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Structure Factor of a Semidilute Solution of Polydisperse Rodlike Macromolecules

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ABSTRACT: The static structure factor of a semidilute solution of polydisperse rodlike macromolecules interacting via a hard core repulsion is calculated in the second virial approximation. A suitable substitution reduces the governing set of coupled integral equations to a single integral equation, which is attacked analytically by applying a variational principle. It is shown that the resulting expression for the structure factor is thermodynamically consistent. By way of example the structure factor of a bidisperse solution of rods is discussed and the marked effect of very small amounts of the higher molecular weight species demonstrated.

I. Introduction

There has been a considerable interest in the theory of light scattering by semidilute solutions of rodlike macromolecules recently. Structure factors have been calculated of solutions of various types of stiff polymers, including those interacting via a harshly repulsive "excluded volume",[1–4] electrostatic repulsion,[5–9] and van der Waals attraction.[10] The influence of macromolecular flexibility has also been addressed.[11,12] These studies focus on scattering from monodisperse solutions, and as polymers are often polydisperse, comparison to experimental results may therefore not always be straightforward. We recall that a number of properties of solutions of rodlike polymers are sensitive to polydispersity, e.g., the osmotic pressure, the concentration at which the fluid becomes liquid crystalline, and so forth (see refs 13 and 14, and references cited therein). Intuitively one would assume that the effect of polydispersity on the structure factor is also sizeable.

In this paper we calculate the structure factor of a semidilute solution of polydisperse stiff macromolecules by extending the theory presented in refs 1, 4, 7, and 22. We consider only those stiff polymers that may be viewed as perfectly rigid rods, implying that the contour length of every macromolecule should not be much greater than its persistence length. The structure factor can then be described in terms of local rod density functions, of which we have one for every molecular weight present in the sample (section II). Since the structure factor gauges density fluctuation correlations, quite a few self- and cross-correlation functions would have to be determined, at least in principle. We show in section III, however, that for hard rods, i.e., for rods interacting via their excluded volumes, this is possible by solving a single integral equation, although we do restrict ourselves to the regime where the second virial approximation is valid. This integral equation is solved approximately in section IV, providing a closed expression for the structure factor. Next we show that the obtained expression is thermodynamically consistent (section V) and finally discuss in section VI by way of example the marked behavior of the structure factor of a bidisperse solution.

II. Structure Factor

We focus on an isotropic solution of slender, rodlike macromolecules of number density ν, the total number of rods per unit volume. The rods all have an equal diameter D but may have different lengths. Let the solution contain a mole fraction x_i of the species that has length L_i, with $0 \le x_i \le 1$ and $\sum_i x_i = 1$ ($i = 1, 2, ...$). It will prove useful to replace the actual rodlengths L_i by dimensionless ones $q_i \equiv L_i/\langle L^2\rangle_n^{1/2}$, where $\langle L^2\rangle_n \equiv \sum_i x_i L_i^2$ is the mean square length of the rods. The subscript n indicates that $\langle L^2\rangle_n$ is a number average. Similarly, weight averages and z averages will be denoted by the subscripts w and z.

The configuration of a rod is characterized by two vectors $\mathbf{r}$ and $\mathbf{u}$: the former is the position vector of the center of mass in a Cartesian coordinate system, while the latter represents a unit vector pointing along the rod's main axis. The number of rods per unit volume of a particular species i and configuration $(\mathbf{r},\mathbf{u})$ is then described by a function $f_i(\mathbf{r},\mathbf{u})$, normalized such that

$$V^{-1}\int\int f_i(\mathbf{r},\mathbf{u})\, d\mathbf{r}\, d\mathbf{u} = x_i\nu \tag{2.1}$$

where V is the system's volume.

Thermally induced fluctuations of the number densities cause the solution to scatter light. The scattered intensity resulting from those fluctuations we loosely refer to as fluctuations of the local orientational order will be assumed to be negligible because of the usually small anisotropy of polarizability exhibited by stiff macromolecules. Hence, we only consider a certain type of concentration fluctuation, i.e., the type associated with isotropic scattering.

The rods are viewed as consisting of a number of (isotropic) scattering units or "segments" of length D. The structure factor[23] is accordingly defined in terms of the Fourier transform of the local segment density $c(\mathbf{k})$:

$$S(\mathbf{k}) = \langle c(-\mathbf{k})c(\mathbf{k})\rangle_s/\nu V \tag{2.2}$$

Here $\mathbf{k}$ denotes the usual scattering vector and $\langle ...\rangle_s$ a statistical average. The Fourier transforms of the local segment and rod densities are related through

$$c(\mathbf{k}) = \sum_i c_i(\mathbf{k})$$

$$c_i(\mathbf{k}) = q_i\int j_0(q_i\mathbf{K}\cdot\mathbf{u}) f_i(\mathbf{k},\mathbf{u})\, d\mathbf{u} \tag{2.3}$$

with spherical Bessel function $j_0(x) \equiv x^{-1}\sin x$ and dimensionless scattering vector $K \equiv {}^1/_2\mathbf{k}\langle L^2\rangle_n{}^{1/2}$. The Fourier transform of the local rod density is denoted by $f_i(\mathbf{k},\mathbf{u})$. Our definition of $c_i(\mathbf{k})$ is somewhat different from that of ref 1 and ensures that in the limit of zero concentration the structure factor becomes unity at vanishing scattering angles.

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Although eqs 2.2 and 2.3 seem to indicate that we have to evaluate an arbitrary number of correlation functions, it so happens that these can be dealt with simultaneously, albeit in the second virial approximation.

III. Second Virial Approximation

The equilibrium properties of the isotropic solution are accurately described at the level of the second virial approximation, provided the rods have large enough aspect ratios. When $L_i/D \gg 1$, the volume fraction of the solute is always much smaller than 1, the nematic phase setting in at volume fractions somewhat lower than $4D/\langle L\rangle_w$, with $\langle L\rangle_w$ the weight-average rod length.[14] We therefore write for the free energy of our suspension[7] (k_B is Boltzmann's constant and T the absolute temperature)

$$F/k_BT = \text{constant} + \sum_i \int\int f_i(\mathbf{r},\mathbf{u}) \ln f_i(\mathbf{r},\mathbf{u})\, d\mathbf{r}\, d\mathbf{u} - {}^1\!/_2\sum_i\sum_j \int\int\int\int f_i(\mathbf{r},\mathbf{u}) f_j(\mathbf{r}',\mathbf{u}') \times \Phi_{ij}(\mathbf{r},\mathbf{r}',\mathbf{u},\mathbf{u}')\, d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{u}\, d\mathbf{u}' + \sum_i \int\int \phi_i(\mathbf{r},\mathbf{u}) f_i(\mathbf{r},\mathbf{u})\, d\mathbf{r}\, d\mathbf{u} \quad (3.1)$$

The respective terms of eq 3.1 are (1) a for our ends inessential constant, (2) an ideal entropy, (3) a second virial term involving the Mayer function Φ_{ij}, and (4) a term accounting for a hypothetical external field ϕ_i acting on each rod, the purpose of which will become clear below. Since we assume the rods to interact only via their mutual impenetrabilities, we have

$$\Phi_{ij}(\mathbf{r},\mathbf{r}',\mathbf{u},\mathbf{u}') = \Phi_{ij}(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}') = \begin{cases} -1 & \text{if two rods of species } i \text{ and } j \text{ overlap} \\ 0 & \text{otherwise} \end{cases} \quad (3.2)$$

Functional minimization of the free energy with respect to f_i yields the equilibrium rod densities in the presence of the external field

$$\ln f_i(\mathbf{r},\mathbf{u}) = \lambda_i - \phi_i + \sum_j \int\int f_j(\mathbf{r}',\mathbf{u}')\, \Phi_{ij}(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')\, d\mathbf{r}'\, d\mathbf{u}' \quad (3.3)$$

with λ_i a constant determined by normalization (2.1). Equation 3.3 is a generalization of the integral equation derived by Onsager for a monodisperse solution of hard rods.[20] For weak external fields f_i is expected to be close to its value in the absence of a field, $f_i^0 = x_i\nu/4\pi$. We accordingly write $f_i = f_i^0 + \delta f_i$ and presume the perturbation δf_i is linear in ϕ_i. Insertion in eq 3.3, linearization, and Fourier transformation then lead to

$$\delta f_i(\mathbf{k},\mathbf{u}) = -f_i^0\phi_i(\mathbf{k},\mathbf{u}) + f_i^0\sum_j \int \Phi_{ij}(\mathbf{k},\mathbf{u},\mathbf{u}')\delta f_j(\mathbf{k},\mathbf{u}')\, d\mathbf{u}' \quad (3.4)$$

where the vector $\mathbf{k}$ indicates that we are dealing with Fourier transforms. The Fourier transform of the Mayer function of two thin rods skewed at an angle $\gamma = \gamma(\mathbf{u},\mathbf{u}')$ is given by[15]

$$\Phi_{ij}(\mathbf{k},\mathbf{u},\mathbf{u}') = -2q_iq_j\langle L^2\rangle_n D j_0(q_i\mathbf{K}\cdot\mathbf{u}) j_0(q_j\mathbf{K}\cdot\mathbf{u}') \sin\gamma(\mathbf{u},\mathbf{u}') \quad (3.5)$$

and is a straightforward generalization of the result obtained by Doi et al. for two like rods.[1]

To generate the type of concentration fluctuation monitored by isotropic scattering, we impose an external field that acts on each individual segment with a strength $-\epsilon$. In terms of the rod-related potential ϕ_i this field amounts to (see also ref 1)

$$\phi_i(\mathbf{k},\mathbf{u}) = -\epsilon q_i j_0(q_i\mathbf{K}\cdot\mathbf{u}) \quad (3.6)$$

If we insert eqs 3.5 and 3.6 into eq 3.4, we find for the perturbation of the local rod density

$$\delta f_i(\mathbf{k},\mathbf{u}) = x_iq_ij_0(q_i\mathbf{K}\cdot\mathbf{u})\left\{\frac{\epsilon\nu}{4\pi} - 8\,c\pi^{-1}\sum_j q_j\langle j_0(q_j\mathbf{K}\cdot\mathbf{u}')\delta f_j(\mathbf{k},\mathbf{u}') \sin\gamma(\mathbf{u},\mathbf{u}')\rangle'\right\} \quad (3.7)$$

where

$$c \equiv \langle L^2\rangle_n D\nu\pi/4 \quad (3.8)$$

denotes a dimensionless concentration and $\langle...\rangle' \equiv (4\pi)^{-1}\int(...)\, d\mathbf{u}'$ an orientational average with a similar prescription for the unprimed variable. One can show[14] that $c < 4$ in the isotropic phase. From eq 3.7 it follows that the δf_i's are not independent. In fact

$$q_jx_jj_0(q_j\mathbf{K}\cdot\mathbf{u})\delta f_i(\mathbf{k},\mathbf{u}) = q_ix_ij_0(q_i\mathbf{K}\cdot\mathbf{u})\delta f_j(\mathbf{k},\mathbf{u}) \quad (3.9)$$

It should be stressed that the validity of this identity is restricted to rods and that it does not apply to other systems. Equation 3.9 greatly facilitates the calculation of external field driven perturbation of the segment density

$$\delta c(\mathbf{k}) = \sum_j \delta c_j(\mathbf{k}) = \sum_j q_j \int j_0(q_j\mathbf{K}\cdot\mathbf{u})\delta f_j(\mathbf{k},\mathbf{u})\, d\mathbf{u} \quad (3.10)$$

After substituting

$$g(\mathbf{k},\mathbf{u}) \equiv 4\pi J(\mathbf{k},\mathbf{u})\delta f_i(\mathbf{k},\mathbf{u})/q_ix_ij_0(q_i\mathbf{K}\cdot\mathbf{u})\epsilon\nu \quad (3.11)$$

and

$$J(\mathbf{k},\mathbf{u}) \equiv \left(\sum_j x_jq_j^2j_0^{\,2}(q_j\mathbf{K}\cdot\mathbf{u})\right)^{1/2} \quad (3.12)$$

in eqs 3.7 and 3.10, we obtain

$$\delta c(\mathbf{k}) = \chi(\mathbf{k})\epsilon$$

$$\chi(\mathbf{k}) \equiv \nu\,\langle J(\mathbf{k},\mathbf{u})g(\mathbf{k},\mathbf{u})\rangle \quad (3.13)$$

The function g is the solution of

$$g(\mathbf{k},\mathbf{u}) + 8c\pi^{-1}\langle J(\mathbf{k},\mathbf{u}) \sin\gamma(\mathbf{u},\mathbf{u}')J(\mathbf{k},\mathbf{u}')g(\mathbf{k},\mathbf{u}')\rangle' = J(\mathbf{k},\mathbf{u}) \quad (3.14)$$

A theorem by Yvon[16,21] finally links the response function $\chi(\mathbf{k})$ to the static structure factor.

$$S(\mathbf{k}) = \chi(\mathbf{k})/\nu = \langle J(\mathbf{k},\mathbf{u})g(\mathbf{k},\mathbf{u})\rangle \quad (3.15)$$

This establishes our expression for the structure factor of a solution of polydisperse rigid rods, though still in terms of an as yet unknown function g. We remark that for the case of monodisperse rods the result by Doi et al.[1] is retrieved.

IV. Approximate Solution

It has been shown elsewhere[4,22] that integral equations like eq 3.14 can be attacked analytically with the aid of a variational principle. We refer to these works for details and merely give the final result.

$$S(\mathbf{k}) = \frac{\langle J^2(\mathbf{k},\mathbf{u})\rangle^2}{\langle J^2(\mathbf{k},\mathbf{u})\rangle + 8c\pi^{-1}\langle\langle J^2(\mathbf{k},\mathbf{u})J^2(\mathbf{k},\mathbf{u}') \sin\gamma(\mathbf{u},\mathbf{u}')\rangle\rangle'} \quad (4.1)$$

Here

$$\langle J^2(\mathbf{k},\mathbf{u})\rangle \equiv F_z(K) = \sum_i x_i q_i^2 F(q_i K) \tag{4.2}$$

is the polydisperse equivalent of the single rod form factor (actually a z average), with

$$F(q_i K) = \langle j_0^{\,2}(q_i \mathbf{K}\cdot\mathbf{u})\rangle = (q_i K)^{-1}\,\mathrm{Si}(2q_i K) - j_0^{\,2}(q_i K) \tag{4.3}$$

$\mathrm{Si}(x)$ the sine integral and $K = |\mathbf{K}|$. It is not difficult to see that $F_z(0) = \sum_i x_i q_i^2 = 1$. The remaining integral is tackled as follows.

(1) We let $\mathbf{K}$ be the z axis of our coordinate system and introduce the polar coordinates θ and ϕ. Then $J(\mathbf{k},\mathbf{u}) = J(k,\cos\theta)$.

(2) Since J does not depend on ϕ, we apply the addition theorem to $\sin\gamma$ and perform the ϕ integration

$$(2\pi)^{-1}\int_0^{2\pi} \sin\gamma \,\mathrm{d}\phi = \frac{\pi}{4} - \frac{5\pi}{32}P_2(\cos\theta)P_2(\cos\theta') - \ldots \tag{4.4}$$

where we only retain the first two terms of the expansion in Legendre polynomials P_n. This gives

$$\langle\langle J^2(\mathbf{k},\mathbf{u})J^2(\mathbf{k},\mathbf{u}')\sin\gamma(\mathbf{u},\mathbf{u}')\rangle\rangle' \cong \frac{\pi}{4}F_z^2(K) - \frac{5\pi}{32}G_z^2(K) \tag{4.5}$$

and

$$G_z(K) = \sum_j x_j q_j^2 G(q_j K)$$

$$G(q_j K) = {}^3/_4 (q_j K)^{-2}(1 - j_0(2q_j K)) - {}^1/_2 F(q_j K) \tag{4.6}$$

We thus arrive at

$$S(K) = \frac{F_z^2(K)}{F_z(K) + 2cF_z^2(K) - 5cG_z^2(K)/4} \tag{4.7}$$

Variants of this expression pertaining to monodisperse hard and charged rods have been compared to results obtained by a numerical evaluation of the appropriate integral equations and were found to be very accurate.[4,5] In addition, eq 4.7 is in accordance with the general expression derived by Stockmayer[25] for multicomponent systems with no angular dissymmetry, valid in the limit $K = 0$.

Our expression for the structure factor bears some resemblance to the one obtained by Benoit and Benmouna for flexible polymers on the basis of an extension of the so-called single contact model.[19] Their result lacks a term equivalent to our G_z, which signifies the coupling of translational and rotational degrees of freedom. With regard to $S(0)$, we remark that the usual relation with the isothermal osmotic compressibility does not hold.[16] Instead, we have a more complicated expression involving the partial structure factors of the various species. This is addressed in the following section, where we show that eq 4.7 is thermodynamically consistent.

V. Osmotic Compressibility

Kirkwood and Buff[16,17] derived a relation between the isothermal compressibility and the partial structure factors of a multicomponent system. A polydisperse solution is essentially a multicomponent system, so we apply their result and get[18]

$$\nu k_B T \kappa_T = \frac{|\mathbf{S}(0)|}{\sum_i \sum_j x_i x_j q_i q_j |\mathbf{S}(0)|_{ij}} \tag{5.1}$$

Here κ_T denotes the isothermal (osmotic) compressibility, $|\mathbf{S}(0)|$ the determinant of the matrix $\mathbf{S}(0)$ of partial structure factors $S_{ij}(0)$ at zero scattering angle, and $|\mathbf{S}(0)|_{ij}$ the cofactor of $S_{ij}(0)$ in this determinant. The dimensionless lengths q_i appear because of our normalization of the local segment density and hence of the total and partial structure factors

$$S(\mathbf{k}) = \sum_i \sum_j S_{ij}(\mathbf{k})$$

$$S_{ij}(\mathbf{k}) = \langle c_i(-\mathbf{k})c_j(\mathbf{k})\rangle_s/\nu V \tag{5.2}$$

To keep the analysis simple, we restrict ourselves to the bidisperse case and set $x \equiv x_2$ and $1 - x \equiv x_1$ so that

$$\nu k_B T \kappa_T = \frac{S_{11}(0)S_{22}(0) - S_{12}(0)S_{21}(0)}{q_1^2(1-x)^2 S_{22}(0) - q_1 q_2 x(1-x)(S_{12}(0) + S_{21}(0)) + q_2^2 x^2 S_{11}(0)} \tag{5.3}$$

The partial structure factors can be determined along similar lines as the structure factor itself. We focus on the limit $K = 0$ and switch on a hypothetical external field that couples only to segments of type "1". If we apply a field of the kind put forward in eq 3.6, we find for the perturbation of the single rod densities ($\delta f_i(\mathbf{u}) \equiv \delta f_i(0,\mathbf{u})$)

$$\delta f_1(\mathbf{u}) = (1-x)q_1(\epsilon\nu/4\pi) - (1-x)q_1\sum_{j=1}^{2} q_j 8c\pi^{-1}\langle\delta f_j(\mathbf{u}')\sin\gamma(\mathbf{u},\mathbf{u}')\rangle'$$

$$\delta f_2(\mathbf{u}) = -xq_2\sum_{j=1}^{2} q_j 8c\pi^{-1}\langle\delta f_j(\mathbf{u}')\sin\gamma(\mathbf{u},\mathbf{u}')\rangle' \tag{5.4}$$

Clearly

$$xq_2\delta f_1(\mathbf{u}) = (1-x)q_1\delta f_2(\mathbf{u}) + (1-x)q_1\epsilon\nu/4\pi \tag{5.5}$$

This enables us to calculate the segment density response functions from eqs 2.3 and 5.4

$$\chi_{11} \equiv \delta c_1(0)/\epsilon = \nu(1-x)q_1^2(1 + 2cxq_2^2)\langle g(\mathbf{u})\rangle$$

$$\chi_{21} \equiv \delta c_2(0)/\epsilon = -2c(1-x)xq_1^2 q_2^2\nu\langle g(\mathbf{u})\rangle \tag{5.6}$$

with the function g the solution of

$$g(\mathbf{u}) + 8c\pi^{-1}\langle g(\mathbf{u}')\sin\gamma(\mathbf{u},\mathbf{u}')\rangle' = 1 \tag{5.7}$$

The exact solution of integral eq 5.7 is given by $g = (1 + 2c)^{-1}$, so that

$$S_{11}(0) = \chi_{11}/\nu = (1-x)q_1^2(1 + 2cxq_2^2)(1 + 2c)^{-1}$$

$$S_{21}(0) = \chi_{21}/\nu = -2c(1-x)xq_1^2q_2^2(1 + 2c)^{-1} \tag{5.8}$$

By analogy

$$S_{12}(0) = S_{21}(0)$$

$$S_{22}(0) = xq_2^2(1 + 2c(1-x)q_1^2)(1 + 2c)^{-1} \tag{5.9}$$

We note that use of the variational principle would give identical results. Also, the total structure factor as calculated from eqs 5.2, 5.8, and 5.9 is consistent with the *variational expression eq 4.7, at least for $K = 0$.* The cross-terms related to the interaction between unlike particles and that appear in all four partial structure factors apparently cancel out in the total structure factor.

If eqs 5.8 and 5.9 are inserted into eq 5.3, we finally obtain

$$\nu k_B T \kappa_T = \{1 + 2c((1-x)^2 q_1^2 + 2x(1-x)q_1 q_2 + q_2^2 x^2)\}^{-1} \tag{5.10}$$

This expression should be identical to the one obtained directly from its thermodynamic definition[16]

$$\nu k_B T \kappa_T = -\nu(V(\partial/\partial V)\Pi/k_B T)^{-1} \tag{5.11}$$

Here Π denotes the osmotic pressure of the solution. In the second virial approximation[24]

$$\Pi/k_B T = \nu\{1 + c((1-x)^2 q_1^2 + 2x(1-x)q_1 q_2 + x^2 q_2^2)\} \tag{5.12}$$

from which it is easy to prove that eqs 5.3 and 5.11 are indeed consistent.

VI. Discussion

The main result of this paper is given by eq 4.7. It provides a closed expression for the structure factor of a semidilute suspension of rodlike macromolecules with an arbitrary length distribution. Although quite simple in appearance, its behavior is in fact far from simple. This is demonstrated for the special case of a bidisperse solution.

Let the solution contain rods of lengths L_1 and L_2 with $Q \equiv L_2/L_1 > 1$. The respective mole fractions are $x = x_2$ and $1 - x = x_1$. We focus on the limits $q_i K \ll 1$ and $q_i K \gg 1$.

(I) $q_i K \ll 1$. Equation 4.7 reduces to

$$S(K_z) = \frac{1 - K_z^2/9}{1 + 2c - 2cK_z^2/9} \tag{6.1}$$

Here $K_z = {}^1/_2|\mathbf{k}|(L^2)_z{}^{1/2} \ll 1$ is a natural dimensionless magnitude of the scattering vector, with $(L^2)_z = \sum_i x_i L_i^4/\sum_i x_i L_i^2 = L_1^2(1 - x + xQ^4/1 - x + xQ^2)$. Equation 6.1 does not represent a "master curve" as c still depends on the length distribution.

$$c = (\pi/4)L_1^2 D\nu(1 - x + xQ^2) \tag{6.2}$$

Of experimental interest is the effect on $S(K_z)$ of a varying bidispersity given some fixed volume fraction υ, implying that ν is to be varied along with x to keep υ constant. To this end, c is written as

$$c \equiv c_\upsilon(x) = c_\upsilon(0)(1 - x + xQ^2)/(1 - x + xQ) \tag{6.3}$$

where the subscript υ indicates that irrespective of the actual values of x and Q the total volume fraction has a constant value $\upsilon = c_\upsilon(0)D/L_1$. Two regimes emerge.

(i) $xQ \lesssim 1$. $c_\upsilon(x)$ increases and hence $S(K_z)$ decreases rapidly with increasing x, especially when Q is quite larger than 1. This implies that the structure factor is very sensitive to the presence of very small amounts of a rather larger molecular weight species.

(ii) $xQ \gg 1$. In that case $c_\upsilon(x) \approx c_\upsilon(0)Q$ and $S(K_z)$ become virtually independent of x. As a consequence, the presence of even a relatively larger fraction of a *smaller* molecular weight species does not necessarily influence $S(K_z)$ much, provided Q is large enough.

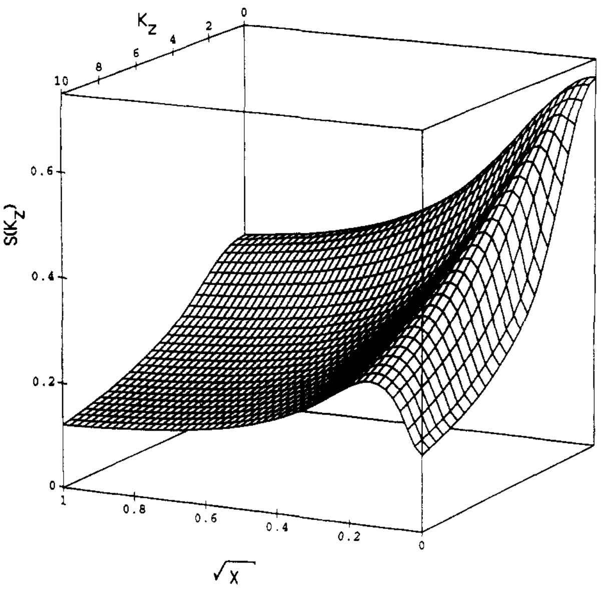

Figure 1. Structure factor of a bidisperse solution of rodlike macromolecules according to eq 4.7. The length ratio of the rods is $Q = L_2/L_1 = 5$. Results are shown as a function of the scaled magnitude of the scattering vector K_z and of the mole fraction x of the longer rods. The total volume fraction of rods is kept at a constant value of $0.2D/L_1$.

Both effects clearly result from the strong length dependence of the excluded volume inteaction between rods.

(II) $q_i K \gg 1$. The limiting behavior of eq 4.7 for $q_i K \gg 1$ is given by

$$S^{-1}(K_w) = \frac{2}{\pi}K_w + \frac{27}{16}c \tag{6.4}$$

Here $K_w \equiv {}^1/_2|\mathbf{k}|(L)_w \gg 1$ and $(L)_w \equiv \sum_i x_i L_1^2/\sum_i x_i L_i$. K_w and K_z are related through

$$K_w = K_z\left(\frac{1 - x + xQ^2}{1 - x + xQ}\right)\left(\frac{1 - x + xQ^2}{1 - x + xQ^4}\right)^{1/2} \tag{6.5}$$

We distinguish three regimes.

(i) $xQ^3 \ll 1$. $S^{-1}(K_z) \approx 2\pi^{-1}(1 + xQ^4)^{-1/2}K_z$ so that $S(K_z)$ *increases* with increasing x.

(ii) $xQ^3 \gtrsim 1$, in which case $S(K_z)$ decreases when x increases.

(iii) $xQ \gg 1$. The structure factor becomes almost independent of x, $S(K_z) \approx 2\pi^{-1}K_z + 27c_\upsilon(0)Q/16$.

To sum up, if we gradually increase the mole fraction of the higher molecular weight species in a bidisperse solution from 0 to 1 at a constant volume fraction, $S(K_z)$ always decreases at small K_z but increases initially at large K_z to decrease again further on. The point at which $S(K_z)$ is (nearly) equal to that of the monodisperse solution of the longer rods is governed by the condition $xQ \gtrsim 1$, implying that if $Q \gg 1$, x may be substantially smaller than 1.

Some of the above features are exemplified in Figure 1, in which we have plotted $S(K_z)$ for $Q = 5$, $c_\upsilon(0) = 1/5$ and varying values of x. The marked influence of even tiny quantities of the longer rods is clearly shown.

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(15) Implied is the condition $|\mathbf{k}|D \ll 1$. Since typically $|\mathbf{k}|L_i \simeq O(1)$ and since $L_i \gg D$ for the second virial approximation to be applicable, this condition is automatically met.

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