Developments and Trends in Light Scattering on Macromolecular Solutions

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The-agony-of-getting-older.

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LIGHT SCATTERING by small particles

by

H.C. van de Hulst
Leiden Observatory

THE SCATTERING OF LIGHT AND OTHER ELECTROMAGNETIC RADIATION

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STATIC LIGHT SCATTERING

Rayleigh ratio from a solution with solute concentration $c$

$$R_{Si}(q,c) = r^2 I_{Si}(\theta)/V_{obs} I_{INC}$$

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

- $k_0$ vectoral wave number along the incident beam
- $k$ vectoral wave number along the scattered beam
- $q$ is the vector difference between the and scattered light, respectively:
  $$q = k_0 - k$$
- $|k_0| = |k| = (4\pi n/\lambda)$ for static scattering, with $\lambda$ the wavelength in vacuum
- The modulus $|q|$ of the scattering vector $q$ becomes
  $$q = (4\pi/\lambda)\sin(\theta/2)$$
$R_{Hv}(q,c)$ and $R_{Vv}(q,c)$ are given by (Using $I_{\text{solution}} - I_{\text{solvent}}$):

$$R_{Hv}(q,c) = R_{\text{aniso}}(q,c)$$

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

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

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

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

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

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

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

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

\[ \frac{K_{op}cM}{R(q,c)} = \frac{1}{S(q,c)} = \frac{1}{P(q,c)} + c\Gamma(c)H(q,c) \]
For a **monodisperse solute (only)**, \( F(0,c) \) is related to the equilibrium osmotic modulus \( K_{OS} \):

\[
F(0,c) = \left( \frac{M}{cRT} \right) K_{OS}
\]

\[
K_{OS} = c \frac{\partial \Pi}{\partial c}
\]

where \( \Pi \) is the osmotic pressure.

With this expression, for a **monodisperse** solute,

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

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

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

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

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

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

\[ a_{LS}(c) = \frac{kT}{6\pi\eta D_M(c)}; \quad \lim_{c=0} a_{LS}(c) = R_H: \text{ Hydrodynamic Radius} \]
Static scattering extrapolated to infinite dilution:

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

LS denotes an averaging over heterodispersity appropriate for scattering; \( K' = 4\pi^2/\Lambda_0^4 \),

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

In the RGD limit for a solute:

\[ M_{LS} = \psi^{-2} \sum \nu \omega_{\nu} M_{\nu}^{-1} \left\{ \sum \nu \psi_{\nu,j} m_{j,\nu} \right\}^2 \]

For identical isotropic scattering elements:

<table>
<thead>
<tr>
<th>Single solvent component</th>
<th>Multiple solvent components</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_{LS} = \sum \nu \omega_{\nu} M_{\nu} = M_w )</td>
<td>( M_{LS} = \frac{\left( \frac{\partial \hat{n}}{\partial c} \right)_\Pi^2}{\left( \frac{\partial \hat{n}}{\partial c} \right)_w^2} M_w )</td>
</tr>
</tbody>
</table>
Two, optically distinct scattering elements, single solvent component:

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

\[ Y = \frac{\Psi_A - \Psi_B}{\Psi} \approx \frac{n_A - n_B}{w_A n_A + (1 - w_A)n_B} \]

\[ \mu_n = \sum_{v=1}^{C} w_v M_v \Delta w_v^n / M_w; \quad n = 1, 2 \]

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

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. $(ν_A - ν_B)/ν_0$.

(Benoit)
Depolarized scattering in the RGD regime:

Identical cylindrically symmetric polarizabilities for all chain elements:

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

\[
\delta_{LS}^2 = M_w^{-1} \sum_{\nu} C \nu M_\nu \delta_{\nu}^2 ; \quad \delta_{\nu}^2 = \delta_0^2 \sum_{j}^{n_\nu} \sum_{k}^{n_\nu} \left( \frac{3}{2} \right) \left( \cos^2 \beta_{ij} \right) - 1
\]

- \( \beta_{ij} \) 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:

\[
M_{LS,H\nu} = (3/5) \delta_{LS}^2 M_w ; \quad M_{LS,V\nu} = \left\{ 1 + \left( 4/5 \right) \delta_{LS}^2 \right\} M_w
\]
Wormlike chain model:

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

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

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

coil: \quad 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 $M_{LS}$:

1. $\widetilde{\psi} \Rightarrow h_{sph}(\check{n})\widetilde{\psi}; \quad h_{sph}(\check{n}) = \frac{3(\check{n} + 1)}{2(\check{n}^2 + 2)}; \quad \check{n} = \frac{n_{solute}}{n_{medium}}$

2. A function $m(\check{n}, \lambda, M_{\nu})$ specific for each particle shape is required:

$$M_{LS} = \sum_{\nu} C \ w_{\nu} M_{\nu} \ [m(\check{n}, \lambda, M_{\nu})]^2$$
Special case, **Mie scattering** for spherical particles:

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

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

\[
M_{LS} \approx M\left\{\frac{3}{2\tilde{\alpha}^2(\tilde{n} - 1)}h_{sph}(\tilde{n})\right\}^2
\]
Scattering at infinite dilution and "small" scattering angle in the RGD regime:

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

(Optically isotropic scattering elements)

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

\[
R_{G,LS}^2 = \sum_{c} w_v M_v^{-1} \sum_{\nu} \sum_{\nu} \psi_{j,\nu} \bar{\psi}_{k,\nu} m_{j,\nu} m_{k,\nu} \langle |r_{jk}|^2 \rangle
\]

\[
\sum_{\nu} w_v M_v^{-1} [\sum_{j} \psi_{j,\nu} m_{j,\nu}]^2
\]
Identical scattering elements:

\[ R_{G,LS}^2 = \frac{1}{M_w} \sum_v w_v M_v R_{G,v}^2; \quad R_{G,v}^2 = \frac{1}{2n_v^2} \sum_j \sum_k \langle |r_{jk}|^2 \rangle \approx \left( \frac{R_G^2}{M^\epsilon} \right) M_v^\epsilon \]

Similarly, for the Hydrodynamic Radius:

\[ R_{H,LS} = M_w / \sum_v w_v M_v R_{H,v}^{-1}; \quad R_{H,v} \approx \left( \frac{R_H}{M^\mu} \right) M_v^\mu \]

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

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**Mean-square radius of gyration for some models**

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

\[ S(Z) = 1 - 3Z + 6Z^2 - 6Z^3 [1 - \exp(-Z^{-1})] \approx (1 + 4Z)^{-1}; \quad Z = \hat{a}/L \]
**$R_{G,LS}^2$ and $R_{H,LS}$ for some power-law approximations**

<table>
<thead>
<tr>
<th></th>
<th>$R_{G,LS}$</th>
<th>$R_{H,LS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exact Relation</strong>&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td>$(1/M_w)\sum_{\nu} w_{\nu} M_{\nu} R_{G,\nu}^2$</td>
<td>$C \frac{M_w}{\sum_{\nu} w_{\nu} M_{\nu} R_{H,\nu}^{-1}}$</td>
</tr>
<tr>
<td><strong>Approximation for</strong>&lt;sup&gt;(b)&lt;/sup&gt; $R_G \propto R_H \propto M^{\varepsilon/2}$</td>
<td>$(R_G^2/M^\varepsilon) M^{\varepsilon+1}_{\varepsilon+1}/M_w$</td>
<td>$(R_H/M^{\varepsilon/2}) M_w/M^{1-\varepsilon}_{1-\varepsilon}$</td>
</tr>
<tr>
<td>Random-flight coil&lt;sup&gt;(c)&lt;/sup&gt;; $\varepsilon = 1$</td>
<td>$(R_G^2/M) M_z$</td>
<td>$(R_H/M^{1/2}) M_w/M^{1/2}_{(1/2)} \approx$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(R_H/M^{1/2}) M_w^{1/2}(M_w/M_n)^{0.10}$</td>
</tr>
<tr>
<td>Rodlike chain (thin)&lt;sup&gt;(c)&lt;/sup&gt;; $\varepsilon \approx 2$</td>
<td>$(R_G^2/M^2) M_z M_{z+1}$</td>
<td>$(R_H/M) M_w$</td>
</tr>
<tr>
<td>Sphere&lt;sup&gt;(c)&lt;/sup&gt;; $\varepsilon = 2/3$</td>
<td>$(R_G^2/M^{2/3}) M_z^{5/3}/M_w \approx$</td>
<td>$(R_H/M^{1/3}) M_w^{2/3}_{(2/3)} \approx$</td>
</tr>
<tr>
<td></td>
<td>$(R_G^2/M^{2/3}) M_z^{2/3}(M_w/M_z)^{0.10}$</td>
<td>$(R_H/M^{1/3}) M_w^{1/3}(M_w/M_n)^{0.10}$</td>
</tr>
</tbody>
</table>

$M^{(\mu)}_{(\mu)} = \sum_{\nu} w_{\nu} M^{(\mu)}_{\nu}$; $M^{(\mu)}_{(\mu)}$ is $M_n$, $M_w$, $(M_w M_z)^{1/2}$ and $(M_w M_z M_{z+1})^{1/3}$ for $\mu = -1, 1, 2$ and $3$
Wormlike Chain (not a power-law):

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

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

\[ \approx [1 + 4Z_z(h + 2)/(h + 3)]^{-1} = [1 + 4\hat{a}/L_{z+1}]^{-1} \]
**Branched flexible chain polymers:**

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

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

- \( f \) 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

\[ R_{G,LS}^2 = \frac{\sum \sum \sum \psi_{j,v} \psi_{k,v} m_{j,v} m_{k,v} \langle |r_{jk}|^2 \rangle}{2[\sum \psi_{j,v} m_{j,v}]^2} \]

Special case:

- two scattering elements, A and B
- weight fraction \( w_A = 1 - w_B \)
  \[ = n_A m_A / (n_A m_A + n_B m_B) \]

- \( \psi = w_A \psi_A + w_B \psi_B \)
- \( \bar{w}_A = 1 - \bar{w}_B = w_A \psi_A / \psi; \) \( \bar{\psi}_A \) and \( \bar{\psi}_B \) many be +, −, or 0.

\[ R_{G,LS}^2 = \bar{w}_A R_{G,A}^2 + (1 - \bar{w}_A) R_{G,B}^2 + \bar{w}_A (1 - \bar{w}_A) \Delta_{AB}^2 \]

\( \Delta_{AB}^2 \) 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 $R_A$ ($\Delta_{AB} = 0$)

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

For a thin shell enclosing the solvent, such that $\omega_A = 0$:

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

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

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

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

Homopolymer comprising cylindrically symmetric scattering elements:

\[
\left[ R_{Si}(q,c)/c \right]_0^0 = K' \hat{n}_s^2 (\partial \hat{n}/\partial c)_w^2 M_{LS, Si} P_{LS, Si}(q,0)
\]

\[
P_{LS, Hv}(q,0) = 1 - (3/7) R_{G, LS, Hv}^2 q^2 + \ldots
\]

\[
P_{LS, VV}(q,0) = 1 - (1/3) R_{G, LS, VV}^2 q^2 + \ldots
\]

For the persistent coil model,

\[
R_{G, LS, Hv}^2 = \frac{\sum_{\nu}^{C} w_{\nu} M_{\nu} \delta_{\nu}^2 f_{3,\nu}^2 R_{G, \nu}^2}{\sum_{\nu}^{C} w_{\nu} M_{\nu} \delta_{\nu}^2}; \quad R_{G, LS, VV}^2 = \frac{\sum_{\nu}^{C} w_{\nu} M_{\nu}(1 + 4\delta_{\nu}^2/5) J(\delta_{\nu}) R_{G, \nu}^2}{\sum_{\nu}^{C} w_{\nu} M_{\nu}(1 + 4\delta_{\nu}^2/5)}
\]

\[
J(\delta_{\nu}) = \frac{1 - (4/5)f_{1,\nu}\delta_{\nu} + (4/7)(f_{2,\nu}\delta_{\nu})^2}{1 + (4/5)\delta_{\nu}^2}
\]
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 $\hat{\lambda}$: 

$\cdots$, $f_1$; $- - -$, $f_2$; $- - -$, $f_3$; and $- - -$, $f_4$.

Owing to the decrease in $\delta/\delta_0$ with increasing $L/\hat{\lambda}$, the influence of the depolarized components decreases rapidly for $L/\hat{\lambda} > 1$, and one can simply put all $f_i \approx 1$ with negligible error in the analysis of data.
Upper:
$[Kc/R_{Vv}(0,c)]^{1/2}$ for cis-PBO.

Middle:
$Kc/R_{Hv}(0,c)$ for cis-PBO.

Lower:
$[Kc/R_{Vv}(0,c)]^{1/2}$ for ab-PBO.
Scattering beyond the RGD regime

\[ R_{G,LS}^2 = \frac{\sum_{\nu} w_\nu M_\nu y(\tilde{n}, \lambda, M_\nu) [m(\tilde{n}, \lambda, M_\nu)]^2 R^{2}_{G,\text{RGD},\nu}}{\sum_{\nu} w_\nu M_\nu [m(\tilde{n}, \lambda, M_\nu)]^2} \]

Mie scattering theory:

\[ R_{G,LS}^2 = (3/5) \frac{\sum_{\nu} w_\nu M_\nu [m_{\text{sph}}(\tilde{n}, \tilde{\alpha}_\nu)]^2 y_{\text{sph}}(\tilde{n}, \tilde{\alpha}_\nu) R_\nu^2}{\sum_{\nu} w_\nu M_\nu [m_{\text{sph}}(\tilde{n}, \tilde{\alpha}_\nu)]^2} \]

Evaluation of an average R from \( R_{G,LS}^2 \) requires an iterative process.
Scattering at infinite dilution and arbitrary $q$

\[
P_{LS}(q,0) = \frac{\sum_{\nu}^C w_{\nu}M_{\nu}^{-1} \sum_{j,k} \bar{\psi}_{j,\nu} \bar{\psi}_{k,\nu} m_{j,\nu} m_{k,\nu} \langle \sin(q|r_{jk}|) / q|r_{jk}| \rangle}{\sum_{\nu}^C w_{\nu}M_{\nu}^{-1} \left[ \sum_{j} \bar{\psi}_{j,\nu} m_{j,\nu} \right]^2}
\]

Identical scattering elements

\[
P_{LS}(q,0) = \frac{1}{M_w} \sum_{\nu}^C w_{\nu} M_{\nu} P_{\nu}(q,0); \quad P_{\nu}(q,0) = \frac{1}{n_{\nu}^2} \sum_{j,k} \langle \sin(q|r_{jk}|) / q|r_{jk}| \rangle
\]

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## Particle scattering functions for some optically isotropic models

<table>
<thead>
<tr>
<th>Model</th>
<th>$R_G^2$</th>
<th>$P(q,0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random-flight linear coil</td>
<td>$\frac{\lambda L}{3}$</td>
<td>$u = \frac{\lambda q^2}{3}$ $p_c(u) = (2/u^3)[u - 1 + \exp(-u)]$</td>
</tr>
<tr>
<td>Disk (&quot;infinitely thin&quot;)</td>
<td>$R^2/2$</td>
<td>$y = Rq$ $p_q(2y^2)[1 - J_1(2y)/y]$</td>
</tr>
<tr>
<td>Sphere</td>
<td>$3R^2/5$</td>
<td>$y = Rq$ $p_q(9/y^6)[\sin(y) - y\cos(y)]^2$</td>
</tr>
<tr>
<td>Shell (&quot;infinitely thin&quot;)</td>
<td>$R$</td>
<td>$y = Rq$ $p_q[\sin(y)/y]^2$</td>
</tr>
<tr>
<td>Rod (&quot;infinitely thin&quot;)</td>
<td>$L^2/12$</td>
<td>$x = Lq$ $p_1(x) = (2/x^2)[x\sin(x) - 1 + \cos(x)]$</td>
</tr>
</tbody>
</table>

### 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 $M$:

$$P_{LS}(q,0) = \frac{2}{rMw}q^2\left\{1 - \frac{1}{rM_nq^2}\left[1 - M_n\sum_{v} w_vM_v^{-1}\exp(-rM_vq^2)\right]\right\}$$

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

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

$$P_{LS}(q,0) = \frac{2M_L}{qM_w} \arctan \frac{qM_w}{2M_L}, \text{ For a most-probable distribution of } M$$
\( g^{(1)}(\tau; q, c) \approx \sum_r r_{\mu}(q, c)\exp[-\tau \gamma_{\mu}(q, c)]; \quad \sum_r r_{\mu} = 1 \)

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

Inverse Laplace transform of \( g(1)(t; q, c) \):
Behavior at large $R_G^2 q^2$

Random-flight chain:

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

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

$$\lim_{u \gg 1} \left[ K_{op c/H(q,c)} \right]^0 = \frac{1}{2} [M^{-1} + (R_G^2/M)q^2 + \ldots]$$

where $C = 1/2$ for a linear chain. Note: $\partial [K_{op c/H(q,c)}]^0/\partial q^2 = \hat{a}/2M_L$

Rodlike chain:

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

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

where $C = 2/\pi^2$ and $u = R_G^2 q^2 = L^2 q^2/12$. Note: $\partial [K_{op c/H(q,c)}]^0/\partial q = L/\pi M = 1/\pi M_L$
Kraty-Porod wormlike chain model

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

I. Wormlike chain behavior for $R_G^2 q^2 < 1$

II. Flexible chain like asymptote ($q^2 P(q,0) \propto 2$) for $1/R_G < q < 1/\lambda$

III. Rodlike asymptotic behavior ($q^2 P(q,0) \propto q$) for $\lambda q > 1$

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

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

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

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

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

Holtzer Plot

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

\[ R_G q^{**} = 1.466 \]

\[ L/\hat{a} = 640, 160, 80, 40, 20, 10, 5 \text{ top to bottom} \]
In neutron scattering, the effect of the chain element diameter may be seen in region III, and modeled by replacing multiplying $\pi/Lq$ by $P_{section}(q,0)$,

$$P_{section}(q,0) \approx \left(\frac{2J_1(R_cq)}{R_cq}\right)^2 \approx \exp[-(R_cq)^2/4]$$

Two different wormlike micelles
Optically diverse scattering elements

Limiting to two scattering elements, A and B, with \( w_A = 1 - w_B = w_A \psi_A / \psi \):

\[
P_{LS}(q,0) = w_A P_A(q,0) + (1 - w_A)P_B(q,0) + w_A(1 - w_A)P_{AB}(q,0)
\]

\[
P_{\nu}(q,0) = \left( \frac{1}{2} \sum_n^{n_A} \sum_k^{n_B} \langle \sin(q|\vec{r}_{jk}|) / q|\vec{r}_{jk}| \rangle \right); \quad \nu = A, B
\]

\[
P_{AB}(q,0) = \frac{1}{n_A n_B} \sum_j^n \sum_k^n \langle \sin(q|\vec{r}_{jk}|) / q|\vec{r}_{jk}| \rangle - [P_A(q,0) + P_A(q,0)];
\]

\[
P_{AB}(q,0) \approx (\Delta_{AB} q)^2 / 3 + \ldots
\]

- Note the similarity in form to the expression the for \( R_G^{2,LS} \).
- Has been applied to mixtures of chemically diverse polymers.
**Example:**  

_Stratified sphere (2-layers):_

\[
P_{LS}(q,0) = \left( \bar{w}_A [P_A(q,0)]^{1/2} + (1 - \bar{w}_A) \frac{R_B^3[P_B(q,0)]^{1/2} - R_A^3[P_A(q,0)]^{1/2}}{R_B^3 - R_A^3} \right)^2
\]

where \( P_A(q,0) \) and \( P_B(q,0) \) are the functions for spheres with radii \( R_A \) and \( R_B \), respectively.

- Reduces to a solvent-filled shell with thickness \( R_B - R_A \) if \( \bar{w}_A = 0 \)

- If \( \bar{\psi} = 0 \), this form may be recast to give \( [R(q,c)/c]^0 \) that exhibits min and max similar to those for charged spheres, discussed later, but for an entirely different reason.
Optically anisotropic scattering elements

\[
[R_{Si}(q,c)/c]^0 = K' \hat{n}_s^2 (\partial \hat{n}/\partial c)^2 w M_{LS,Sl} P_{LS,Sl}(q,0)
\]

For rodlike chains monodisperse in M, with \( x = Lq \):

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

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

The functions of \( x \) are known trigonometric functions:

<table>
<thead>
<tr>
<th>( p_1(x) )</th>
<th>( m_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (2/x^2)[xSi(x) - 1 + \cos(x)] )</td>
<td>( p_1 - p_2 )</td>
</tr>
<tr>
<td>( p_2(x) )</td>
<td>( m_2 )</td>
</tr>
<tr>
<td>( (6/x^3)[x - \sin(x)] )</td>
<td>( 3p_1 - p_2 - p_3 )</td>
</tr>
<tr>
<td>( p_3(x) )</td>
<td>( m_3 )</td>
</tr>
<tr>
<td>( (10/x^5)[x^3 + 3x\cos(x) - 3\sin(x)] )</td>
<td>( p_3 - p_2 )</td>
</tr>
</tbody>
</table>
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 \( |\tilde{n} - 1| > 10 \), the angular dependence is independent of \( \tilde{n} \), and is the same for absorbing and nonabsorbing particles.

Spheres:

\[
\lim_{R/\lambda \gg 1} P_{VV}(q,0) = \left\{ \frac{2J_1(\tilde{\alpha} \sin(\theta))}{\tilde{\alpha} \sin(\theta)} \right\}^2
\]

\[
\lim_{R/\lambda \gg 1} \left[ R_{VV}(q,c)/c \right]^0 \propto \sum_v \tilde{\alpha}_v^6 \left\{ \frac{2J_1(\tilde{\alpha}_v \sin(\theta))}{\tilde{\alpha}_v \sin(\theta)} \right\}^2
\]

Cylinders of length \( L_{cyl} \) and radius \( R \), with \( L_{cyl} \gg R \gg \lambda \),

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

Extrema pattern similar for the functions for spheres and cylinders
Data on Hollow Spherical Shells
Scattering from a dilute solution

\[ R(q,c) = K_{op}cM S(q,c) \]

\[ S(q,c) = P(q,c)F(q,c) \]

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

\[ \Gamma(c) = B(c)/[1 - cB(c)] \]

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

\[ B(c) = M\tilde{B}(c) \]

\[ \tilde{B}_{LS}(c)Q_{LS}(q,c) = \frac{\sum_{\nu} \sum_{\mu} w_{\nu}w_{\mu} \tilde{\psi}_{\nu}\tilde{\psi}_{\mu} M_{\nu}M_{\mu} P_{\nu}(q,c)P_{\mu}(q,c)\tilde{B}_{\nu\mu}(c)Q_{\nu\mu}(q,c)}{[M_{LS}P_{LS}(q,c)]^2} \]
Scattering in the RGD regime at zero scattering angle:

\[ \tilde{B}_{LS}(c) = M_{LS}^2 \sum_{\nu} \sum_{\mu} w_{\nu} w_{\mu} \tilde{\psi}_{\nu} \tilde{\psi}_{\mu} M_{\nu} M_{\mu} \tilde{B}_{\nu \mu}(c) \]

For a solute with optically identical scattering elements,

\[ \tilde{B}_{LS}(c) = M_{w}^2 \sum_{\nu} \sum_{\mu} w_{\nu} w_{\mu} M_{\nu} M_{\mu} \tilde{B}_{\nu \mu}(c) \]

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

\[ \Gamma_{LS}(c) = 2A_{2,LS}M_w + 3A_{3,LS}M_wc + \ldots \]
\[ \frac{K_{\text{op}c}}{R(q,c)} = M_w^{-1}\{1 + c\Gamma_{\text{LS}}(c)\} \]
\[ = M_w^{-1}\{1 + 2A_{2,\text{LS}}M_w c + 3A_{3,\text{LS}}M_w c^2 + \ldots\} \]

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

\[ \frac{\Pi}{RTc} = M_n^{-1}\{1 + A_{2,\Pi}M_n c + A_{3,\Pi}M_n c^2 + \ldots\} \]

\[ A_{2,\text{LS}} = A_{2,\Pi}, \text{ etc., only for a monodisperse solute} \]
Special case:

Solution with $A_2 >> 0$: Put $A_{3,LSM} = \gamma_3 (A_{2,LSM_w})^2$

\[
\frac{K_{op c}}{R(q,c)} = M_w^{-1} \{ 1 + 2A_{2,LSM_w}c + 3\gamma_3 (A_{2,LSM_w}c)^2 + \ldots \}
\]

\[
\left( \frac{K_{op c}}{R(q,c)} \right)^{1/2} = M_w^{1/2} \{ 1 + A_{2,LSM_w}c + [(3\gamma_3 - 1)/2](A_{2,LSM_w}c)^2 + \ldots \}
\]

Monodisperse spheres interacting through a hard-core potential:

\[
\gamma_3 = 5/8; \quad (3\gamma_3 - 1)/2 = 7/16 \approx 0.44
\]
Representative behavior for a flexible chain in a 'very good solvent'
Heterodisperse solute, identical optically isotropic scattering elements

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

By comparison,

\[ \frac{\Pi M_n}{RTc} = 1 + A_{2,\Pi} M_n c + \ldots \]

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

\( A_{2,LS} \) 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).

\[ \Omega_{LS} \propto A_{2,LS}/M_w^{\gamma} \text{ (curves 2 and 3) and } \Omega_{\Pi} \propto A_{2,\Pi}/M_n^{\gamma} \text{ (curves 1 and 4)} \]

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

3 and 4: \( A_{2,v\mu} = (A_{2,vv} A_{2,\mu\mu})^{1/2} \)
Optically diverse, isotropic scattering elements

\[ A_{2,LS} = M_w^{-2} \sum_v \sum_{\mu} w_v w_{\mu} \bar{\psi}_v \bar{\psi}_\mu M_v M_{\mu} A_{2,\nu \mu} \]

- 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

\[ \frac{K_c}{R_{VV}(0,c)} = \left( \frac{1}{M(1 + 4\delta^2/5)} \right) \left\{ 1 + 2 \left( \frac{1 - \delta^2/10}{1 + 4\delta^2/5} \right) A_2 M c + \ldots \right\} \]

\[ \frac{K_c}{R_{HV}(0,c)} = \frac{5}{3M\delta^2} \left\{ 1 - A_2 M c/4 + \ldots \right\} \]

with the latter limited to rodlike chains.

Note the weak dependence of \( K_c/R_{HV}(0,c) \) on \( c \).
Upper: $[Kc/R_{Vv}(0,c)]^{1/2}$ for solutions of \textit{cis}-PBO.
Middle: $Kc/R_{Hv}(0,c)$ for solutions of \textit{cis}-PBO.
Lower: $[Kc/R_{Vv}(0,c)]^{1/2}$ \textit{ab}-PBO.

Upper: $[Kc/R_{Vv}(0,c)]^{0}$ for solutions of \textit{cis}-PBO.
Middle: $[Kc/R_{Hv}(0,c)]^{0}$ for solutions of \textit{cis}-PBO.
Lower: $[Kc/R_{Vv}(0,c)]^{0}$ for solutions of \textit{ab}-PBO.
Concentrated and moderately concentrated solutions at zero scattering angle

\[ \frac{K_{\text{op}} c M}{R(q,c)} = 1 + c \Gamma(c) \]

With this expression, for a monodisperse solute,

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

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:

\[ \Pi V_1/RT = -\{\ln(1 - \phi) + (1 - 1/r)\phi + \chi\phi^2\} \]

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

\( \chi \) 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 \( Y_3 = A_3M_c/(A_2M_c)^2 \):

\[
\Pi M/RT_c \approx 1 + A_2M_c\{1 + (Y_3/p)A_2M_c\}^p
\]

\[
KcM/R(0,c) \approx 1 + 2A_2M_c\{1 + (3Y_3/4p)(2A_2M_c)\}^p
\]

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

- \( A_2M^2/N_AR_G^3 \) 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

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

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

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

\[
H(q,c) = \frac{P(2q,0)^{1/2}}{P(q,0)}
\]

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

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

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

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

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

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):

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

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

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

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

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

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 \( L_B = e^2/\varepsilon kT \) is the Bjerrum length, with \( \varepsilon \) the dielectric strength (\( L_B/\text{nm} \approx 57/\varepsilon \) at 25°C, or \( L_B \approx 0.7 \) nm for water), and \( I_0 \) is the ionic strength (\( I_0 = \Sigma \nu_i^2 m_i/2 \), with \( \nu_i \) and \( m_i \) the molarity and charge of species \( i \)).
\[
\ln[g^{(2)}(\tau; q, c) - 1]^{1/2} = \ln[f_c]^{1/2} - K^{(1)}(q, c)\tau + \frac{1}{2!} K^{(2)}(q, c)\tau^2 + \ldots
\]

\[
\lim_{q \to 0} K^{(1)}(q, c) = D_M(c) q^2
\]

Data for a variety of M and solvents

Upper curve:
Good solvents

Lower Curve
Flory Theta Solvent conditions

ISPAC - 2005
Carnegie Mellon University
Non Ergodic Behavior, e.g., Many Gels

\[ g^{(2)}_i(\tau; q, c) = 1 + x(1 - x)f_C^{1/2}|f_E(\tau, q) - f_E(\infty, q)| + \]
\[ x^2f_C[f_E^2(\tau, q)(\tau, q) - f_E^2(\tau, q)(\infty, q)] \]

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):
\[ R(q,c) = \sum_{\mu} R_{\mu}(q,c) \approx K \sum_{\mu} \frac{M_c}{P(q,c) + 2A_2 M_c}_{\mu,c} \]
Thanks for your patience and attention!
Low concentrations: The third virial coefficient (isotropic elements)

\[ \tilde{B}_{LS}(c) \approx M_{LS}^2 \sum_v \sum_\mu \bar{\psi}_v \bar{\psi}_\mu \left( w_v w_\mu M_v M_\mu \tilde{B}_v^0 + \sum_k w_k [\tilde{B}_{v\mu k}^0 - M_k \tilde{B}_{vk}^0 \tilde{B}_{\mu k}^0]c \right) \]

Optically identical scattering elements:

\[ A_{3,LS} \approx M_w^{-2} \sum_v \sum_\mu \sum_k w_v w_\mu w_k M_v M_\mu A_{3,v\mu k} \]

\[ - \frac{4}{3} M_w^3 \sum_v \sum_\mu \sum_k \sum_\sigma w_v w_\mu w_k w_\sigma M_v M_\mu M_k M_\sigma [A_{2,vk} A_{2,\mu k} - A_{2,vk} A_{2,\mu \sigma}] \]

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

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

