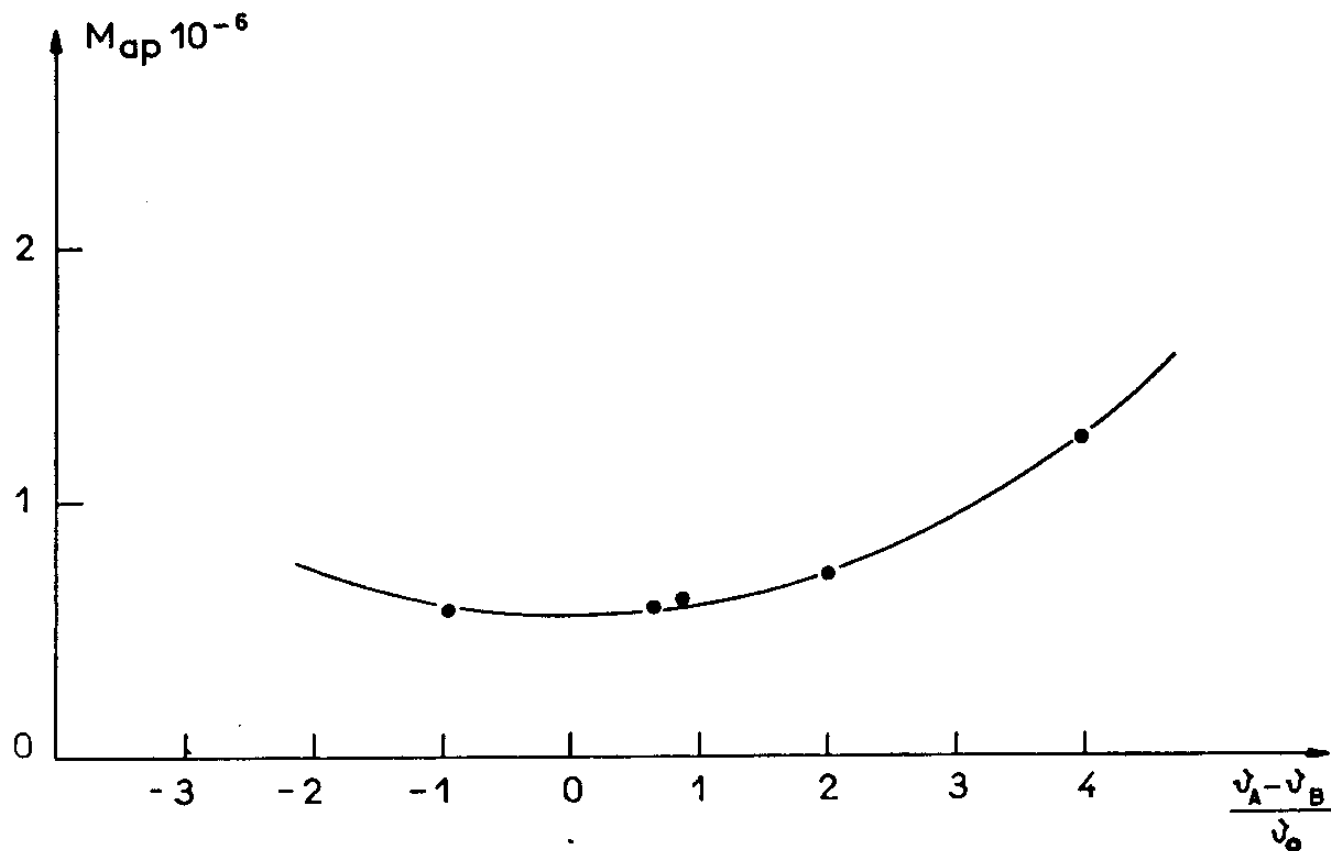


FIG. 3. Experimental results for a copolymer. Apparent molecular weight of polystyrene polymethylmethacrylate in various solvents plotted vs.  $(\nu_A - \nu_B)/\nu_0$ .

(Benoit)

## Depolarized scattering in the RGD regime:

Identical cylindrically symmetric polarizabilities for all chain elements:

$$\frac{[\mathbf{R}_{\text{aniso}}(0, \mathbf{c})/\mathbf{c}]^0}{K' \hat{n}_s^2 (\partial \hat{n} / \partial \mathbf{c})_w^2} = (3/5) M_w \delta_{\text{LS}}^2$$

$$\delta_{\text{LS}}^2 = M_w^{-1} \sum_v^C w_v M_v \delta_v^2 ;$$

$$\delta_v^2 = \frac{\delta_0^2}{n_v} \sum_j^{n_v} \sum_k^{n_v} (3/2) [\langle \cos^2 \beta_{ij} \rangle - 1]$$

- $\beta_{ij}$  is the angle between the major axes of scattering elements  $i$  and  $j$

- $\delta_0 = \frac{\alpha_{\parallel} - \alpha_{\perp}}{\alpha_{\parallel} + 2\alpha_{\perp}}$

*For an optically anisotropic homogeneous solute:*

$$M_{\text{LS}, \text{Hv}} = (3/5) \delta_{\text{LS}}^2 M_w ;$$

$$M_{\text{LS}, \text{Vv}} = \{1 + (4/5) \delta_{\text{LS}}^2\} M_w$$

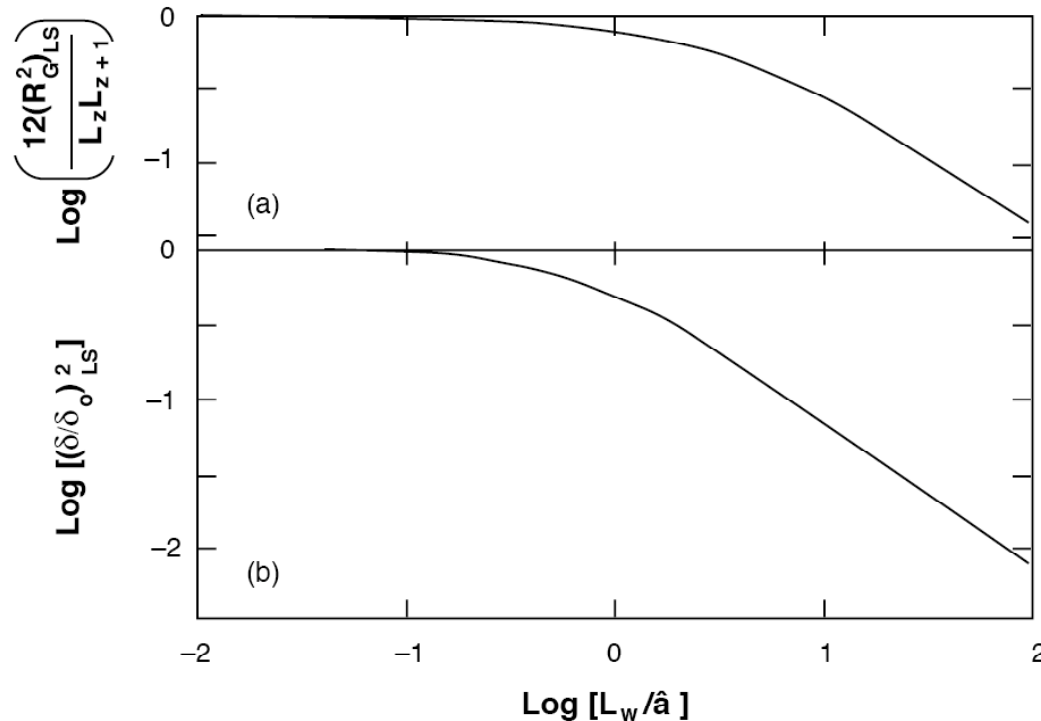
## Wormlike chain model:

- persistence length  $\hat{a}$
- contour length  $L$
- mass per unit length  $M_L = M/L$

$$\delta_v^2/\delta_0^2 = (2Z_v/3)\{1 - (Z_v/3)[1 - \exp(-3Z_v^{-1})]\}; \quad Z_v = \hat{a}/L_v.$$

$$\text{rod: } M_w \delta_{LS}^2 = \delta_0^2 M_w$$

$$\text{coil: } M_w \delta_{LS}^2 = \delta_0^2 m_0 \ll \delta_0^2 M_w$$



## ***Scattering beyond the Rayleigh-Gans-Debye (RGD) regime:***

- RGD approximation that the electric field giving rise to the dipole radiation of the scattered light is that of the incident radiation propagating in the medium is the same as that acting on the solvent is usually valid for "*threadlike*" molecules;
- RGD approximation may fail for large particles, particularly if the particle refractive index is very different from the suspending medium.

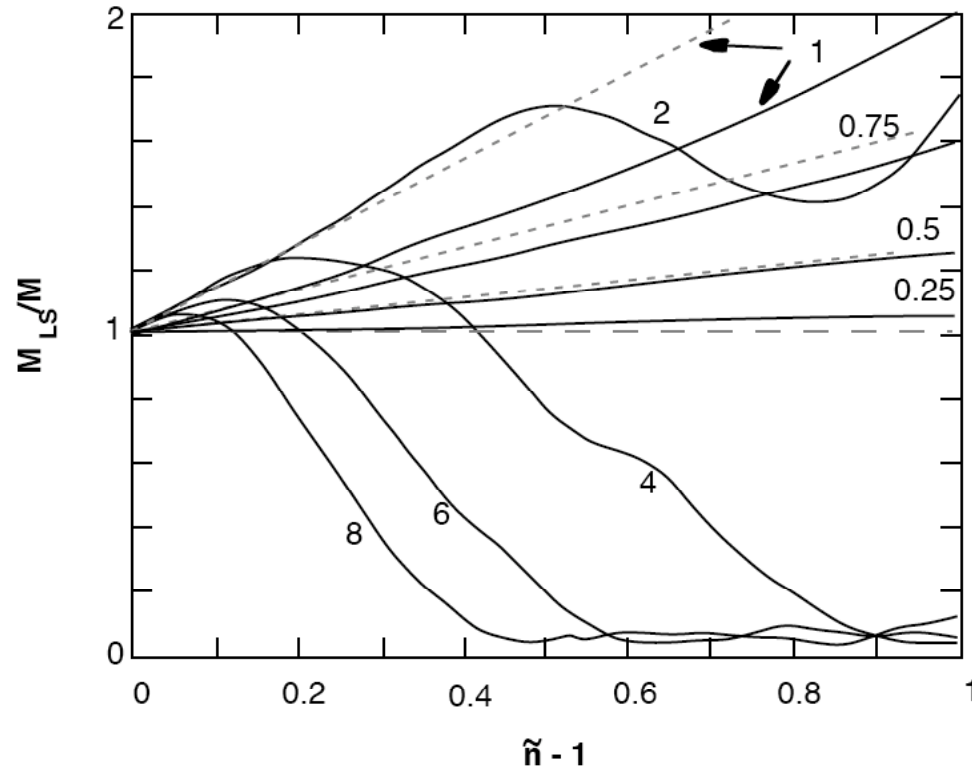
For nonabsorbing, optically homogeneous particles, two modifications are required to compute  $M_{LS}$ :

- $\Psi \Rightarrow h_{\text{sph}}(\tilde{n})\Psi$ ;  $h_{\text{sph}}(\tilde{n}) = 3(\tilde{n} + 1)/2(\tilde{n}^2 + 2)$ ;  $\tilde{n} = \hat{n}_{\text{solute}}/\hat{n}_{\text{medium}}$
- A function  $m(\tilde{n}, \lambda, M_v)$  *specific for each particle shape* is required:

$$M_{LS} = \sum_v^C w_v M_v [m(\tilde{n}, \lambda, M_v)]^2$$

Special case, *Mie scattering* for spherical particles:

$$M_{LS} = \sum_{\nu}^C w_{\nu} M_{\nu} [m_{\text{sph}}(\tilde{n}, \tilde{\alpha}_{\nu})]^2; \quad \tilde{\alpha}_{\nu} = 2\pi R_{\nu} / \lambda$$



**Fraunhofer scattering regime** for monodisperse spheres ( $\tilde{\alpha} > 4$  and  $\tilde{n} > 1.4$ ),

$$M_{LS} \approx M \{ 3/2 \tilde{\alpha}^2 (\tilde{n} - 1) h_{\text{sph}}(\tilde{n}) \}^2$$

**Scattering at infinite dilution and "small" scattering angle in the RGD regime:**

$$[\mathbf{R}(q,c)/c]^0 = K' \hat{n}_s^2 (\partial \hat{n} / \partial c)_w^2 M_{LS} \mathbf{P}_{LS}(q,0)$$

(Optically isotropic scattering elements)

$$P_{LS}(q,0) = 1 - (1/3)q^2 R_{G,LS}^2 + \dots$$

$$R_{G,LS}^2 = \frac{\sum_v^C w_v M_v^{-1} \sum_j^{n_v} \sum_k^{n_v} \Psi_{j,v} \Psi_{k,v} m_{j,v} m_{k,v} \langle |r_{jk}|_v^2 \rangle}{2 \sum_v^C w_v M_v^{-1} \left[ \sum_j^{n_v} \Psi_{j,v} m_{j,v} \right]^2}$$

## *Identical scattering elements:*

$$R_{G,LS}^2 = \frac{1}{M_w} \sum_v^C w_v M_v R_{G,v}^2; \quad R_{G,v}^2 = \frac{1}{2n_v} \sum_j^{n_v} \sum_k^{n_v} \langle |r_{jk}|^2 \rangle \approx (R_G^2/M^\varepsilon) M_v^\varepsilon$$

Similarly, for the *Hydrodynamic Radius*:

$$R_{H,LS} = M_w / \sum_v^C w_v M_v R_{H,v}^{-1}; \quad R_{H,v} \approx (R_H/M^\mu) M_v^\mu$$

Note: The "*power-law*" approximations do not apply to the wormlike chain

## Mean-square radius of gyration for some models

Model	Length scales	$R_G^2$
Random-flight linear coil ("infinitely thin")	$L = \text{contour length}$ $\hat{a} = \text{persistence length}$	$\hat{a}L/3$
Persistent (wormlike) chain <sup>(a)</sup> ("infinitely thin")	$L = \text{contour length}$ $\hat{a} = \text{persistence length}$	$(\hat{a}L/3)S(\hat{a}/L)$ $\approx [(\hat{a}L/3)^{-1} + (L^2/12)^{-1}]^{-1}$
Rod ("infinitely thin")	$L = \text{length}$	$L^2/12$
Disk ("infinitely thin")	$R = \text{radius}$	$R^2/2$
Cylinder	$L = \text{length}$ $R = \text{radius}$	$L^2/12 + R^2/2$
Sphere	$R = \text{radius}$	$3R^2/5$
Spherical shell	$R = \text{radius (outer)}$ $\Delta = \text{shell thickness}$	$(3R^2/5) \left( \frac{1 - [1 - (\Delta/R)^5]}{1 - [1 - (\Delta/R)^3]} \right)$
Spherical shell ("infinitely thin")	$R = \text{radius (outer)}$	$R$
Spheroid	$2R_1 = \text{unique axis}$ $2R_2 = \text{transverse axis}$	$R_1^2 \left( \frac{2 + (R_2/R_1)^2}{5} \right)$

a)  $S(Z) = 1 - 3Z + 6Z^2 - 6Z^3[1 - \exp(-Z^{-1})] \approx (1 + 4Z)^{-1}$ ;  $Z = \hat{a}/L$

## $R_{G,LS}^2$ and $R_{H,LS}$ for some power-law approximations

	$R_{G,LS}^2$	$R_{H,LS}$
Exact Relation <sup>(a)</sup>	$(1/M_w) \sum_v w_v M_v R_{G,v}^2$	$M_w / \sum_v w_v M_v R_{H,v}^{-1}$
Approximation for <sup>(b)</sup> $R_G \propto R_H \propto M^{\varepsilon/2}$	$(R_G^2/M^\varepsilon) M_{(\varepsilon+1)}^{\varepsilon+1}/M_w$	$(R_H/M^{\varepsilon/2}) M_w/M_{(1-\varepsilon)}^{1-\varepsilon}$
Random-flight coil <sup>(c)</sup> ; $\varepsilon = 1$	$(R_G^2/M) M_z$	$(R_H/M^{1/2}) M_w/M_{(1/2)}^{1/2} \approx$ $(R_H/M^{1/2}) M_w^{1/2} (M_w/M_n)^{0.10}$
Rodlike chain (thin) <sup>(c)</sup> ; $\varepsilon \approx 2$	$(R_G^2/M^2) M_z M_{z+1}$	$(R_H/M) M_w$
Sphere <sup>(c)</sup> ; $\varepsilon = 2/3$	$(R_G^2/M^{2/3}) M_{(5/3)}^{5/3}/M_w \approx$ $(R_G^2/M^{2/3}) M_z^{2/3} (M_w/M_z)^{0.10}$	$(R_H/M^{1/3}) M_w/M_{(2/3)}^{2/3} \approx$ $(R_H/M^{1/3}) M_w^{1/3} (M_w/M_n)^{0.10}$

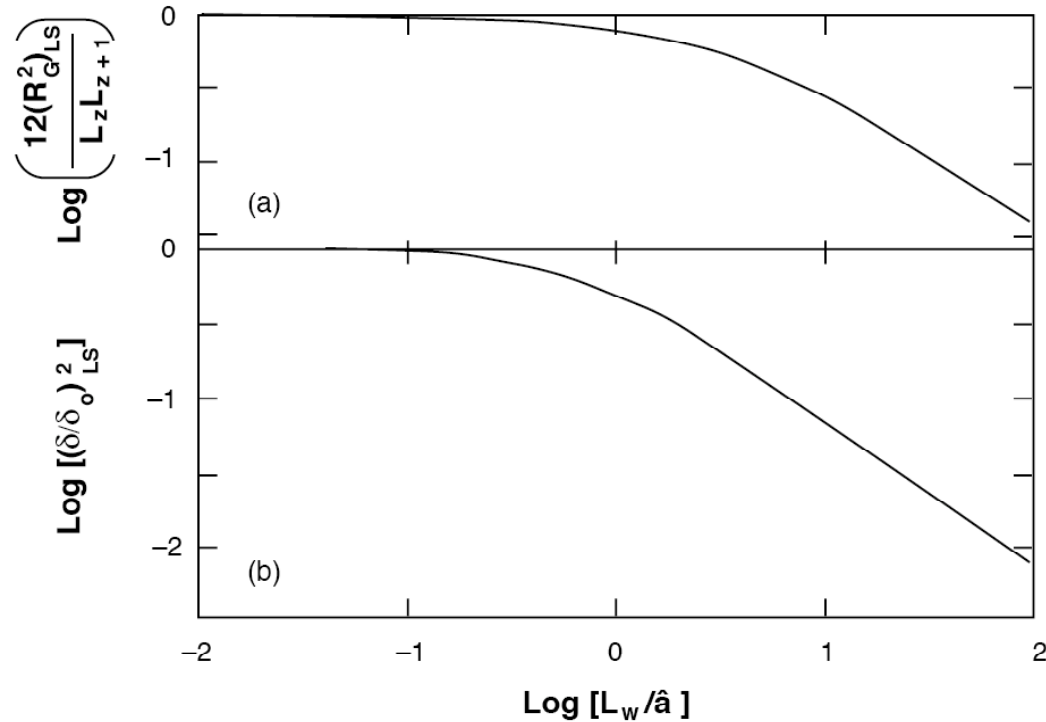
$$M_{(\mu)}^\mu = \sum_v w_v M_v^\mu; \quad M_{(\mu)} \text{ is } M_n, M_w, (M_w M_z)^{1/2} \text{ and } (M_w M_z M_{z+1})^{1/3} \text{ for } \mu = -1, 1, 2 \text{ and } 3$$

## Wormlike Chain (not a power-law):

$$R_{G,LS}^2 = (L_z \hat{a}/3) S_{LS}(\hat{a}/L_z)$$

$$S_{LS}(Z_z) = 1 - 3Z_z + 6Z_z^2 \frac{h+2}{h+1} - 6Z_z^3 \frac{(h+2)^2}{h(h+1)^2} \{1 - [1 + (Z_z(h+2))^{-1}]^{-h}\}$$

$$\approx [1 + 4Z_z(h+2)/(h+3)]^{-1} = [1 + 4\hat{a}/L_{z+1}]^{-1}$$



### ***Branched flexible chain polymers:***

For regular star- and comb-shaped branched random-flight chains:

$$R_G^2 = gR_{G,LIN}^2 ; \quad g \approx \lambda_{br} + g_{star}(1 - \lambda_{br})^{7/3}$$

- $f$  is the number of branches
- $\lambda_{br}$  is the fraction of the mass in the backbone, i.e.,  $\lambda_{br} = 0$  for a star-shaped molecule, and  $\lambda_{br} = 1$  for a linear chain.

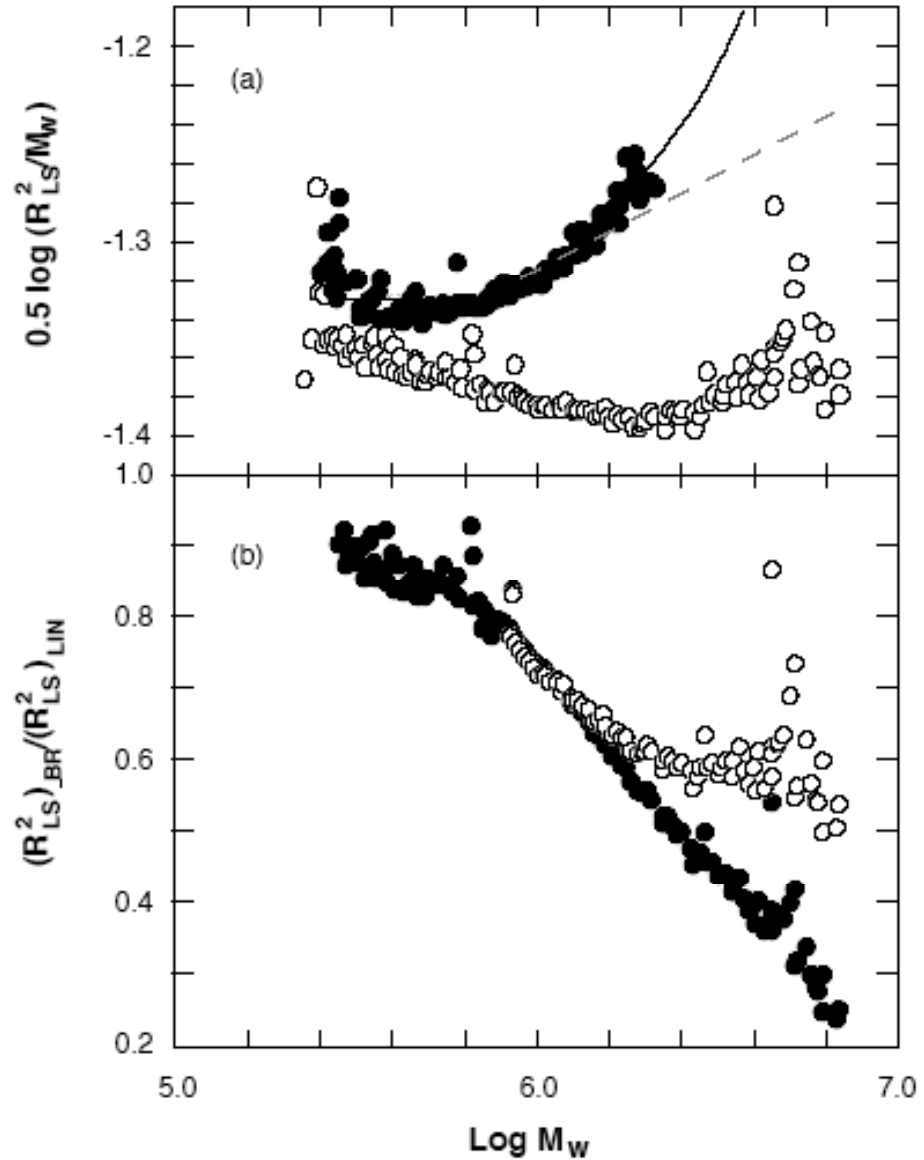
Theoretical expressions for  $g$  are available for a variety of structures, including randomly branched chains.

The combination of SEC with light scattering measurements of  $M$  and  $R_G^2$  for the eluent is particularly useful, especially if a model is available for  $g$  for the anticipated branched chains (e.g., randomly branched "fractions"):

Randomly branched poly(methyl methacrylate), PMMA.

(a) linear (●), branched polymers (○)

(b) The ratio using the power-law (○) and polynomial (●) extrapolations



## Optically diverse scattering elements

$$R_{G,LS}^2 = \frac{\sum_{\nu} \sum_j^C \sum_k^{n_{\nu}} \tilde{\Psi}_{j,\nu} \tilde{\Psi}_{k,\nu} \mathbf{m}_{j,\nu} \mathbf{m}_{k,\nu} \langle |\mathbf{r}_{jk}|_{\nu}^2 \rangle}{2 \left[ \sum_{\nu} \sum_j^C \tilde{\Psi}_{j,\nu} \mathbf{m}_{j,\nu} \right]^2}$$

### Special case:

<ul style="list-style-type: none"> <li>• two scattering elements, A and B</li> <li>• weight fraction <math>w_A = 1 - w_B</math>  <math>= n_A m_A / (n_A m_A + n_B m_B)</math></li> </ul>	<ul style="list-style-type: none"> <li>• <math>\tilde{\Psi} = w_A \tilde{\Psi}_A + w_B \tilde{\Psi}_B</math></li> <li>• <math>\tilde{w}_A = 1 - \tilde{w}_B = w_A \tilde{\Psi}_A / \tilde{\Psi}</math> ;  <math>\tilde{w}_A</math> and <math>\tilde{w}_B</math> may be +, -, or 0.</li> </ul>
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$$R_{G,LS}^2 = \tilde{w}_A R_{G,A}^2 + (1 - \tilde{w}_A) R_{G,B}^2 + \tilde{w}_A (1 - \tilde{w}_A) \Delta_{AB}^2$$

$\Delta_{AB}^2$  is the mean-square separation of the c.g.'s of the A & B constellations.

$$R_{G,geo}^2 = w_A R_{G,A}^2 + (1 - w_A) R_{G,B}^2 + w_A (1 - w_A) \Delta_{AB}^2$$

## Example:

A stratified sphere: outer diameter  $R_B$  and inner core diameter  $R_A$  ( $\Delta_{AB} = 0$ )

$$R_{G,LS}^2 = (3/5) \left( \tilde{w}_A R_A^2 + (1 - \tilde{w}_A) \frac{R_B^5 - R_A^5}{R_B^3 - R_A^3} \right)$$

For a thin shell enclosing the solvent, such that  $\tilde{w}_A = 0$ :

$$R_{G,LS}^2 = (3/5) R_B^2 \left( \frac{1 - [1 - (\Delta_{shell}/R_B)^5]}{1 - [1 - (\Delta_{shell}/R_B)^3]} \right); \quad \Delta_{shell} = R_B - R_A$$

The expression for the ratio of the volume of the shell to its surface area in terms of experimentally determined parameters may be solved to give

$$\Delta_{shell} \approx (v_2 M_w / 4\pi N_A R_{G,LS}^2) \{ 1 + (1.3)\beta^2 + 0.06\beta^3 + \dots \}^{-1}$$

where  $\beta = v_2 M / 4\pi N_A (R_G^2)^{3/2} \ll 1$

## Optically anisotropic scattering elements

Homopolymer comprising cylindrically symmetric scattering elements:

$$[\mathbf{R}_{Si}(\mathbf{q},c)/c]^0 = K' \hat{n}_s^2 (\partial \hat{n} / \partial c)_w^2 \mathbf{M}_{LS,si} \mathbf{P}_{LS,si}(\mathbf{q},0)$$

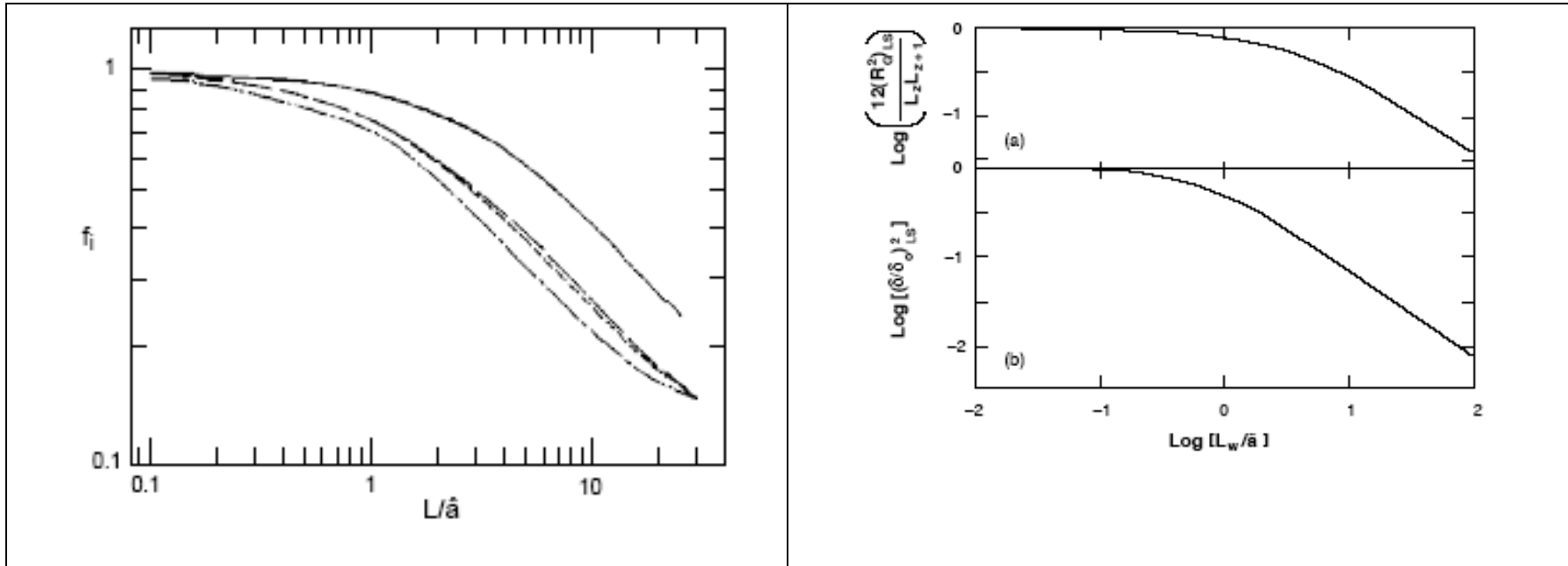
$$P_{LS,Hv}(\mathbf{q},0) = 1 - (3/7)R_{G,LS,Hv}^2 q^2 + \dots$$

$$P_{LS,Vv}(\mathbf{q},0) = 1 - (1/3)R_{G,LS,Vv}^2 q^2 + \dots$$

For the **persistent coil model**,

$$R_{G,LS,Hv}^2 = \frac{\sum_v^C w_v M_v \delta_v^2 f_{3,v}^2 R_{G,v}^2}{\sum_v^C w_v M_v \delta_v^2} ; \quad R_{G,LS,Vv}^2 = \frac{\sum_v^C w_v M_v (1 + 4\delta_v^2/5) J(\delta_v) R_{G,v}^2}{\sum_v^C w_v M_v (1 + 4\delta_v^2/5)}$$

$$J(\delta_v) = \frac{1 - (4/5)f_{1,v}\delta_v + (4/7)(f_{2,v}\delta_v)^2}{1 + (4/5)\delta_v^2}$$



The functions  $f_i$ , appearing in the reciprocal scattering factors for anisotropic chains as a function of the contour length  $L$  divided by the persistence length  $\hat{a}$ :  
 —,  $f_1$ ; — - —,  $f_2$ ; - - -,  $f_3$ ; and — — —,  $f_4$  .

Owing to the decrease in  $\delta/\delta_0$  with increasing  $L/\hat{a}$ , the influence of the depolarized components decreases rapidly for  $L/\hat{a} > 1$ , and one can simply put all  $f_i \approx 1$  with negligible error in the analysis of data.

**Upper:**

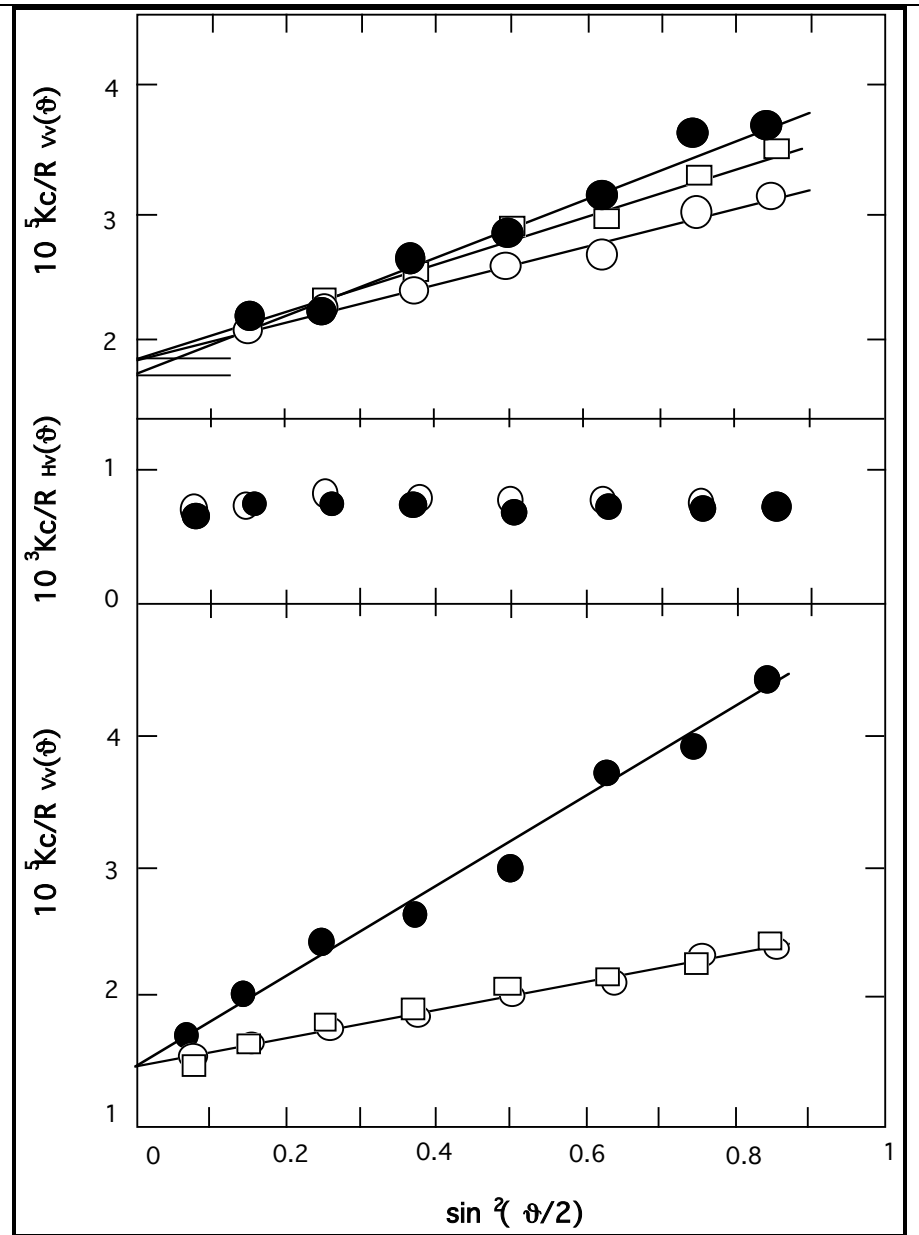
$[Kc/R_{V_V}(0,c)]^{1/2}$  for *cis*-PBO.

**Middle:**

$Kc/R_{H_V}(0,c)$  for *cis*-PBO.

**Lower:**

$[Kc/R_{V_V}(0,c)]^{1/2}$  for *ab*-PBO.



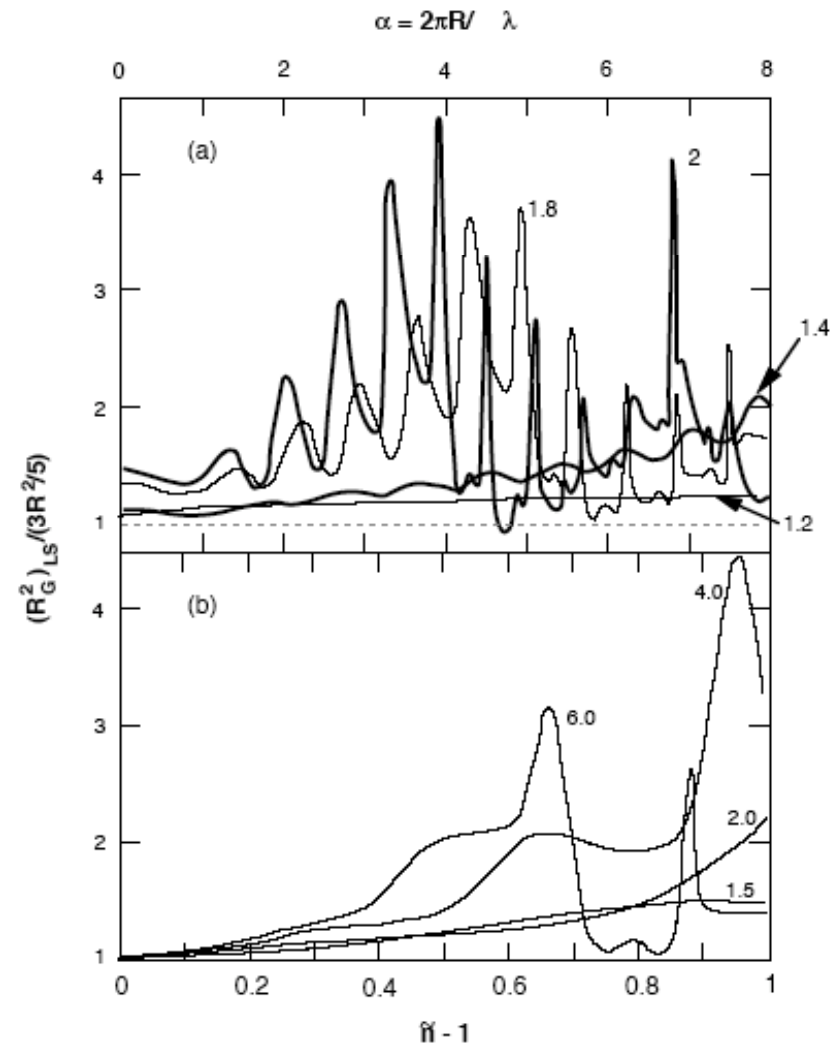
## Scattering beyond the RGD regime

$$R_{G,LS}^2 = \frac{\sum_v^C w_v M_v y(\tilde{n}, \lambda, M_v) [m(\tilde{n}, \lambda, M_v)]^2 R_{G,RGD,v}^2}{\sum_v^C w_v M_v [m(\tilde{n}, \lambda, M_v)]^2}$$

Mie scattering theory:

$$R_{G,LS}^2 = (3/5)^v \frac{\sum_v^C w_v M_v [m_{sph}(\tilde{n}, \tilde{\alpha}_v)]^2 y_{sph}(\tilde{n}, \tilde{\alpha}_v) R_v^2}{\sum_v^C w_v M_v [m_{sph}(\tilde{n}, \tilde{\alpha}_v)]^2}$$

Evaluation of an average R from  $R_{G,LS}^2$  requires an iterative process.



## *Scattering at infinite dilution and arbitrary q*

$$P_{LS}(q,0) = \frac{\sum_v^C w_v M_v^{-1} \sum_j^{n_v} \sum_k^{n_v} \tilde{\psi}_{j,v} \tilde{\psi}_{k,v} m_{j,v} m_{k,v} \langle [\sin(q|r_{jk}|_v)]/q|r_{jk}|_v \rangle}{\sum_v^C w_v M_v^{-1} \left[ \sum_j^{n_v} \tilde{\psi}_{j,v} m_{j,v} \right]^2}$$

## *Identical scattering elements*

$$P_{LS}(q,0) = \frac{1}{M_w} \sum_v^C w_v M_v P_v(q,0); \quad P_v(q,0) = \frac{1}{n_v} \sum_j^{n_v} \sum_k^{n_v} \langle [\sin(q|r_{jk}|)]/q|r_{jk}| \rangle$$

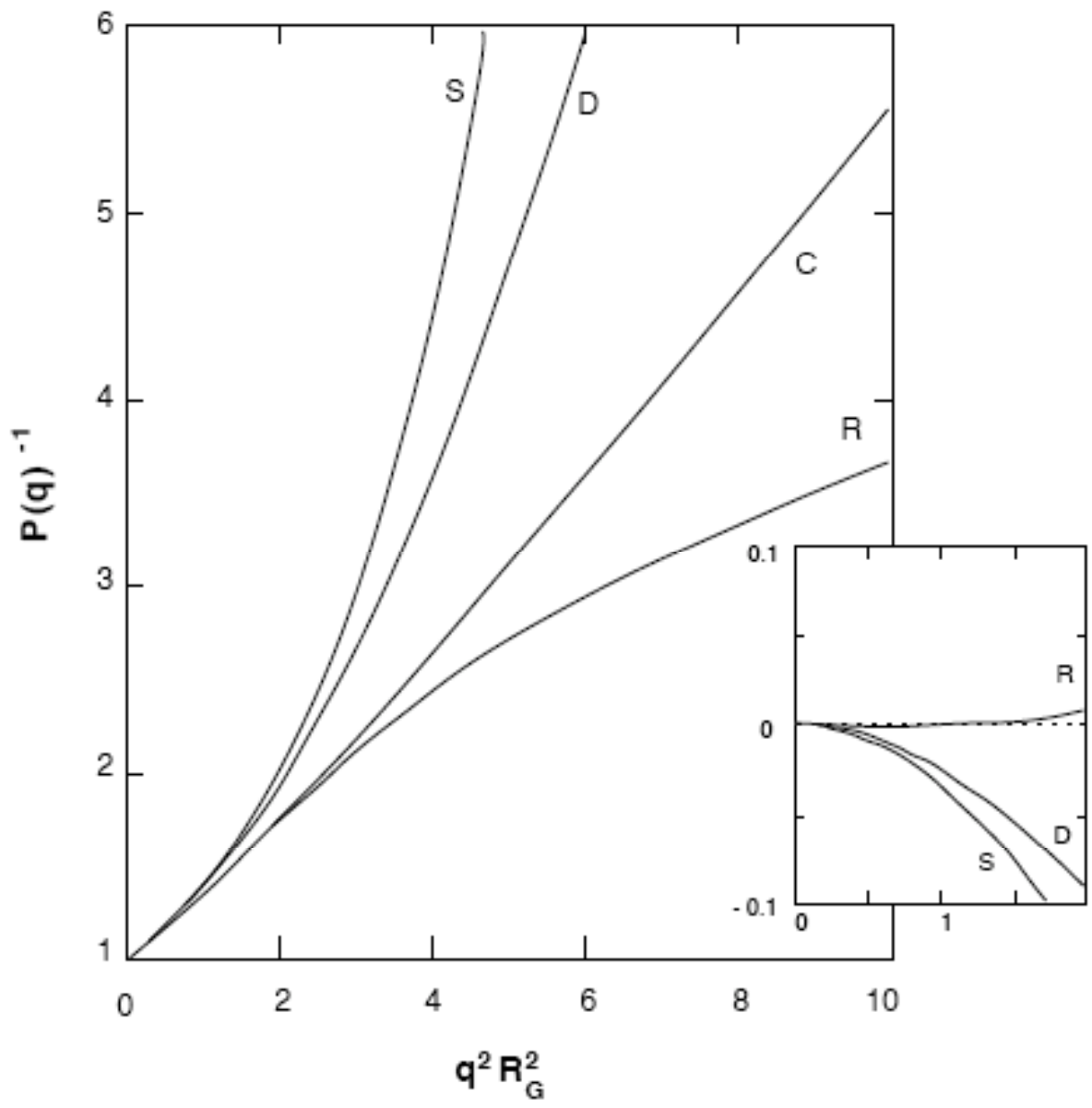
## Particle scattering functions for some optically isotropic models

Model	$R_G^2$		$P(q,0)$
Random-flight linear coil	$\hat{a}L/3$	$u = \hat{a}Lq^2/3$	$p_c(u) = (2/u^2)[u - 1 + \exp(-u)]$
Disk ("infinitely thin")	$R^2/2$	$y = Rq$	$(2y^2)[1 - J_1(2y)/y]$
Sphere	$3R^2/5$	$y = Rq$	$(9/y^6)[\sin(y) - y\cos(y)]^2$
Shell ("infinitely thin")	$R$	$y = Rq$	$[\sin(y)/y]^2$
Rod ("infinitely thin")	$L^2/12$	$x = Lq$	$p_1(x) = (2/x^2)[x\text{Si}(x) - 1 + \cos(x)]$

### Monodisperse Random-Flight model:

$$P(q,0)^{-1} = 1 + \frac{1}{3}u + \frac{1}{36}u^2 - \frac{1}{540}u^3 + O(u^4)$$

$$P(q,0)^{-1/2} = 1 + \frac{1}{6}u - 0 \times u^2 - \frac{1}{1080}u^3 + O(u^4)$$



## Chain length dispersion:

### Linear random-flight chain heterodisperse in M:

$$P_{LS}(q,0) = (2/rM_w q^2) \left\{ 1 - (1/rM_n q^2) \left[ 1 - M_n \sum_v^C w_v M_v^{-1} \exp(-rM_v q^2) \right] \right\}$$

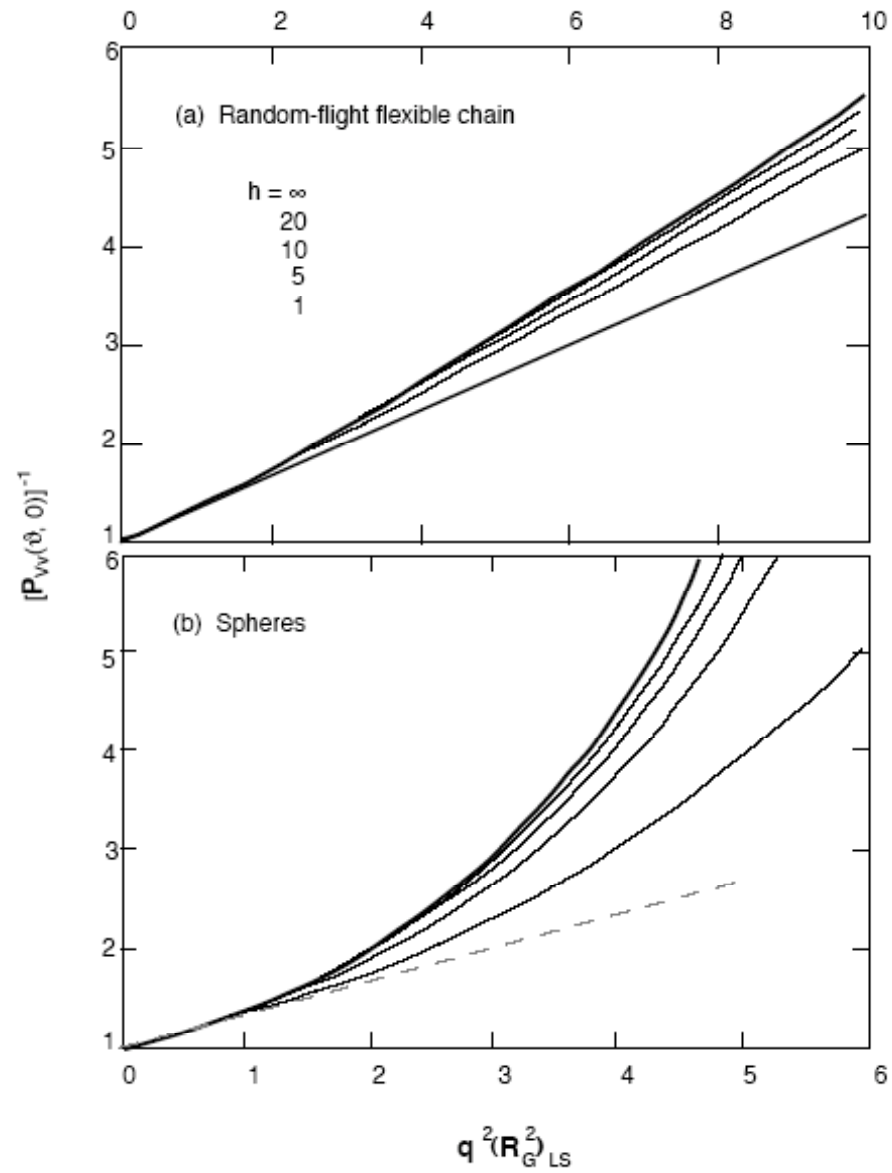
$$P_{LS}(q,0)^{-1} = 1 + rM_z q^2/3; \text{ For the most-probable distribution of M}$$

### Linear rodlike chain with a Schulz-Zimm distribution in M:

$$P_{LS}(q,0) = \frac{2}{(1+h)\xi} \left\{ \arctan(\xi) + \sum_{j=1}^{h-1} \left( \frac{1}{h-j} - \frac{1}{h} \right) (1 + \xi^2)^{(j-h)/2} \sin[(h-j)\arctan(\xi)] \right\}$$

where  $\xi = qM_w/M_L(1+h)$ .

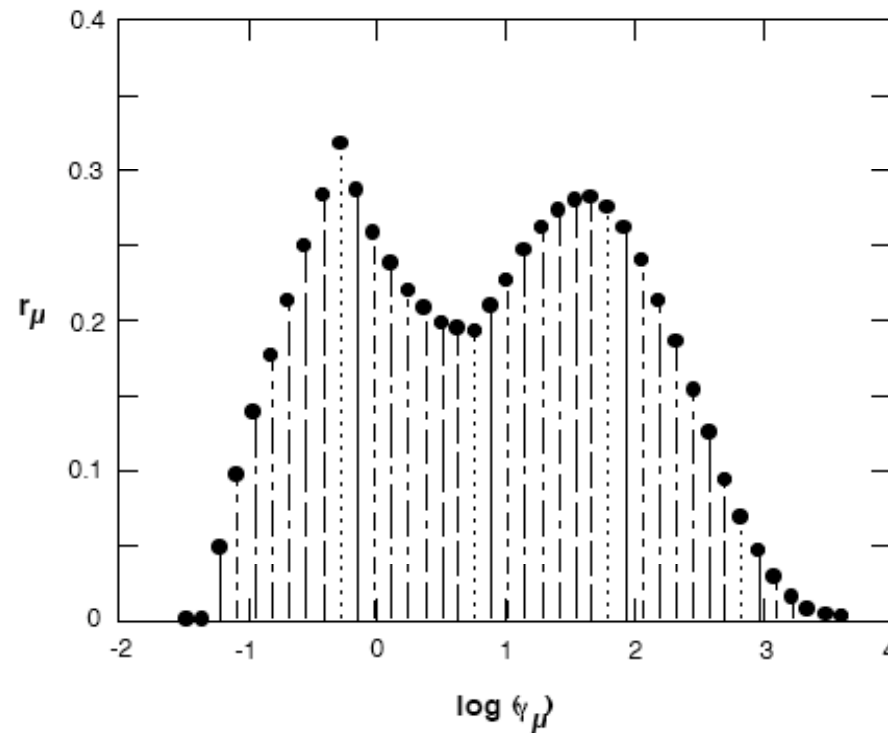
$$P_{LS}(q,0) = \frac{2M_L}{qM_w} \arctan \frac{qM_w}{2M_L}; \text{ For a most-probable distribution of M}$$



$$g^{(1)}(\tau; q, c) \approx \sum_{\mu} r_{\mu}(q, c) \exp[-\tau \gamma_{\mu}(q, c)]; \quad \sum_{\mu} r_{\mu} = 1$$

$$\gamma_{\mu}(q, c) = \frac{kTq^2}{6\pi\eta\hat{a}_{\mu}(c)} ; \quad \lim_{c \rightarrow 0} a_{\mu}(c) = R_{H,\mu}; \quad \text{Hydrodynamic Radius}$$

Inverse Laplace transform of  $g^{(1)}(t; q, c)$ :



## Behavior at large $R_G^2 q^2$

Random-flight chain:

$$\lim_{u \gg 1} P(q,0)^{-1} = C + u/2 + O(u^{-1})$$

$$\lim_{u \gg 1} uP(q,0) \approx 2$$

$$\lim_{u \gg 1} [K_{op}c/\mathbf{R}(q,c)]^0 = (1/2)[M^{-1} + (R_G^2/M)q^2 + \dots]$$

where  $C = 1/2$  for a linear chain.

Note:  $\partial[K_{op}c/\mathbf{R}(q,c)]^0/\partial q^2 = \hat{a}/2M_L$

Rodlike chain:

$$\lim_{u \gg 1} P(q,0)^{-1} = C + Lq/\pi + O(q^{-1})$$

$$\lim_{u \gg 1} uP(q,0) \approx \pi Lq/12$$

where  $C = 2/\pi^2$  and  $u = R_G^2 q^2 = L^2 q^2/12$ . Note:  $\partial[K_{op}c/\mathbf{R}(q,c)]^0/\partial q = L/\pi M = 1/\pi M_L$

## Kratky-Porod wormlike chain model

Three ranges of behavior in  $q^2P(q,0)$  vs  $q$ :

- I. Wormlike chain behavior for  $R_G^2 q^2 < 1$
- II. Flexible chain like asymptote ( $q^2P(q,0) \propto 2$ ) for  $1/R_G < q < 1/\hat{a}$
- III. Rodlike asymptotic behavior ( $q^2P(q,0) \propto q$ ) for  $\hat{a}q > 1$

Approximate models to mimic this behavior may be fitted by a Padé relation:

$$P(q,0) \approx \left( P_{RF}(q,0)^m + \left( \frac{1 - \exp(-(\hat{a}q)^2)}{1 + Lq^2/\pi} \right)^m \right)^{1/m}; \quad m \approx 5-7$$

$P_{RF}(q,0)$  for the random-flight chain, with  $\hat{a}L/3$  replaced by  $R_G^2 = (\hat{a}L/3)S(\hat{a}/L)$

## Kratky-Porod plot

The intersection of the extrapolated lines for regions II and III occurs for

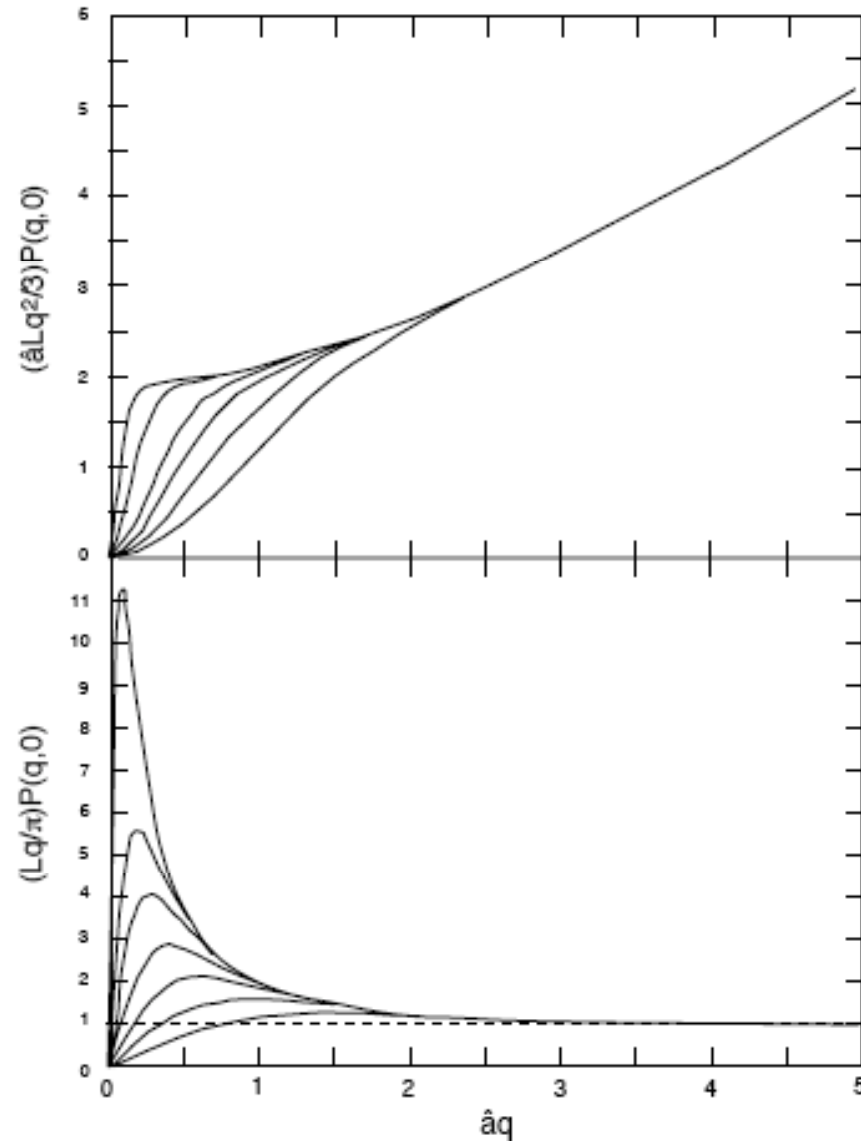
$$\hat{a}q^* \approx (6/\pi)S(\hat{a}/L)^{-1} \\ \approx (6/\pi)(1 + 4\hat{a}/L)$$

---

## Holtzer Plot

A maximum in  $qP(q,0)$  vs  $q$  that marks the transition from regions I to II occurs for

$$R_G q^{**} = 1.466$$

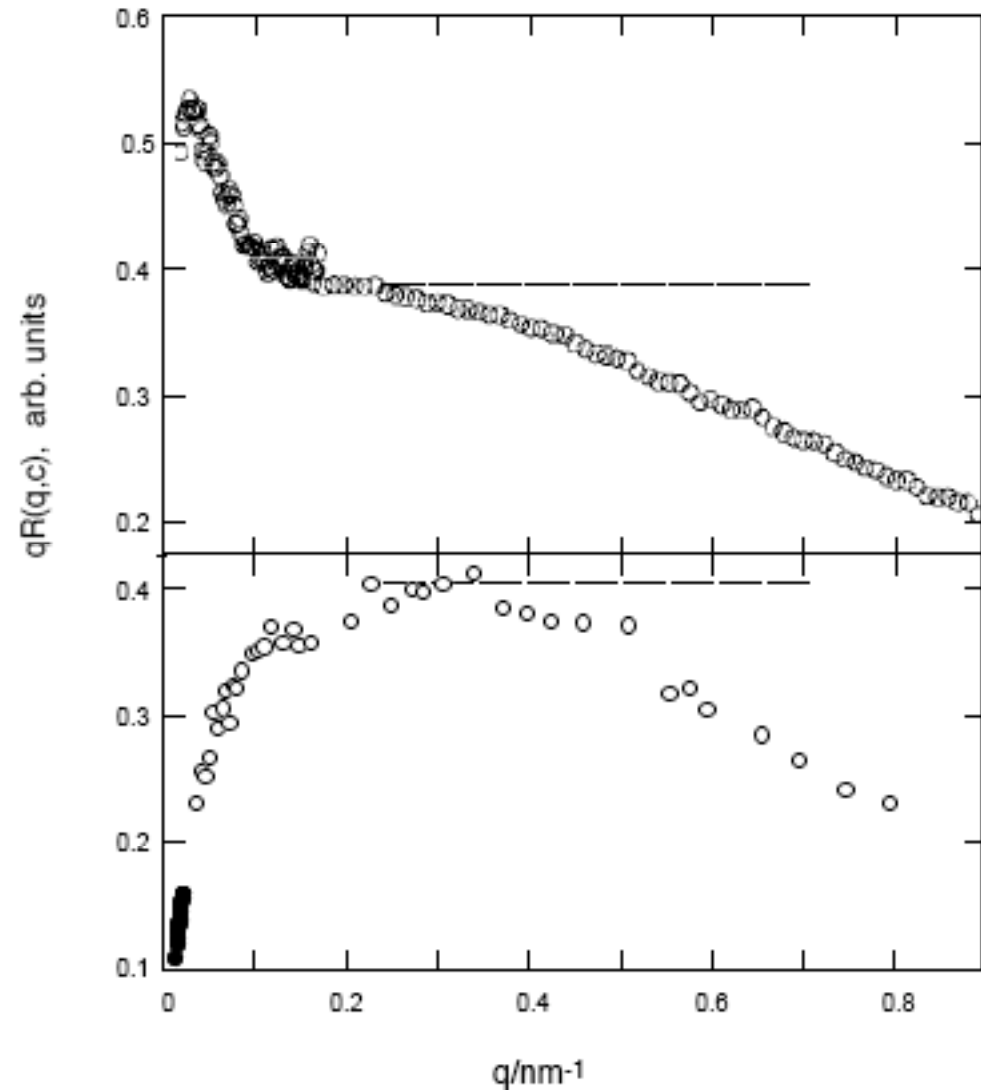


$L/\hat{a} = 640, 160, 80, 40, 20, 10, 5$  top to bottom

In neutron scattering, the effect of the chain element diameter may be seen in region III, and modeled by replacing multiplying  $\pi/Lq$  by  $P_{\text{section}}(q,0)$ ,

$$P_{\text{section}}(q,0) \approx \left( \frac{2J_1(R_c q)}{R_c q} \right)^2$$

$$\approx \exp[-(R_c q)^2/4]$$



Two different wormlike micelles

## *Optically diverse scattering elements*

Limiting to two scattering elements, A and B, with  $\tilde{w}_A = 1 - \tilde{w}_B = w_A \tilde{\Psi}_A / \tilde{\Psi}$ :

$$P_{LS}(q,0) = \tilde{w}_A P_A(q,0) + (1 - \tilde{w}_A) P_B(q,0) + \tilde{w}_A (1 - \tilde{w}_A) P_{AB}(q,0)$$

$$P_v(q,0) = \left( \frac{1}{n_v} \sum_j \sum_k \langle [\sin(q|r_{jk|_v})] / q|r_{jk|_v} \rangle \right); \quad v = A, B$$

$$P_{AB}(q,0) = \frac{1}{n_A n_B} \sum_j \sum_k \langle [\sin(q|r_{jk}|)] / q|r_{jk}| \rangle - [P_A(q,0) + P_B(q,0)];$$

$$P_{AB}(q,0) \approx (\Delta_{AB} q)^2 / 3 + \dots$$

- Note the similarity in form to the expression the for  $R_{G,LS}^2$ .
- Has been applied to mixtures of chemically diverse polymers.



## *Optically anisotropic scattering elements*

$$[\mathbf{R}_{Si}(q,c)/c]^0 = K' \hat{n}_s^2 (\partial \hat{n} / \partial c)_w^2 M_{LS,Si} P_{LS,Si}(q,0)$$

For rodlike chains monodisperse in  $M$ , with  $x = Lq$ :

$$(1 + 4\delta^2/5)P_{Vv}(q,0) = p_1(x) + \delta^2 \left\{ (4/5)p_3(x) - (2 - \delta^{-1})m_1(x) + (9/8)m_2(x) + m_3(x) \right\}$$

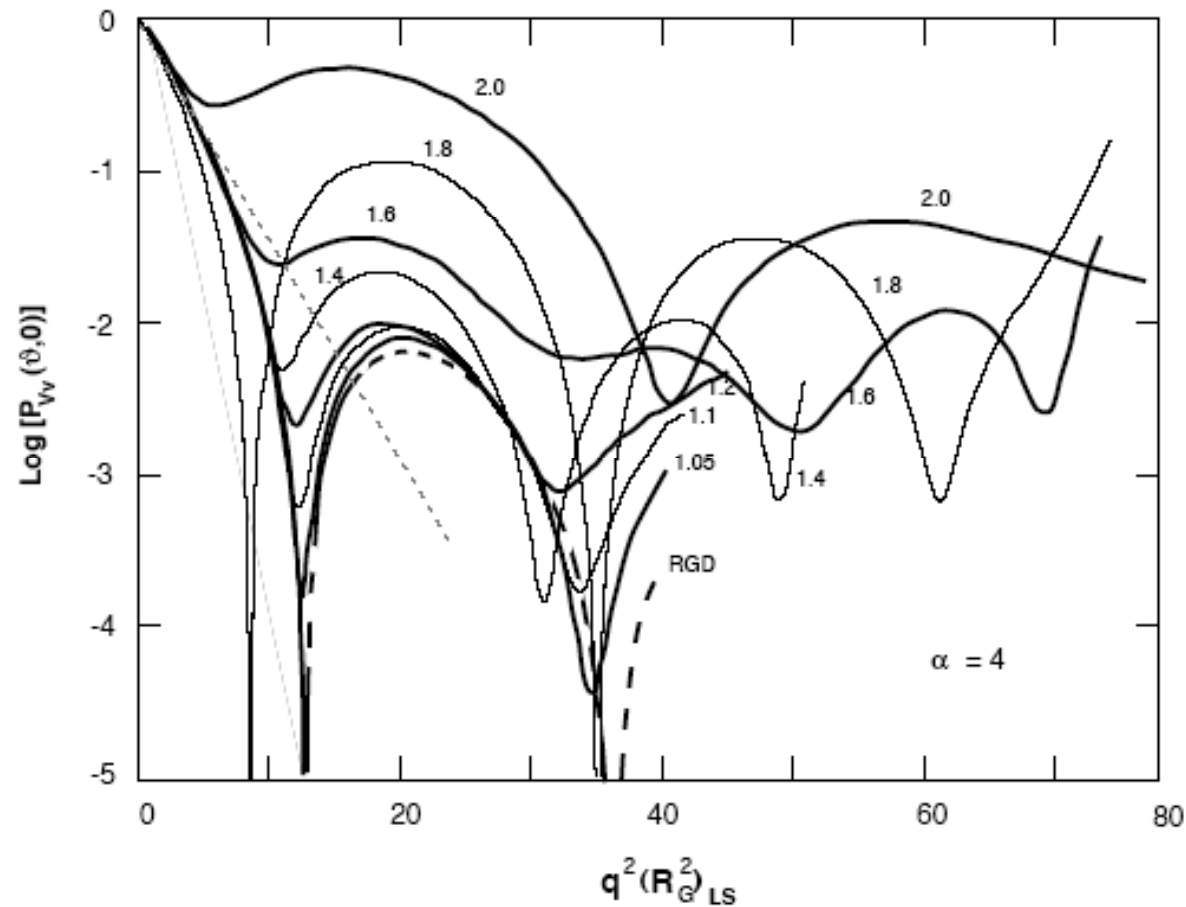
$$P_{Hv}(q,0) = p_3(x) + (5/8)\sin^2(\vartheta/2)m_2(x)$$

The functions of  $x$  are known trigonometric functions:

$p_1(x) = (2/x^2)[x\text{Si}(x) - 1 + \cos(x)]$	$m_1 = p_1 - p_2$
$p_2(x) = (6/x^3)[x - \sin(x)]$	$m_2 = 3p_1 - p_2 - p_3$
$p_3(x) = (10/x^5)[x^3 + 3x\cos(x) - 3\sin(x)]$	$m_3 = p_3 - p_2$

## Scattering Beyond the RGD Regime

- Numerical methods are available to compute the scattering for a number of particle shapes, beyond the scope here.
- $P_{VV}(q,0)$  may be calculated for **homogeneous spheres using the Mie theory** as functions of  $\tilde{\alpha}$  and  $\tilde{n}$ .



## Fraunhofer Limit:

For both  $\tilde{n} \gg 1$  and a phase shift magnitude  $\tilde{\alpha}|\tilde{n} - 1| > 10$ , the angular dependence is independent of  $\tilde{n}$ , and is the same for absorbing and nonabsorbing particles.

## Spheres:

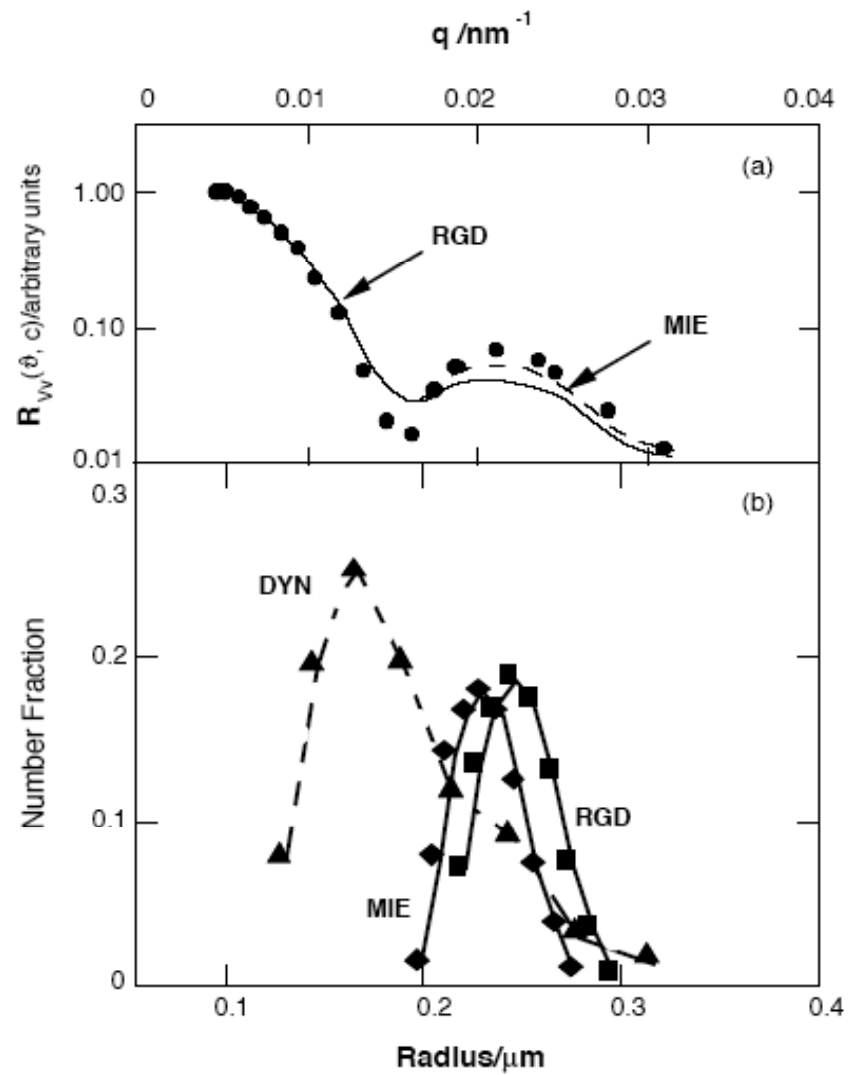
$$\lim_{R/\lambda \gg 1} P_{Vv}(q,0) = \{2J_1(\tilde{\alpha} \sin(\vartheta))/\tilde{\alpha} \sin(\vartheta)\}^2$$

$$\lim_{R/\lambda \gg 1} [\mathbf{R}_{Vv}(q,c)/c]^0 \propto \sum_v n_v \tilde{\alpha}_v^6 \{2J_1(\tilde{\alpha}_v \sin(\vartheta))/\tilde{\alpha}_v \sin(\vartheta)\}^2$$

**Cylinders** of length  $L_{\text{cyl}}$  and radius  $R$ , with  $L_{\text{cyl}} \gg R \gg \lambda$ ,

$$\lim_{R/\lambda \gg 1} P_{Vv}(q,0) = \sin^2(\tilde{\alpha}\vartheta)/(\tilde{\alpha}\vartheta)^3 \quad \text{Note: No dependence on } L$$

Extrema pattern similar for the functions for spheres and cylinders



Data on Hollow Spherical Shells

## Scattering from a dilute solution

$$\mathbf{R}(q,c) = K_{op}cM \mathbf{S}(q,c)$$

$$\mathbf{S}(q,c) = \mathbf{P}(q,c)\mathbf{F}(q,c)$$

$$\mathbf{F}(q,c) = 1 - c\mathbf{B}(c)\mathbf{P}(q,c)\mathbf{Q}(q,c); \quad \mathbf{F}(q,c)^{-1} = 1 + c\mathbf{\Gamma}(c)\mathbf{P}(q,c)\mathbf{H}(q,c)$$

$$\mathbf{\Gamma}(c) = \mathbf{B}(c)/[1 - c\mathbf{B}(c)]$$

$$\mathbf{H}(q,c) = \mathbf{Q}(q,c) \frac{[1 - c\mathbf{B}(c)]}{[1 - c\mathbf{B}(c)\mathbf{P}(q,c)\mathbf{Q}(q,c)]}$$

$$\mathbf{B}(c) = M\tilde{\mathbf{B}}(c)$$

$$\tilde{\mathbf{B}}_{LS}(c)\mathbf{Q}_{LS}(q,c) = \frac{\sum_v^c \sum_\mu^c w_v w_\mu \tilde{\Psi}_v \tilde{\Psi}_\mu M_v M_\mu P_v(q,c) P_\mu(q,c) \tilde{\mathbf{B}}_{v\mu}(c) Q_{v\mu}(q,c)}{[M_{LS}P_{LS}(q,c)]^2}$$

**Scattering in the RGD regime at *zero scattering angle*:**

$$\tilde{B}_{LS}(c) = M_{LS}^{-2} \sum_{\nu}^C \sum_{\mu}^C w_{\nu} w_{\mu} \tilde{\Psi}_{\nu} \tilde{\Psi}_{\mu} M_{\nu} M_{\mu} \tilde{B}_{\nu\mu}(c)$$

For a solute with optically identical scattering elements,

$$\tilde{B}_{LS}(c) = M_w^{-2} \sum_{\nu}^C \sum_{\mu}^C w_{\nu} w_{\mu} M_{\nu} M_{\mu} \tilde{B}_{\nu\mu}(c)$$

For a dilute solution,  $\tilde{B}_{LS}(c)$  may be expanded in a Taylor series and used to compute  $\Gamma_{LS}(c)$ :

$$\Gamma_{LS}(c) = 2A_{2,LS}M_w + 3A_{3,LS}M_w c + \dots$$

$$\begin{aligned}\frac{K_{op}c}{R(q,c)} &= M_w^{-1} \{1 + c\Gamma_{LS}(c)\} \\ &= M_w^{-1} \{1 + 2A_{2,LS}M_w c + 3A_{3,LS}M_w c^2 + \dots\}\end{aligned}$$

By comparison

$$a_{LS}(c) = R_{H,LS} \{1 - [(2 - k_2)(A_2 M / [\eta]) - k_1][\eta]c + \dots\}$$

$$\frac{\Pi}{RTc} = M_n^{-1} \{1 + A_{2,\Pi}M_n c + A_{3,\Pi}M_n c^2 + \dots\}$$

$A_{2,LS} = A_{2,\Pi}$ , etc., only for a monodisperse solute

## Special case:

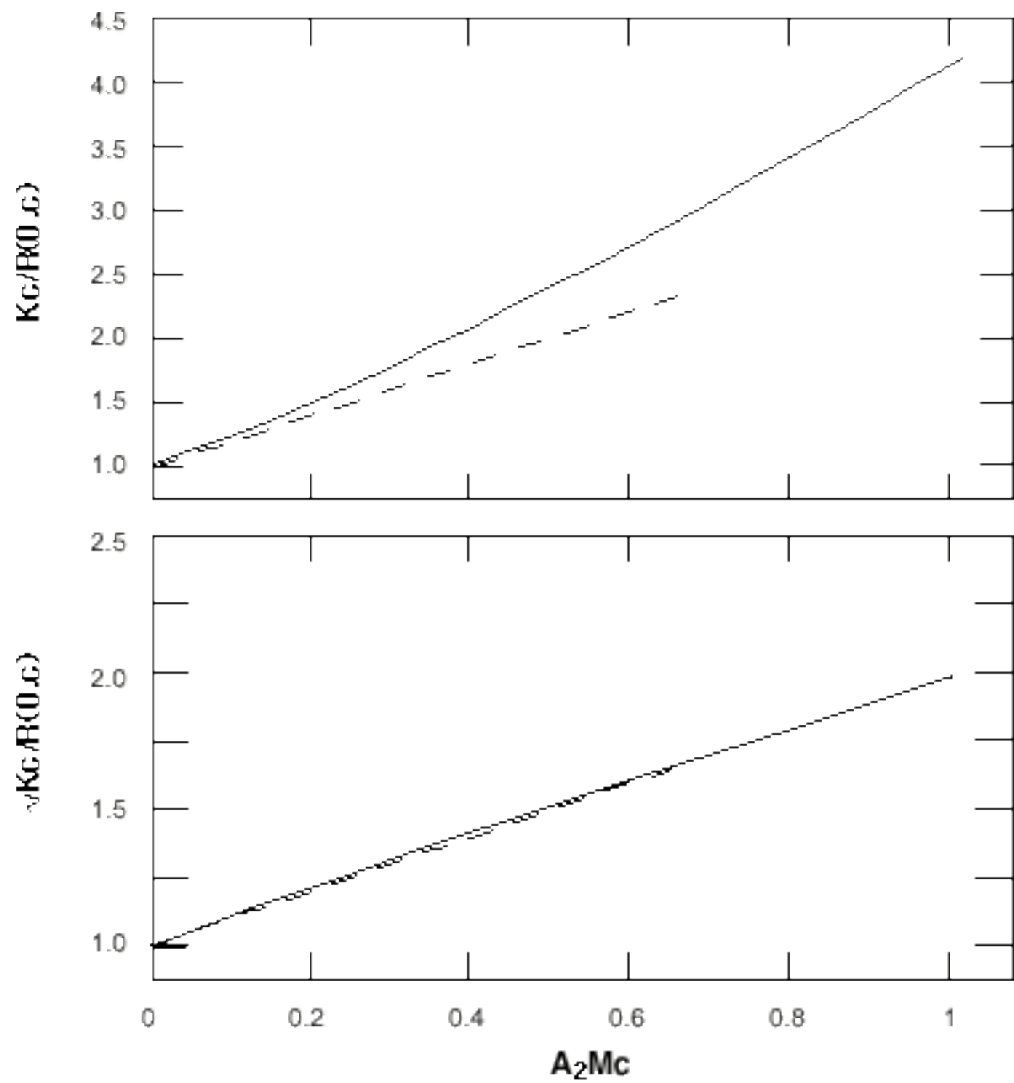
Solution with  $A_2 \gg 0$ : Put  $A_{3,LS}M = \Upsilon_3(A_{2,LS}M_w)^2$

$$\frac{K_{op}c}{R(q,c)} = M_w^{-1} \{1 + 2A_{2,LS}M_w c + 3\Upsilon_3(A_{2,LS}M_w c)^2 + \dots\}$$

$$\left(\frac{K_{op}c}{R(q,c)}\right)^{1/2} = M_w^{-1/2} \{1 + A_{2,LS}M_w c + [(3\Upsilon_3 - 1)/2](A_{2,LS}M_w c)^2 + \dots\}$$

Monodisperse spheres interacting through a hard-core potential:

$$\Upsilon_3 = 5/8; \quad (3\Upsilon_3 - 1)/2 = 7/16 \approx 0.44$$



Representative behavior for a flexible chain in a 'very good solvent'

*Heterodisperse solute, identical optically isotropic scattering elements*

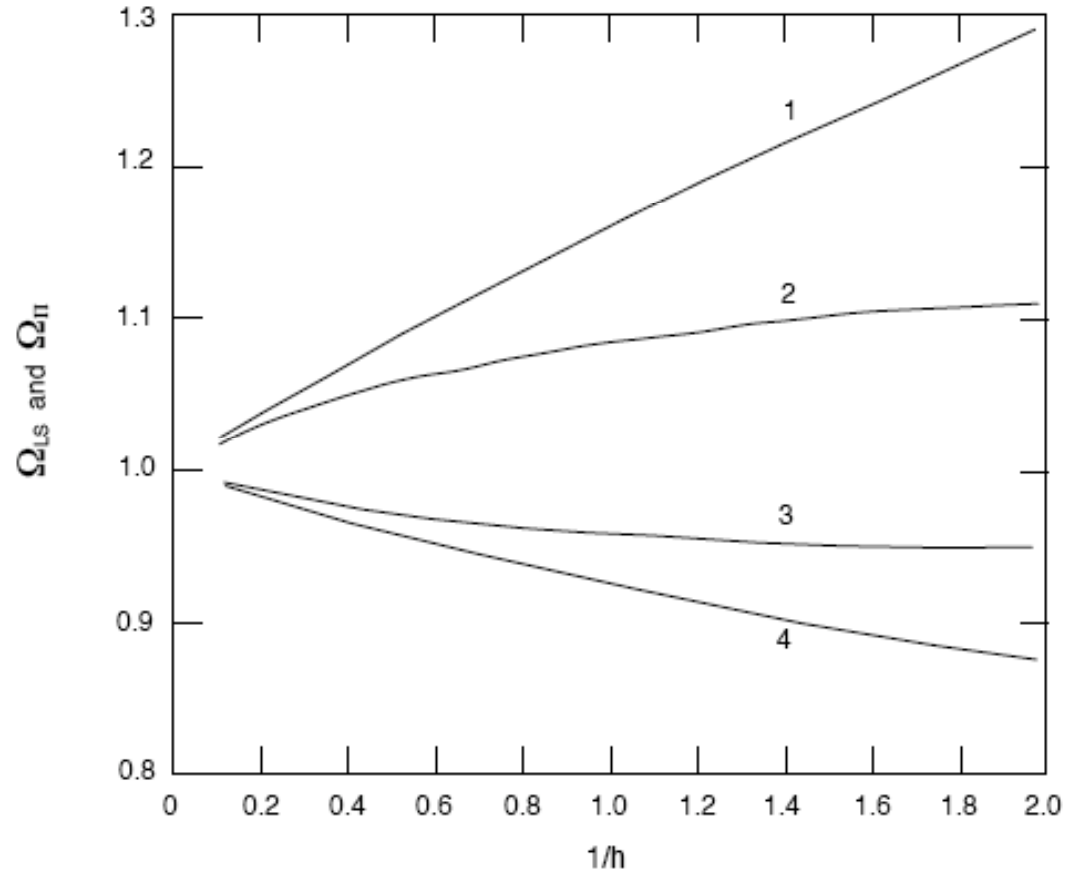
$$A_{2,LS} = M_w^{-2} \sum_v^C \sum_\mu^C w_v w_\mu M_v M_\mu A_{2,v\mu} \approx k_{A_2} M_w^{-\gamma} \Omega_{LS}$$

By comparison, ,

$$\frac{\Pi M_n}{RTc} = 1 + A_{2,\Pi} M_n c + \dots$$

$$A_{2,\Pi} = \sum_v^C \sum_\mu^C w_v w_\mu A_{2,v\mu} \approx k_{A_2} M_n^{-\gamma} \Omega_{\Pi}$$

$A_{2,LS}$  and  $A_{2,\Pi}$  may be correlated with  $M_w$  and  $M_n$ , resp., if the  $\Omega$  are close to unity



$\gamma = 1/5$  (Good solvent).

$\Omega_{LS} \propto A_{2,LS}/M_W^{-\gamma}$  (curves 2 and 3) and  $\Omega_{\Pi} \propto A_{2,\Pi}/M_n^{-\gamma}$  (curves 1 and 4)

$$1 \text{ and } 2: \quad M_v M_\mu A_{2,v\mu} = k_{A_2} [M_v^{(2-\gamma)/3} + M_\mu^{(2-\gamma)/3}]^3 / 2$$

$$3 \text{ and } 4: \quad A_{2,v\mu} = (A_{2,vv} A_{2,\mu\mu})^{1/2}$$

### *Optically diverse, isotropic scattering elements*

$$A_{2,LS} = M_w^{-2} \sum_v^C \sum_\mu^C w_v w_\mu \tilde{\Psi}_v \tilde{\Psi}_\mu M_v M_\mu A_{2,v\mu}$$

- Some work to study the "cross-terms" as a function of composition for mixtures of homopolymers, but theory is lacking.

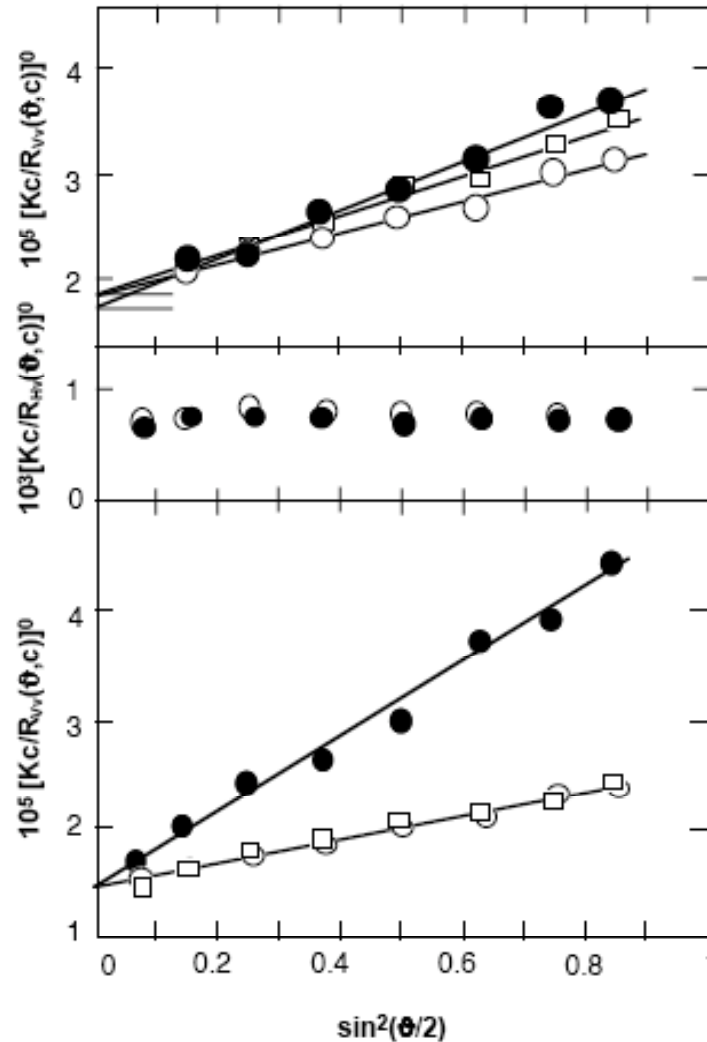
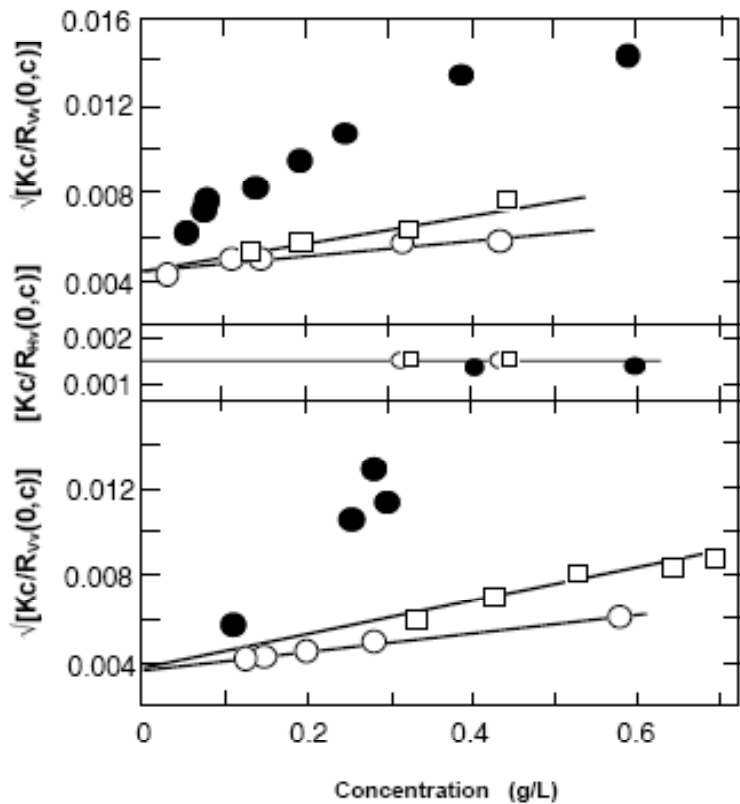
### *Optically identical, anisotropic scattering elements*

$$\frac{Kc}{R_{VV}(0,c)} = \left( \frac{1}{M(1 + 4\delta^2/5)} \right) \left\{ 1 + 2 \left( \frac{1 - \delta^2/10}{1 + 4\delta^2/5} \right) A_2 M c + \dots \right\}$$

$$\frac{Kc}{R_{HV}(0,c)} = \frac{5}{3M\delta^2} \left\{ 1 - A_2 M c/4 + \dots \right\}$$

with the latter limited to rodlike chains.

Note the weak dependence of  $Kc/R_{HV}(0,c)$  on  $c$ .



Upper:  $[Kc/R_{VV}(0,c)]^{1/2}$  for solutions of *cis*-PBO.  
 Middle:  $Kc/R_{HV}(0,c)$  for solutions of *cis*-PBO.  
 Lower:  $[Kc/R_{VV}(0,c)]^{1/2}$  *ab*-PBO.

Upper:  $[Kc/R_{VV}(\vartheta,c)]^0$  for solutions of *cis*-PBO.  
 Middle:  $[Kc/R_{HV}(\vartheta,c)]^0$  for solutions of *cis*-PBO.  
 Lower:  $[Kc/R_{VV}(\vartheta,c)]^0$  for solutions of *ab*-PBO.

***Concentrated and moderately concentrated solutions  
at zero scattering angle***

$$\frac{K_{\text{op}}cM}{R(q,c)} = 1 + c\Gamma(c)$$

With this expression, for a *monodisperse* solute,

$$c\Gamma(c) = \frac{M}{RT} \frac{\partial \Pi}{\partial c} - 1$$

From  $\Pi$  for monodisperse, optically **homogeneous spheres** interacting through a hard-core potential:

$$c\Gamma(c) = \varphi \frac{8 - 2\varphi + 4\varphi^2 - \varphi^3}{(1 - \varphi)^4} \approx \varphi \frac{8 - 2\varphi}{(1 - \varphi)^4}$$

where the volume fraction  $\varphi = (4\pi/3)N_A R^3 c/M$  for spheres of radius  $R$ , and  $A_2Mc = 8\varphi$

Flory-Huggins theory of concentrated polymer solutions:

$$\Pi V_1/RT = -\{\ln(1 - \varphi) + (1 - 1/r)\varphi + \chi\varphi^2\}$$

$$\Gamma(c) = \frac{v_2^2 M}{V_1} \left( \frac{1}{1 - \varphi} - 2\chi - \varphi \frac{\partial \chi}{\partial \varphi} \right)$$

$\chi$  is a constant in FH theory, but it depends on  $\varphi$  in experiment

Data for various concentrated  
polymer solutions over a range of  
M:

Empirical fit:

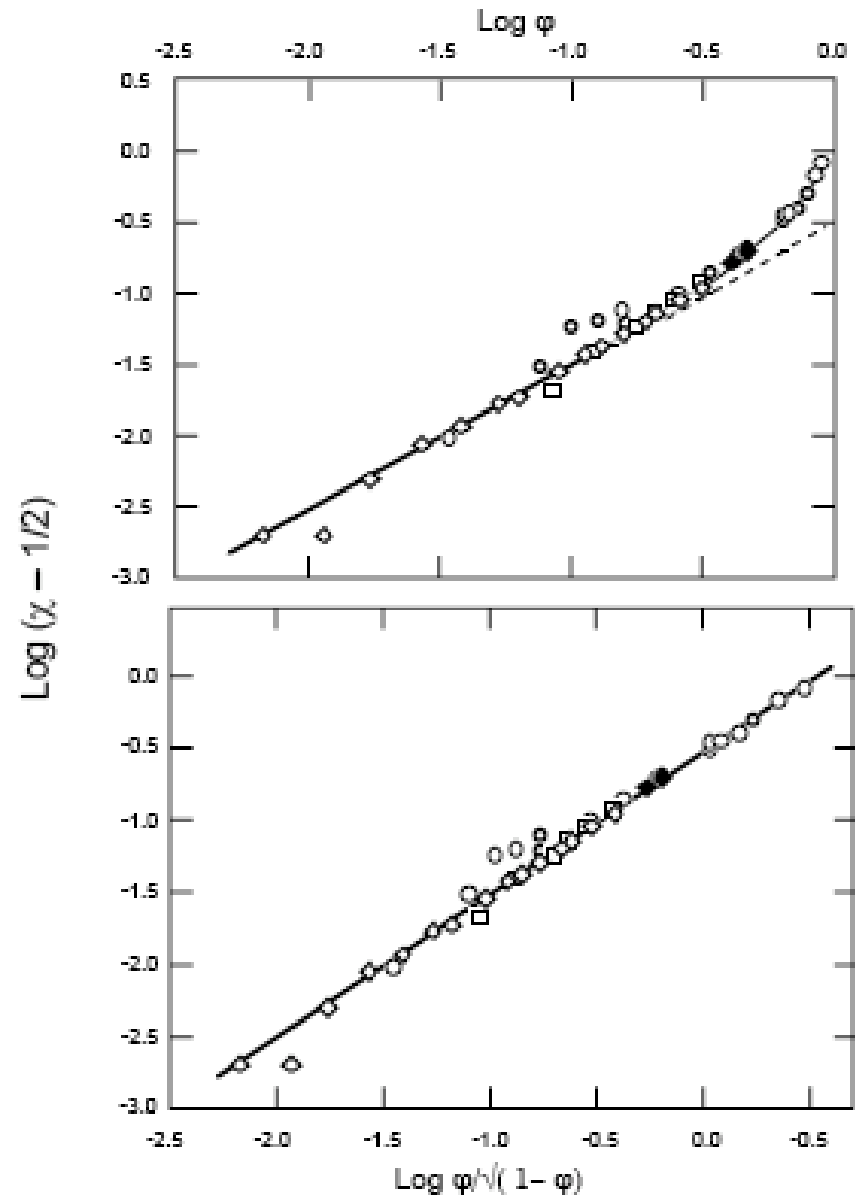
$$\chi = \chi_1 + \chi_2 \frac{\varphi}{\sqrt{1-\varphi}}$$

$$\chi_1 = 1/2$$

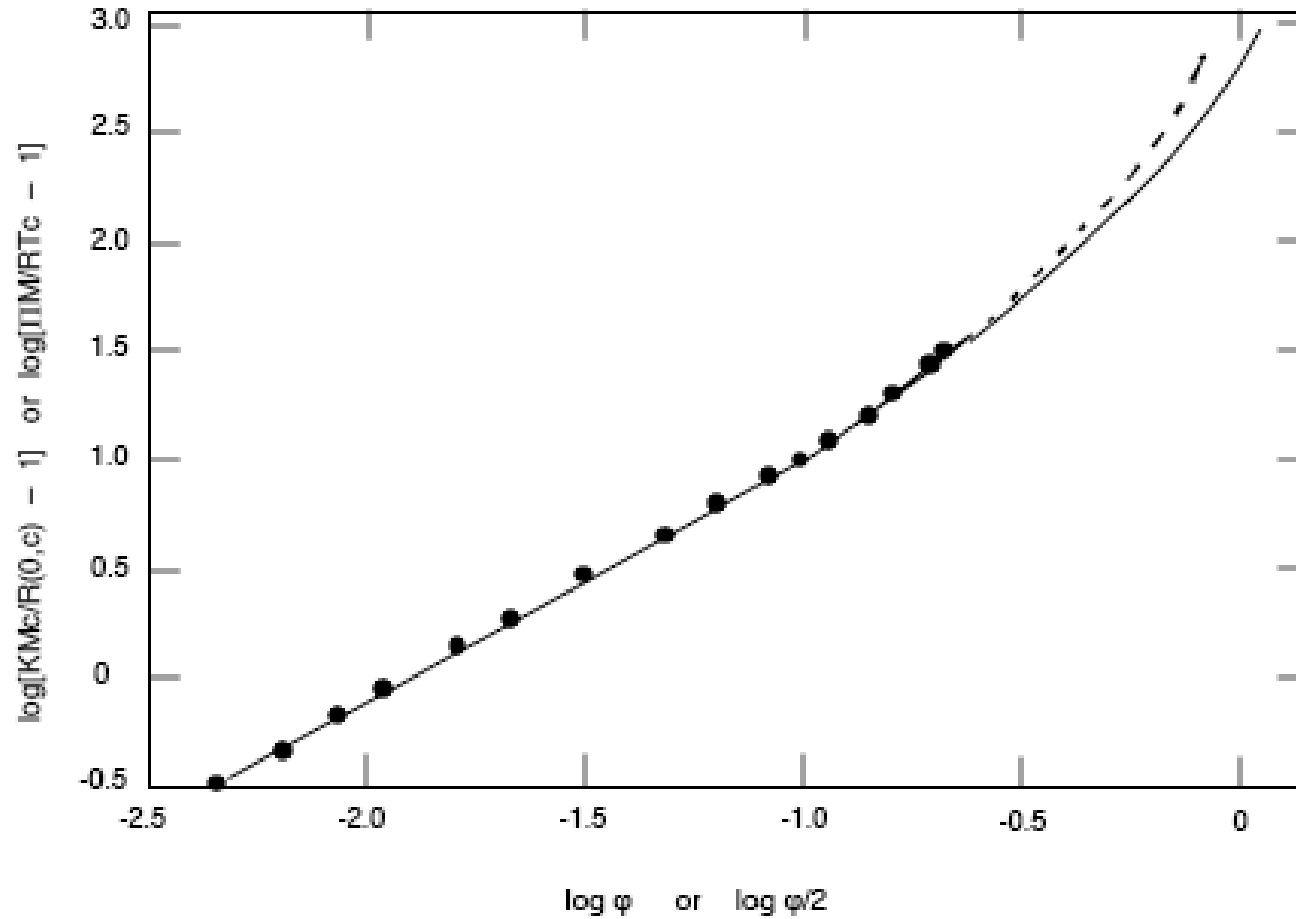
Circle, PStyr/CHx;

Square, PDMS/MEK;

Diamond, PIB/Bz



$$\Gamma(c) = \frac{v_2^2 M}{V_1} \left( \frac{1}{1 - \varphi} - 2\chi_1 - \chi_2 \varphi \left( 2 + \frac{1 - (1 + n)\varphi}{(1 - \varphi)^{1+n}} \right) \right)$$

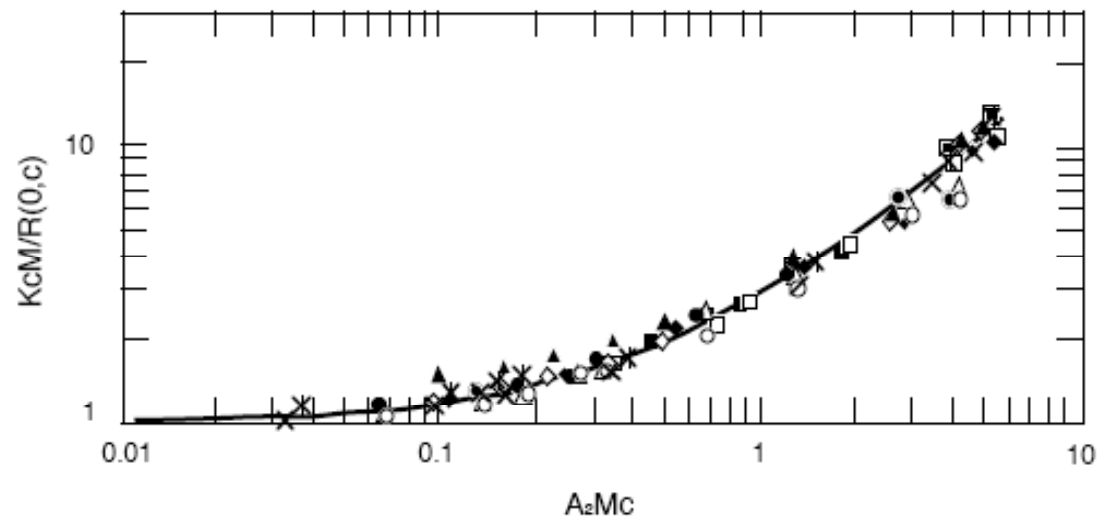


## *Moderately concentrated solutions*

Rodlike chains, for  $c < c_{\text{mesophase transition}}$

$$\Gamma(c) = 2A_2M + 3A_3Mc$$

Solutions of poly(benzyl glutamate):



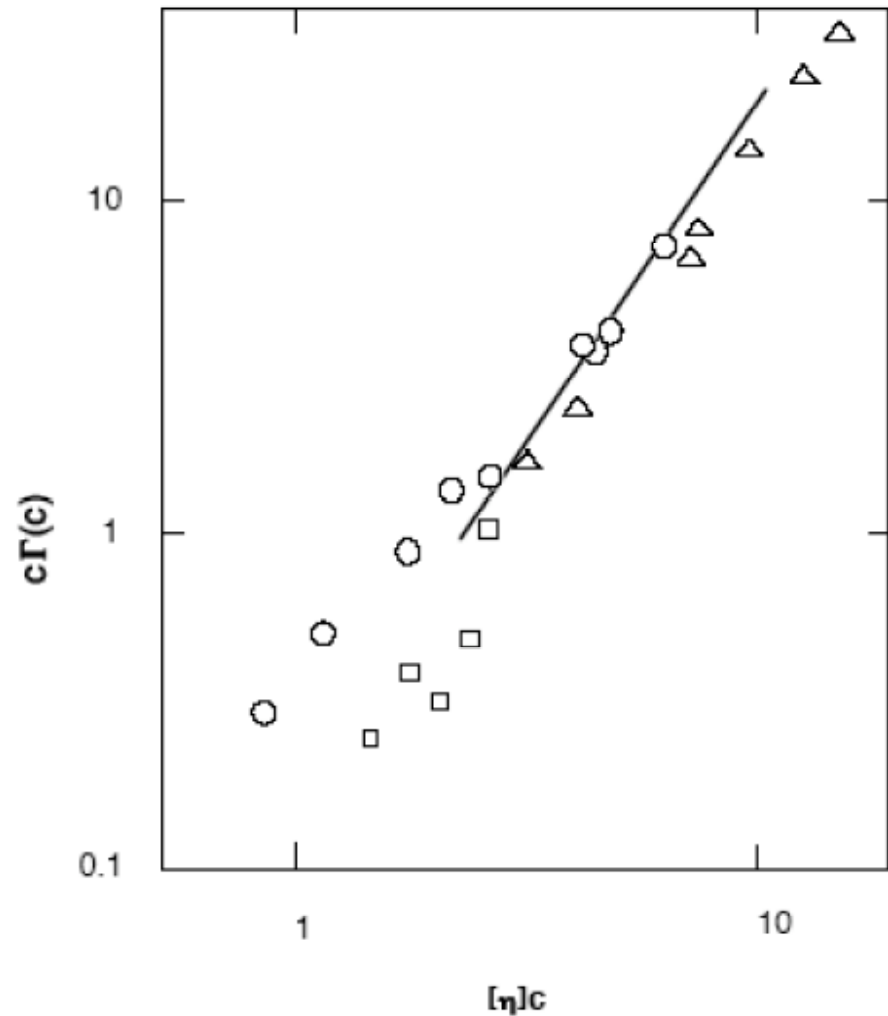
A similar truncation appears to hold for flexible chain polymers under Flory

Theta conditions:

$$c\Gamma(c) \approx 3A_3Mc^2$$

The data are for polystyrene of various  $M$ , under Flory Theta conditions.

Line has slope 2



"Scaling behavior" for moderately concentrated polymer solutions in "good solvents":

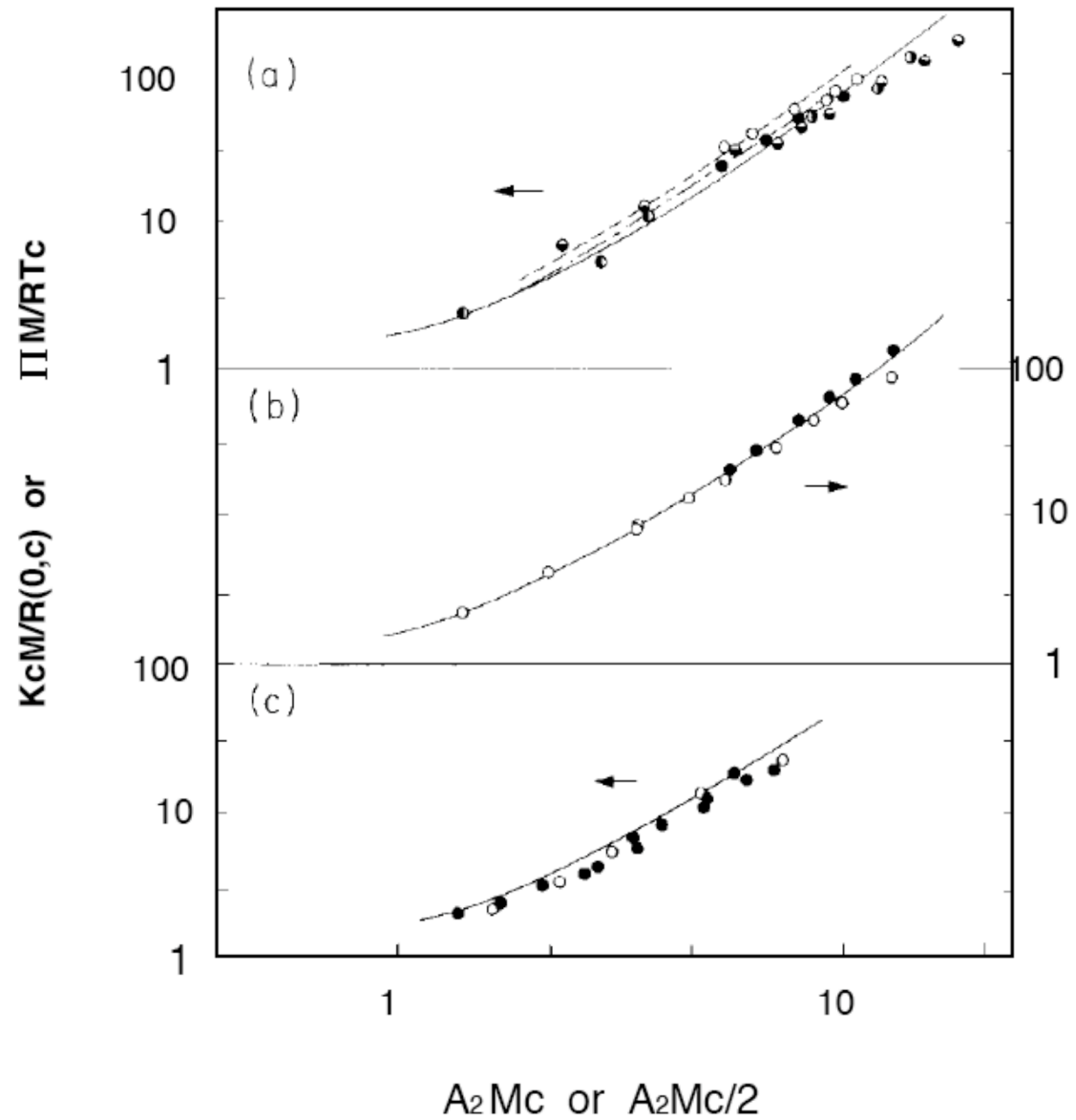
For a monodisperse solute, with  $\Upsilon_3 = A_3Mc/(A_2Mc)^2$ :

$$\Pi M/RTc \approx 1 + A_2Mc\{1 + (\Upsilon_3/p)A_2Mc\}^p$$

$$KcM/R(0,c) \approx 1 + 2A_2Mc\{1 + (3\Upsilon_3/4p)(2A_2Mc)\}^p$$

$p = (4 - 3\varepsilon)/(3\varepsilon - 2) \approx 1/4$  is determined by the stipulations that:

- $A_2M^2/N_A R_G^3$  tends to a constant, with  $R_G^2 \propto M^\varepsilon$  and  $\varepsilon \approx 6/5$ , and
- $\Pi$  should not depend on  $M$  for such a system in moderately concentrated solutions.



**Data on various polymers in systems with  $A_2 > 0$**

## Scattering for arbitrary concentration and $q$

$$\frac{K_{op}cM}{R(q,c)} = \frac{1}{P(q,c)} + c\Gamma(c)H(q,c)$$

### *Dilute to low concentrations*

$$\frac{K_{op}cM}{R(q,c)} = \frac{1}{P(q,0)} + c\Gamma(c)\hat{H}(q,c)$$

$$\hat{H}(q,c) = \frac{2\psi_2 W_2(q)\hat{c} + \{3\psi_3 W_3(q) + 4[P(q,0)W_2(q)]^2 - W_3(q)\}\psi_2^2 \hat{c}^2}{2\psi_2 \hat{c} + 3\psi_3 \hat{c}^2} + \dots$$

$\psi_j = A_j M (M/NAR_G^3)^{j-1}$  are dimensionless virial coefficients

In the "**Single-Contact**" approximation of Zimm,  $\hat{H}(q,c) = 1$ , and  $\Gamma(c)$  is given by the virial expansion discussed above, giving rise to the "Zimm plot".

## Moderately Concentrated and Concentrated Solutions/Suspension

$$\frac{K_{op}cM}{R(q,c)} = \frac{1}{P(q,c)} + c\Gamma(c)H(q,c)$$

For moderately concentrated spheres interacting through a hard-core potential,  $P(q,c) = P(q,0)$ , and a first-order theory, correct to 3-body interactions gives

$$H(q,c) = P(2q,0)^{1/2}/P(q,0)$$

To a first-approximation for polymer solutions, one might adopt the same form, but use  $P(q,c)$  for the random-flight chain, calculated with the value of  $R_G^2$  appropriate for the concentration of interest.

Mean-field theory for concentrated polymer solutions gives  $H(q,c) \approx 1$

Spheres: Hard-core potential

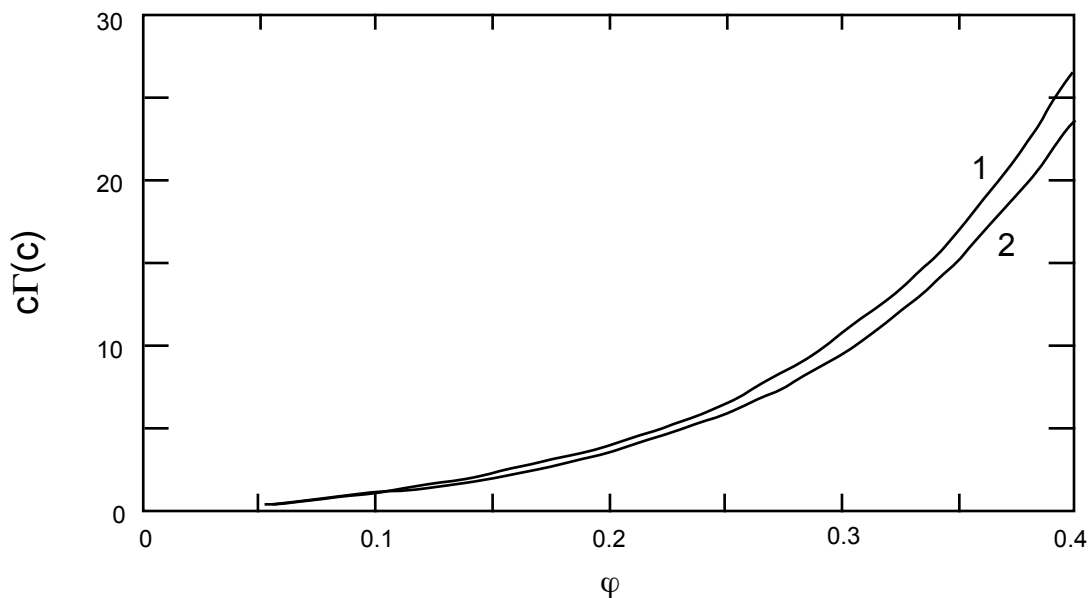
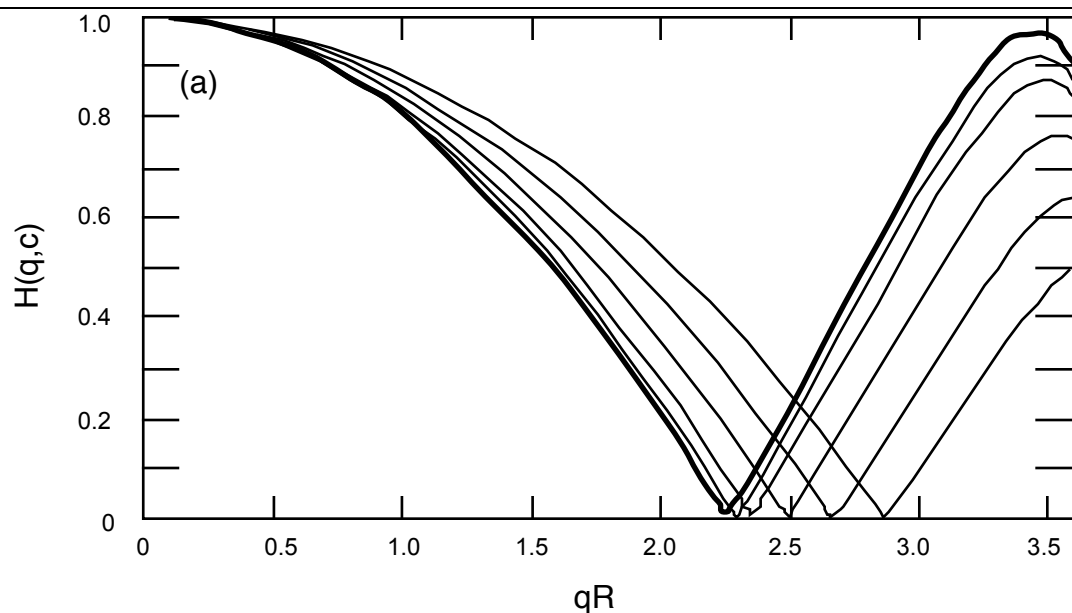
Upper:

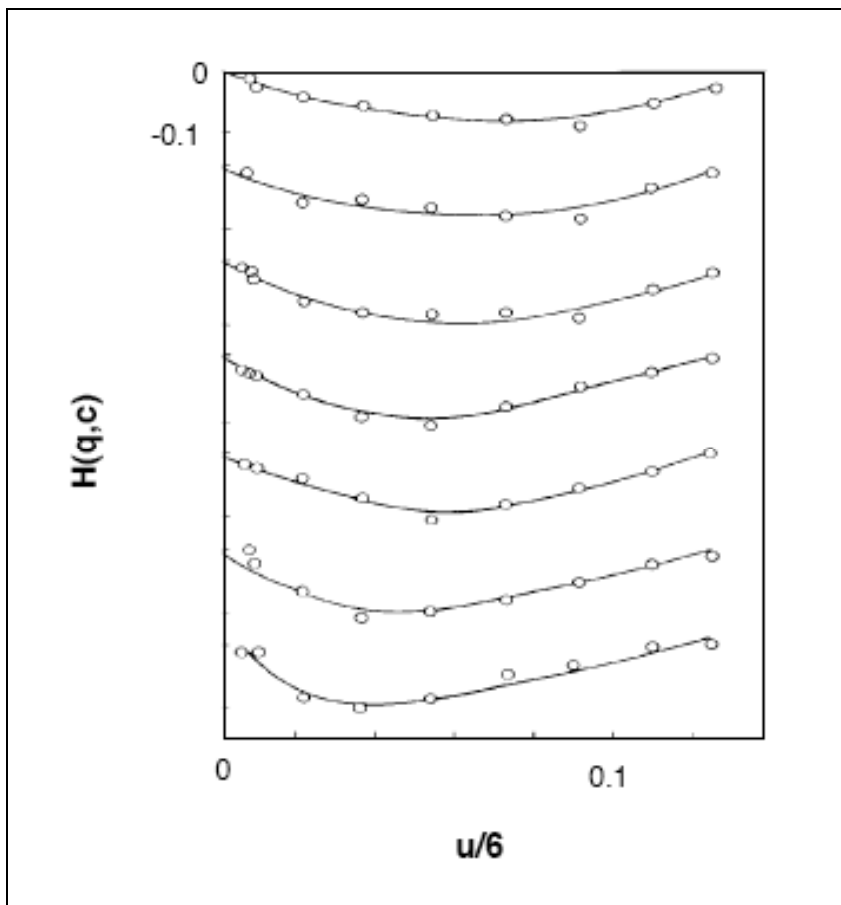
Heavy curve is for 3-body approximation;

Lighter curves are for the all-interactions approximation; these are for  $\varphi = 0.05, 0.1, 0.2, 0.3$  and  $0.4$  (left to right)

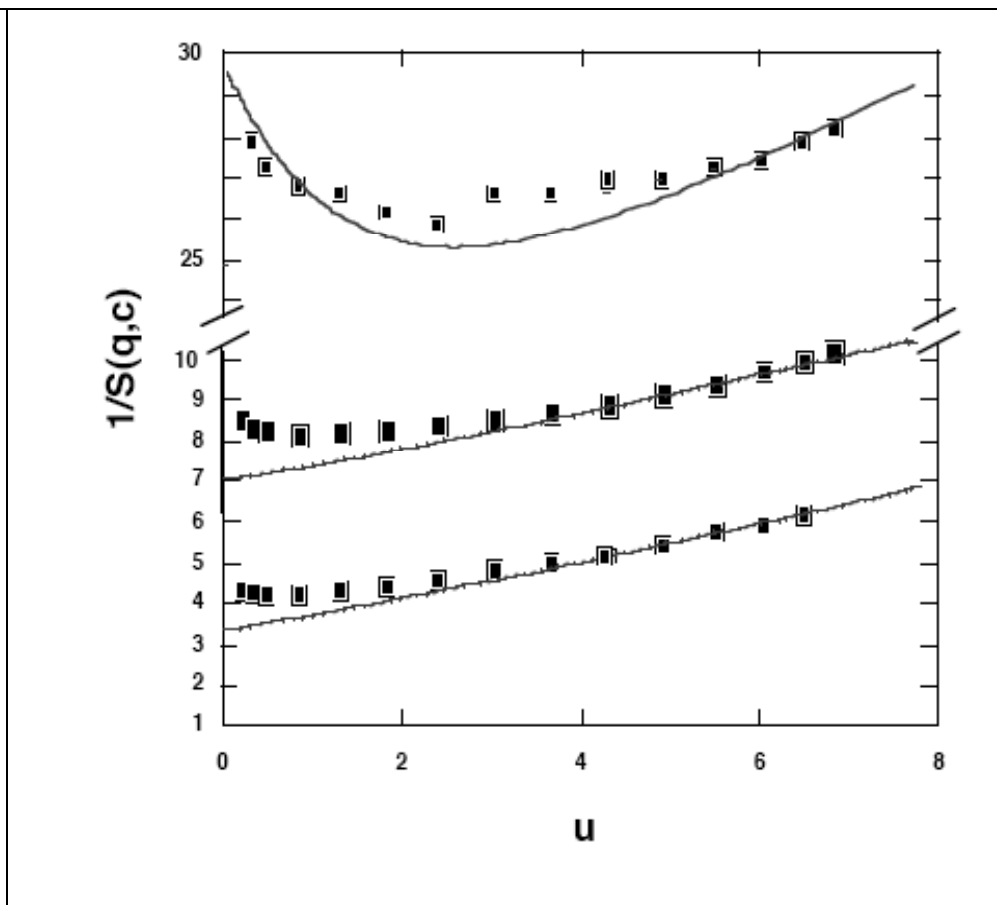
Lower:

Curves 1 and 2 are for the 3-body and full interaction approximations, resp.





Data on polystyrene at Flory Theta conditions,  $c$  increasing from bottom to top from  $[\eta]c = 0.60$  to  $6.54$



Data on poly( $\alpha$ -methyl styrene) in a good solvent,  $c$  increasing from bottom to top.

## *Angular Dependence*

$$b(q,c)^2 = \mathbf{R}(0,c)\{\partial\mathbf{R}^{-1}(q,c)/\partial q^2\}$$

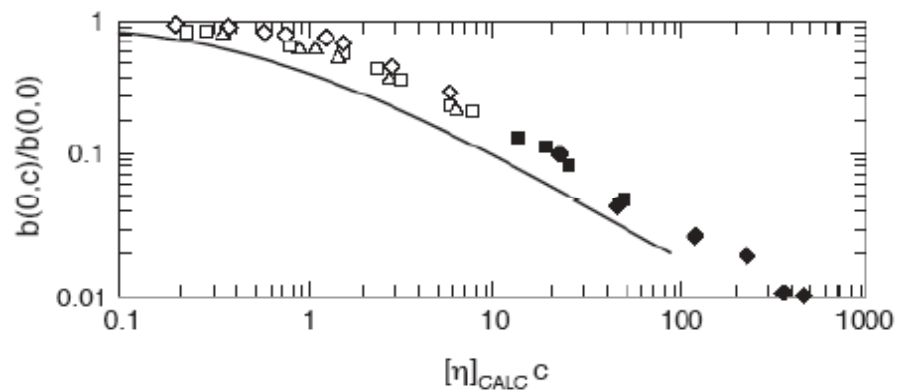
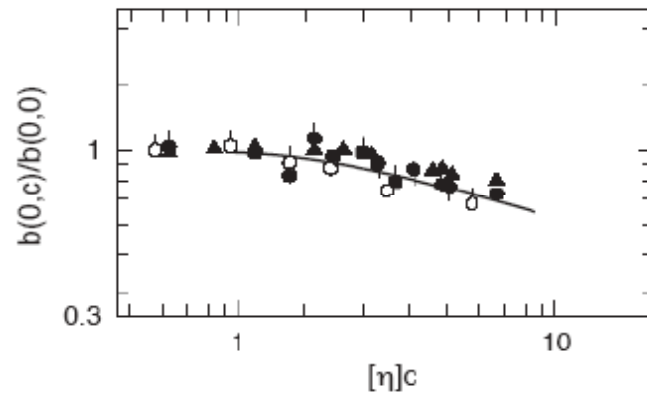
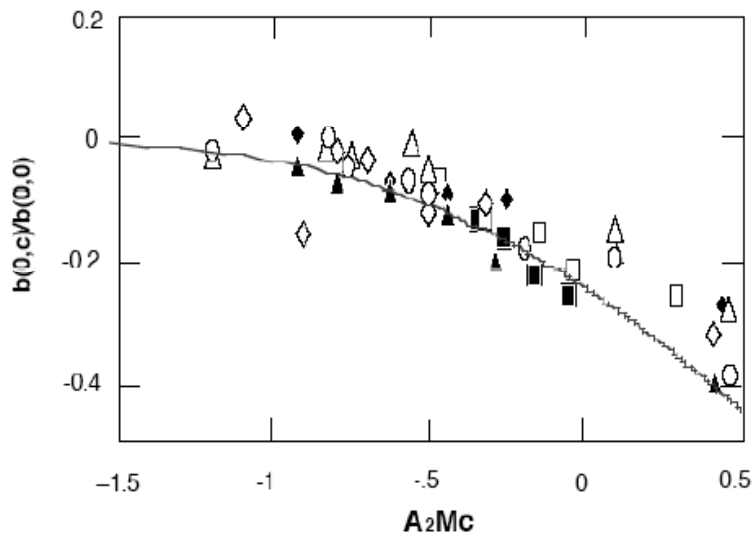
$$b(q,c)^2 = \xi_P(q,c)^2 + \xi_H(q,c)^2$$

$$\xi_P(q,c)^2 = \{1/[1 + c\Gamma(c)]\}\{\partial\mathbf{P}^{-1}(q,c)/\partial q^2\}$$

$$\xi_H(q,c)^2 = \{c\Gamma(c)/[1 + c\Gamma(c)]\}\{\partial H(q,c)/\partial q^2\}$$

For dilute and concentrated polymer solutions,  $H(q,c) \approx 1$

For moderately concentrated polymer solutions,  $\partial H(q,c)/\partial q^2 \leq 0$



Solutions of Poly(benzyl glutamate)

Upper: Polystyrene under Flory Theta Conditions

Lower: Various polymers in Good Solvents (PDMS, Psty, PMMA)

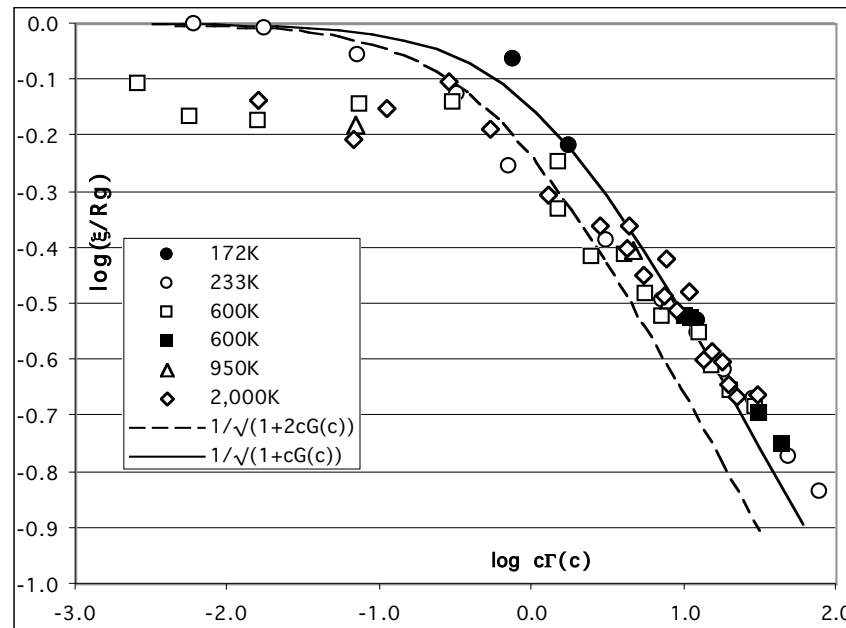
## Behavior for large $u$ (as in neutron scattering):

$$u \gg 1: 1/P(q,0) \approx 1/2[1 + u + O(1/u)]$$

$$2 \frac{K_{OPcM}}{R(q;c)} \approx 1 + u + 2c\Gamma(c)H(q;c)$$

With the assumption that  $H(q;c) \approx 1$  in this regime, the **Ornstein-Zernike** form emerges

$$2 \frac{K_{OPcM}}{R(q;c)} \approx [1 + 2c\Gamma(c)]\{1 + (\xi q)^2\}; \quad \xi^2 = R_g^2/[1 + 2c\Gamma(c)]$$



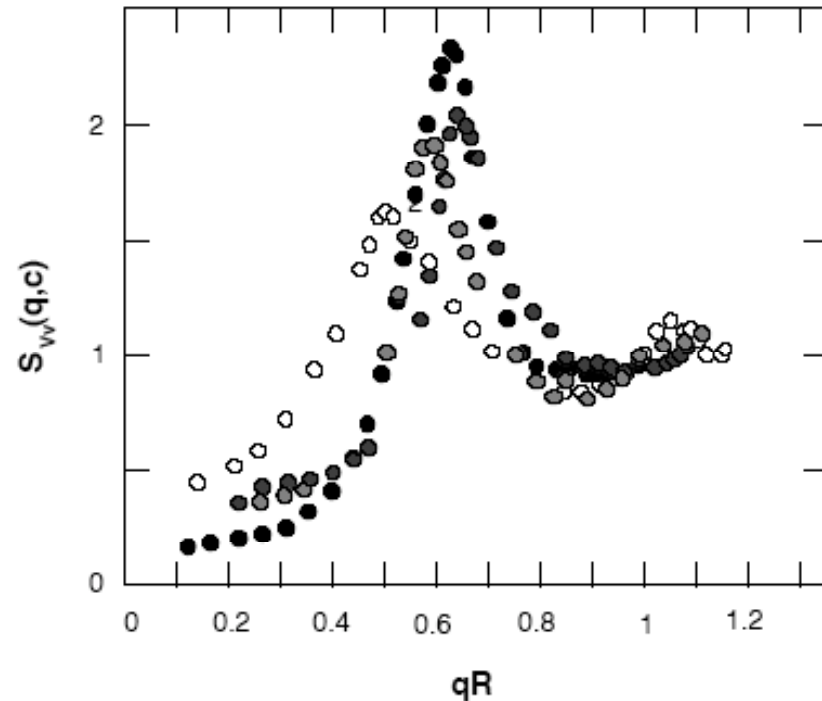
## *Charged Spheres:*

$$\frac{\mathbf{R}(q,c)}{K_{op}cM} = S(q,c) = \frac{P(q,c)}{1 + c\Gamma(c)P(q,c)H(q,c)} \approx \frac{1}{c\Gamma(c)H(q,c)}$$

Debye screening length  $\kappa^{-1}$  provides a measure of the range of the electrostatic interactions, where

$$\kappa^{-1} = (8\pi N_A L_B I_0)^{-1/2}$$

where  $L_B = e^2/\epsilon kT$  is the Bjerrum length, with  $\epsilon$  the dielectric strength ( $L_B/\text{nm} \approx 57/\epsilon$  at 25°C, or  $L_B \approx 0.7$  nm for water), and  $I_0$  is the ionic strength ( $I_0 = \sum v_i^2 m_i/2$ , with  $v_i$  and  $m_i$  the molarity and charge of species  $i$ ).



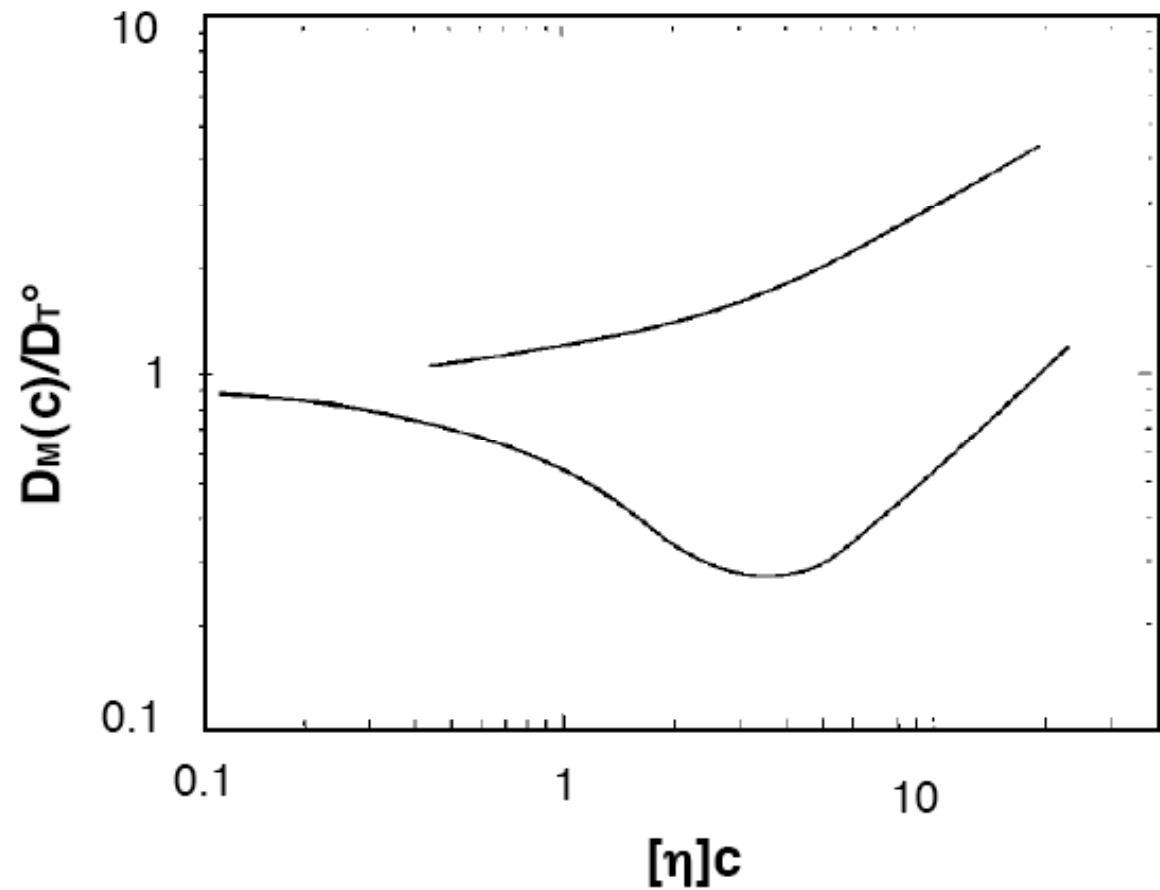
$$\ln[g^{(2)}(\tau; q, c) - 1]^{1/2} = \ln[f_C]^{1/2} - K^{(1)}(q, c)\tau + \frac{1}{2!} K^{(2)}(q, c)\tau^2 + \dots$$

$$\lim_{q \rightarrow 0} K^{(1)}(q, c) = D_M(c) q^2$$

Data for a variety of M  
and solvents

Upper curve:  
Good solvents

Lower Curve  
Flory Theta Solvent  
conditions



## Non Ergodic Behavior, e.g., Many Gels

$$g_t^{(2)}(\tau; q, c) = 1 + x(1 - x)f_c^{1/2} |f_E(\tau, q) - f_E(\infty, q)| + \\ x^2 f_c [f_E^2(\tau, q)(\tau, q) - f_E^2(\tau, q)(\infty, q)]$$

Ensemble-averaged normalized concentration fluctuation correlation function:

$$f_E(\tau, q) = \langle \Delta c(\tau, q) \Delta c(0, q) \rangle_E / \langle \Delta c^2 \rangle_E; \quad 1 \geq f_E(\tau, q) \geq 0$$

Ergodic system,  $f_E(\infty, q) = 0$ ; nonergodic medium,  $1 \geq f_E(\infty, q) \geq 0$

If the gel network with spatial fluctuations in the network junctions:

$$x = \langle n(q) \rangle_E / \langle n(q) \rangle_t; \quad f_E(\infty, q) = \exp(-q^2 \langle \delta^2 \rangle)$$

$\langle \delta^2 \rangle$  is the mean square amplitude of the spatial fluctuation of the constraint

## *Intermolecular association in polymer solutions*

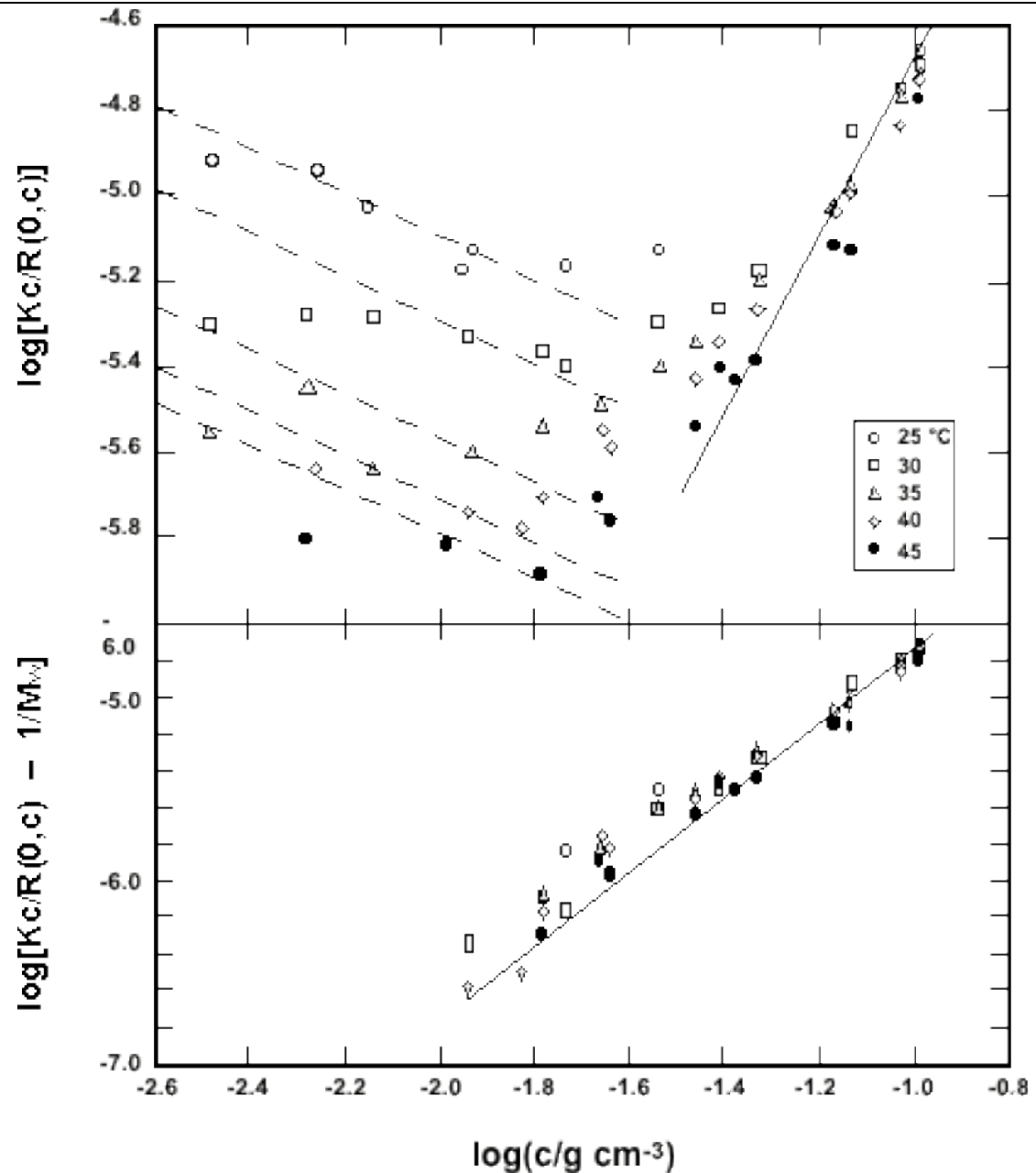
- Association of small molecule surfactants to form wormlike micelles, usually an equilibrium process
- Association of linear flexible chain polymers, often forming meta-stable states, sometimes in the form of quasi-randomly branched structures, and sometimes as more dense, colloidal particles.

***Intermolecular association  
in micelles***

Aqueous solutions of  
wormlike micelles of  
hexaoxyethylene dodecyl  
ether

association-dissociation  
equilibria for wormlike  
micelles suggest that for a  
range of  $c$ ,  $M_w$  might  
increase as  $M_w \propto c^{1/2}$

Dashed lines: Slope  $-1/2$   
Solid lines: Slope 2



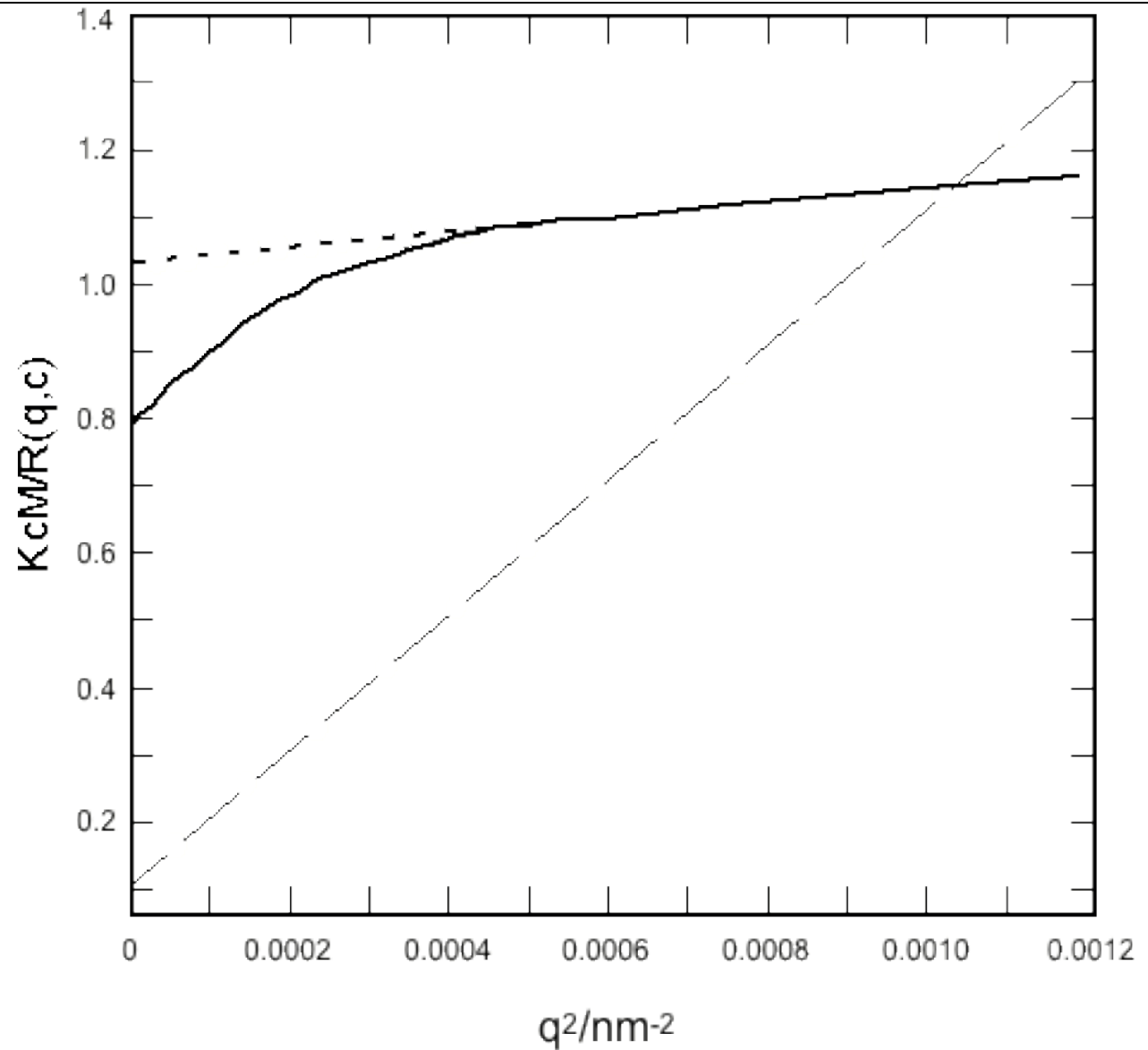
## *Metastable association*

The analysis of metastable behavior is sometimes facilitated by an approximate representation with a few 'pseudo components' (often two or three), each of which dominates the scattering over a limited range of  $q$ , with  $M$ ,  $A_2$  and  $P(q,c)$ :

$$\mathbf{R}(q,c) = \sum_{\mu} \mathbf{R}_{\mu}(q,c)$$

$$\approx K \sum_{\mu}$$

$$\left( \frac{Mc}{P(q,c) + 2A_2Mc} \right)_{\mu,c}$$



*Thanks for your patience and attention!*

***Low concentrations: The third virial coefficient (isotropic elements)***

$$\tilde{B}_{LS}(c) \approx M_{LS}^{-2} \sum_{\nu}^C \sum_{\mu}^C \tilde{\Psi}_{\nu} \tilde{\Psi}_{\mu} \left( w_{\nu} w_{\mu} M_{\nu} M_{\mu} \tilde{B}_{\nu\mu}^0 + \sum_{\kappa}^C w_{\kappa} [\tilde{B}_{\nu\mu\kappa}^0 - M_{\kappa} \tilde{B}_{\nu\kappa}^0 \tilde{B}_{\mu\kappa}^0] c \right)$$

Optically identical scattering elements:

$$A_{3,LS} \approx M_w^{-2} \sum_{\nu}^C \sum_{\mu}^C \sum_{\kappa}^C w_{\nu} w_{\mu} w_{\kappa} M_{\nu} M_{\mu} A_{3,\nu\mu\kappa} \\ - (4/3) M_w^{-3} \sum_{\nu}^C \sum_{\mu}^C \sum_{\kappa}^C \sum_{\sigma}^C w_{\nu} w_{\mu} w_{\kappa} w_{\sigma} M_{\nu} M_{\mu} M_{\kappa} M_{\sigma} [A_{2,\nu\kappa} A_{2,\mu\kappa} - A_{2,\nu\kappa} A_{2,\mu\sigma}]$$

where  $A_{2,\nu\mu} = \tilde{B}_{\nu\mu}^0/2$  (as above) and  $A_{3,\nu\mu\kappa} = \tilde{B}_{\nu\mu\kappa}^0/3$ .

- Very little work to explore the terms in this expression.

1. *Berry, G.C., Total intensity light scattering from solutions of macromolecules, in Soft Matter: Scattering, Manipulation & Imaging, R. Pecora and R. Borsali, Editors. 2005, In Presss.*
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