

Light scattering and sedimentation equilibrium of a concentrated multicomponent hard rod dispersion

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Starting from scaled particle theory, compact expressions for sedimentation equilibrium and light scattering at zero angle for concentrated polydisperse solutions of colloidal hard spherocylinders are derived. These expressions are used to assess the influence of length and diameter polydispersity on the light scattering of dispersions of rod-like particles as a function of the volume fraction.

1. Introduction

Concepts of the theory of simple liquids have been very useful in the description and understanding of concentrated dispersions of colloidal particles [1–3]. For example in the analysis of experimental scattering data for colloidal dispersions, extensive use is made of the structure factors obtained in liquid state theory [4]. A difficulty which arises is that in practice colloidal systems virtually always exhibit some nonuniformity in the particle size. The effect of this polydispersity on the behaviour of a colloidal dispersion can be considerable.

Starting from the Percus–Yevick approximation [4], which may be solved analytically for fluid multicomponent hard sphere systems, Vrij [5,6] and, independently, Blum and Stell [7] have shown how polydispersity influences the scattering intensity of hard sphere colloidal systems. This formalism has been successfully implemented in the analysis of light scattering [8], small angle X-ray (SAXS) [9] and small angle neutron scattering (SANS) [10] on dispersions of colloidal particles with steep short ranged repulsive interactions [11].

In this paper we consider dispersions of polydisperse hard rod colloids which can be seen as the simplest non-trivial extension of hard spheres. Recently Van

der Schoot and Odijk obtained accurate analytical expressions for the structure factor of monodisperse [12] and polydisperse [13] solutions of hard rod-like particles in the second virial approximation but no such results are known for the concentrated case. However, for the thermodynamic properties closed expressions can be obtained using the scaled particle theory (SPT), originally developed by Reiss et al. [14] for spherical particles. Cotter [15] solved the SPT for a system of monodisperse hard spherocylinders (cylinders capped at both ends with hemispheres) whereas the polydisperse results were given by Cotter and Wacker [16]. Starting from the SPT results for multicomponent hard spherocylinders (HSC) assemblies we derive here expressions that can be used directly in the analysis of light scattering intensities and sedimentation equilibria of dispersions of polydisperse rod-like particles. For the monodisperse case the SPT results have been used to interpret sedimentation equilibria and light scattering data from solutions of rod-like macromolecules [17,18]. However, these systems have at least a moderate level of polydispersity and therefore an analysis based on the assumption of monodispersity is not strictly valid.

In section 2 we present the results of SPT for a polydisperse isotropic HSC system. In section 3 we briefly review the relevant equations describing sedimentation equilibrium and the intensity of scattered light at zero angle. The common quantities appearing here are the derivatives $(\partial \rho_i / \partial \mu_k)_{\mu_j}$. In order to obtain these quantities from the SPT results, a matrix inversion is required (section 4). Guided by the work on hard spheres by Vrij [5], we were able to perform this matrix inversion analytically. In section 5 we illustrate the theoretical expressions by presenting the light scattering intensities at zero angle for different degrees of polydispersity and in section 6 we end with some concluding remarks.

2. Scaled particle theory for a polydisperse assembly of hard spherocylinders

In a remarkable paper, Rosenfeld [33] obtained the SPT expressions for the pressure and the chemical potentials for an isotropic fluid mixture of arbitrary hard convex particles in terms of what he refers to as “fundamental measures” of the particles. These expressions were shown to be in full agreement with known results for monodisperse hard spheres [14], polydisperse hard spheres [19] and monodisperse HSC [15]. Here we present the derivation of the SPT results for HSC-mixtures along the traditional lines [15,16] and find that they are also in accordance with the general equations of Rosenfeld.

We consider an isotropic HSC-system consisting of n components with number densities ρ_k ($k = 1, 2, \dots, n$). A particle of the k th component has a length L_k , diameter D_k and an orientation characterized by solid angle Ω . The

basic idea of SPT is to obtain the excess chemical potential by calculating the work $W_k(\Omega)$ needed to insert an additional particle of the k th component with orientation Ω into the system. This work is calculated by expanding (scaling) the added particle from zero to its final size [14,19]. In the case of a HSC of component k with orientation Ω this expansion can be described by the scaling parameters λ_k and ν_k for the length and the diameter respectively, such that the scaled particle has a length $\lambda_k L_k$ and a diameter $\nu_k D_k$.

The work is easily calculated by realising that $\exp(-W_k(\Omega)/kT)$ is equal to the probability that the added particle does not overlap with any of the other particles [20]. In the limit $\lambda_k, \nu_k \rightarrow 0$, the added particle is a mere point and cannot be in contact with more than one particle at the same time and therefore this probability is equal to the accessible volume fraction,

$$\exp[-W_k(\Omega; \lambda_k, \nu_k)/kT] = 1 - \sum_{j=1}^n \int \rho_j f_j(\Omega') \omega_{kj}(\Omega, \Omega'; \lambda_k, \nu_k) d\Omega' \quad (\lambda_k, \nu_k \rightarrow 0). \tag{1}$$

Here, $f_j(\Omega)$ is the orientation distribution of the j th component and $\omega_{kj}(\Omega, \Omega'; \lambda_k, \nu_k)$ refers to the excluded volume of the added scaled particle of the k th component with orientation Ω and a HSC of the j th component with orientation Ω' ,

$$\omega_{kj}(\Omega, \Omega'; \lambda_k, \nu_k) = \frac{1}{6}\pi(D_j + \nu_k D_k)^3 + \frac{1}{4}\pi(D_j + \nu_k D_k)^2(L_j + \lambda_k L_k) + (D_j + \nu_k D_k)\lambda_k L_k L_j |\sin \gamma(\Omega, \Omega')|, \tag{2}$$

where $\gamma(\Omega, \Omega')$ is the angle between the axes of the two particles.

For large values of the scaling parameters λ_k and ν_k , the work required to insert an additional particle is just equal to the work needed to create a hole with a volume equal to that of the scaled particle against the pressure P exerted by the fluid,

$$W_k(\Omega; \lambda_k, \nu_k) = (\frac{1}{6}\pi\nu_k^3 D_k^3 + \frac{1}{4}\pi\nu_k^2 D_k^2 \lambda_k L_k)P \quad (\lambda_k, \nu_k \gg 1). \tag{3}$$

For intermediate values of the scaled particle parameters it is assumed that the work $W_k(\Omega; \lambda_k, \nu_k)$ can be found from a Taylor expansion around $\lambda_k = \nu_k = 0$, with the terms beyond the quadratic being replaced by the expression given in eq. (3),

$$W_k(\Omega; \lambda_k, \nu_k) = \sum_{p,q=0}^2 \frac{1}{p!q!} \frac{\partial^{p+q} W_k}{\partial \lambda_k^p \partial \nu_k^q} \lambda_k^p \nu_k^q + (\frac{1}{6}\pi\nu_k^3 D_k^3 + \frac{1}{4}\pi\nu_k^2 D_k^2 \lambda_k L_k)P. \tag{4}$$

The excess chemical potential of a particle of k th component is obtained by setting the parameters λ_k and ν_k in the above expression for the work equal to 1 and integrating over all possible orientations with the orientation distribution function,

$$\mu_k^{\text{ex}} = \int f_k(\Omega) W_k(\Omega; 1, 1) d\Omega. \tag{5}$$

Since in this derivation an isotropic solution is considered, all orientation distribution functions have the value $1/4\pi$ and therefore the average of the sine of the angle between two HSC's equals $\pi/4$. This leads to the following expression for the excess chemical potential:

$$\beta\mu_k^{\text{ex}} = -\ln(1 - \xi^{(3)}) + \frac{\xi^{(2)}R_k^{(1)} + \xi^{(1)}R_k^{(2)}}{1 - \xi^{(3)}} + \frac{(\xi^{(2)})^2R_k^{(2)}}{8\pi(1 - \xi^{(3)})^2} + \beta R_k^{(3)}P. \tag{6}$$

Here, $\beta = 1/k_B T$ and the quantities $R_k^{(\nu)}$ represent the fundamental measures for HSC introduced by Rosenfeld [33]:

$$\begin{aligned} R_k^{(0)} &= 1, & R_k^{(1)} &= \frac{1}{2}D_k + \frac{1}{4}L_k, \\ R_k^{(2)} &= \pi D_k^2 + \pi D_k L_k, & R_k^{(3)} &= \frac{1}{6}\pi D_k^3 + \frac{1}{4}\pi D_k^2 L_k. \end{aligned} \tag{7}$$

These quantities have a simple geometric meaning: $R_k^{(1)}$ is the radius of curvature integrated over the surface, $R_k^{(2)}$ is the surface area and $R_k^{(3)}$ is the volume of a particle of the k th component. The quantities $\xi^{(\nu)}$ are defined by

$$\xi^{(\nu)} = \sum_{k=1}^n \rho_k R_k^{(\nu)}. \tag{8}$$

By using the Gibbs–Duhem relation, one finally obtains the equation of state,

$$\beta P = \frac{\xi^{(0)}}{1 - \xi^{(3)}} + \frac{\xi^{(1)}\xi^{(2)}}{(1 - \xi^{(3)})^2} + \frac{(\xi^{(2)})^3}{12\pi(1 - \xi^{(3)})^3}. \tag{9}$$

The equations for the excess chemical potentials (6) and the pressure (9) are indeed identical with the expressions given by Rosenfeld [33].

3. Light scattering at $K = 0$ and sedimentation equilibrium of HSC mixtures

Thermodynamic properties of colloidal dispersions can in principle be obtained from light scattering intensities [21] and sedimentation equilibrium data

[22]. Starting from the fluctuation theory of light scattering, developed by Zernike [23,24], it is possible to separate the contributions of the solvent and the solutes [25]. This leads to the following expression for the normalized scattering intensity (Rayleighratio) of the solution, minus that of the solvent, for vertically polarized incident light and extrapolated to zero scattering angle θ :

$$R_{\theta=0} = 4\pi^2 n^2 \lambda_0^{-4} \sum_{i,k=1}^n \gamma_i \gamma_k k_B T \left(\frac{\partial \rho_i}{\partial \mu_k} \right)_{\mu_j} . \tag{10}$$

Here, n is the refractive index of the dispersion, λ_0 is the wavelength of the light used in vacuo and $\gamma_i = (\partial n / \partial \rho_i)_{\rho_k, P}$ is the refractive index increment by the particles of the i th component. The appearance of the quantities $(\partial \rho_i / \partial \mu_k)_{\mu_j}$ in the light scattering intensity expression originates from their connection with concentration fluctuations in a volume V , which, according to thermodynamic fluctuation theory, are given by [26]:

$$\langle \Delta \rho_i \Delta \rho_k \rangle = \frac{k_B T}{V} \left(\frac{\partial \rho_i}{\partial \mu_k} \right)_{\mu_j} . \tag{11}$$

Under the influence of an external field, the spatial distribution of the particles becomes inhomogeneous. For example, in an (ultra) centrifuge the equilibrium concentrations at a distance x will depend on the centrifugal field with strength $\omega^2 x$, where x is the distance from the center of rotation and ω the angular rotation speed. This, in turn, leads to a gradient of the refractive index in the centrifuge cell which can be written as [27]

$$\frac{d(n - n^\circ)}{dx} = -\omega^2 x \sum_{i,k=1}^n \gamma_i \varepsilon_k \left(\frac{\partial \rho_i}{\partial \mu_k} \right)_{\mu_j} . \tag{12}$$

Here n° is the refractive index of the solvent and $\varepsilon_k = (\partial d / \partial \rho_k)_{\rho_j, P}$ with d the mass density of the dispersion.

From eqs. (10) and (12) it follows that both light scattering at zero angle and sedimentation equilibrium of polydisperse colloidal systems depend on the derivatives $(\partial \rho_i / \partial \mu_k)_{\mu_j}$. However, the quantities $(\partial \mu_i / \partial \rho_k)_{\rho_j}$ are directly provided by SPT as given in eq. (6). Therefore a matrix inversion is necessary in order to calculate the light scattering and sedimentation equilibrium.

4. Inversion of the matrix $(\partial \mu_i / \partial \rho_k)_{\rho_j}$

Using the factorization procedure introduced by Baxter [28] to solve the PY integral equations, Vrij [5,27] was able to invert the matrix $(\partial \mu_i / \partial \rho_k)_{\rho_j}$ for hard sphere systems analytically.

The same strategy cannot be applied directly to HSC systems because no factorization procedure that allows the PY equations to be solved analytically is available for these systems. Nevertheless we found that the SPT expressions which apparently have the same roots as the PY approximation [33], are amenable to a similar analysis.

Starting from the SPT expressions for the chemical potentials μ_i (eq. (6)), the derivatives with respect to the densities can be written in the form

$$\frac{(\rho_i \rho_k)^{1/2}}{k_B T} \left(\frac{\partial \mu_i}{\partial \rho_k} \right)_{\rho_j} = \sum_{j=1}^n Q_{ji} Q_{jk} - U_{ik}, \tag{13}$$

where

$$Q_{ji} = \delta_{ji} + (\rho_j \rho_i)^{1/2} Z_{ji} \tag{14}$$

and

$$U_{ik} = \left(\xi^{(1,1)} - \frac{1}{4\pi} \xi^{(2)} \right) Y_i Y_k (\rho_i \rho_k)^{1/2}, \tag{15}$$

with

$$Z_{ji} = \frac{R_i^{(3)} + R_j^{(1)} R_i^{(2)}}{1 - \phi} + \frac{R_j^{(1)} R_i^{(3)} \xi^{(2)}}{(1 - \phi)^2}, \tag{16}$$

$$Y_i = \frac{R_i^{(2)}}{1 - \phi} + \frac{R_i^{(3)} \xi^{(2)}}{(1 - \phi)^2}, \tag{17}$$

$$\xi^{(\nu, \mu)} = \sum_{j=1}^n \rho_j R_j^{(\nu)} R_j^{(\mu)}. \tag{18}$$

Finally $\phi = \xi^{(3)}$ denotes to the total volume fraction. Written in terms of the fundamental measures $R_k^{(\nu)}$, the form of the \mathbf{Q} and \mathbf{Z} matrices is identical to the hard sphere case. However, for HSC systems the factorization is not complete. A correction term U_{ik} arises, due to the fact that for non-spherical particles the square of $R_k^{(1)}$ is not equal to $R_k^{(2)}/4\pi$. The desired inverse of the matrix is given by

$$\frac{k_B T}{(\rho_i \rho_k)^{1/2}} \left(\frac{\partial \rho_i}{\partial \mu_k} \right)_{\mu_j} = \frac{(-1)^{i+k} |(\mathbf{Q}^T \mathbf{Q} - \mathbf{U})^{(i;k)}|}{|\mathbf{Q}^T \mathbf{Q} - \mathbf{U}|}, \tag{19}$$

where \mathbf{Q}^T is the transpose of \mathbf{Q} . Further $|\mathbf{Q}^T \mathbf{Q} - \mathbf{U}|$ denotes the determinant of the matrix $\mathbf{Q}^T \mathbf{Q} - \mathbf{U}$ and the superscript $(i; k)$ indicates that the i th row and the

k th column are deleted from the matrix, i.e. $|(\mathbf{Q}^T\mathbf{Q} - \mathbf{U})^{(i;k)}|$ is a minor of $\mathbf{Q}^T\mathbf{Q} - \mathbf{U}$.

Due to the extra term U_{ik} in eq. (13), one cannot simply adapt the results for the case of hard spheres. Fortunately, as is clear from eq. (15), the elements U_{ik} are bilinear products and therefore the matrix \mathbf{U} has rank 1. This leads immediately to a considerable reduction in the expansion of the determinant appearing in eq. (19) which can be written as

$$|\mathbf{Q}^T\mathbf{Q} - \mathbf{U}| = |\mathbf{Q}^T\mathbf{Q}| - \sum_{i,k=1}^n (-1)^{i+k} \mathbf{U}_{ik} |(\mathbf{Q}^T\mathbf{Q})^{(i;k)}| \tag{20}$$

and

$$|(\mathbf{Q}^T\mathbf{Q} - \mathbf{U})^{(i;k)}| = |(\mathbf{Q}^T\mathbf{Q})^{(i;k)}| - \sum_{(j \neq i, l \neq k)}^n (-1)^{j+l} \mathbf{U}_{jl} |(\mathbf{Q}^T\mathbf{Q})^{(i,j;k,l)}|. \tag{21}$$

By using the Binet–Cauchy formula [29], the determinant and minors of the productmatrix $\mathbf{Q}^T\mathbf{Q}$ can be written as follows:

$$|\mathbf{Q}^T\mathbf{Q}| = |\mathbf{Q}|^2, \tag{22}$$

$$|(\mathbf{Q}^T\mathbf{Q})^{(i;k)}| = \sum_{p=1}^n |\mathbf{q}^{(p;i)}| |\mathbf{q}^{(p;k)}|, \tag{23}$$

$$|(\mathbf{Q}^T\mathbf{Q})^{(i,j;k,l)}| = \sum_{1 \leq p < q \leq n} |\mathbf{q}^{(p,q;i,j)}| |\mathbf{q}^{(p,q;k,l)}|. \tag{24}$$

The next step is to express the determinant and the minors of \mathbf{Q} in terms of the \mathbf{Z} -matrices. Again a considerable simplification occurs, this time due to the fact that \mathbf{Z} is a matrix of rank two,

$$|\mathbf{Q}| = 1 + \sum_{i=1}^n \rho_i Z_{ii} + \frac{1}{2} \sum_{i,j=1}^n \rho_i \rho_j \begin{vmatrix} Z_{ii} & Z_{ij} \\ Z_{ji} & Z_{jj} \end{vmatrix}, \tag{25}$$

$$(-1)^{i+j} |(\mathbf{Q}^{(j;i)})| = |\mathbf{Q}| \delta_{ij} - S_{ij}, \tag{26}$$

$$\begin{aligned} (-1)^{i+j+p+q} |(\mathbf{Q}^{(p,q;i,j)})| &= |\mathbf{Q}| (\delta_{pi} \delta_{qj} - \delta_{pj} \delta_{qi}) - \delta_{qi} S_{ip} - \delta_{pi} S_{jq} + \delta_{qi} S_{jp} \\ &\quad + \delta_{pj} S_{iq} + (\rho_i \rho_j \rho_p \rho_q)^{1/2} \begin{vmatrix} Z_{ip} & Z_{jp} \\ Z_{iq} & Z_{jq} \end{vmatrix}, \end{aligned} \tag{27}$$

where

$$\begin{aligned}
 S_{ij} &= (\rho_i \rho_j)^{1/2} \left(Z_{ij} + \sum_{k=1}^n \rho_k \begin{vmatrix} Z_{ij} & Z_{ik} \\ Z_{kj} & Z_{kk} \end{vmatrix} \right) \\
 &= \frac{(\rho_i \rho_j)^{1/2}}{(1 - \phi)^2} [R_j^{(3)}(\xi^{(1,2)} + 1 - \phi) + R_j^{(2)}(R_i^{(1)} - \xi^{(1,3)})]. \tag{28}
 \end{aligned}$$

The desired quantity $(\partial \rho_i / \partial \mu_k)_{\mu_j}$ now follows from eqs. (13)–(28) after tedious but straightforward algebra:

$$\begin{aligned}
 \frac{kT}{(\rho_i \rho_k)^{1/2}} \left(\frac{\partial \rho_i}{\partial \mu_k} \right)_{\mu_j} &= (\rho_i \rho_k)^{1/2} \left[\left(\frac{\delta_{ik}}{\rho_k} - (R_k^{(3)} + R_i^{(3)}) + \xi^{(3,3)} \right) \right. \\
 &\quad + [(1 - \phi + \xi^{(1,2)})^2 - (\xi^{(1,1)} - \xi^{(2)}/4\pi)\xi^{(2,2)}]^{-1} \\
 &\quad \times \{ \xi^{(2,2)}(R_i^{(1)} - \xi^{(1,3)})(R_k^{(1)} - \xi^{(1,3)}) \\
 &\quad - (1 - \phi + \xi^{(1,2)})[(R_i^{(2)} - \xi^{(2,3)})(R_k^{(1)} - \xi^{(1,3)}) \\
 &\quad + (R_k^{(2)} - \xi^{(2,3)})(R_i^{(1)} - \xi^{(1,3)})] \\
 &\quad \left. + (\xi^{(1,1)} - \xi^{(2)}/4\pi)(R_i^{(2)} - \xi^{(2,3)})(R_k^{(2)} - \xi^{(2,3)}) \right]. \tag{29}
 \end{aligned}$$

Although more elaborate, the above expression has the same structure as the one for polydisperse hard sphere systems [30]. In fact the results obtained here are not limited to HSC mixtures only, but apply quite generally to mixtures of arbitrary hard convex bodies as long as the appropriate expressions for the fundamental measures are used [33].

A quantity of interest for which one can now also obtain a compact expression is the determinant of the matrix $[(\rho_i \rho_k)^{1/2}/kT](\partial \mu_i / \partial \rho_k)_{\rho_j}$,

$$|\mathbf{Q}^T \mathbf{Q} - \mathbf{U}| = \frac{(1 - \phi + \xi^{(1,2)})^2 - (\xi^{(1,1)} - \xi^{(2)}/4\pi)\xi^{(2,2)}}{(1 - \phi)^4}. \tag{30}$$

Note that for hard spheres $\xi^{(1,2)} = 3\phi$ and the final term in the numerator is zero. The resulting expression for the determinant then indeed reduces to the well known result for a multicomponent system of hard spheres in the SPT or equivalently the Percus–Yevick compressibility approximation [5].

5. Light scattering at zero angle for lognormal length and diameter distributions

Taking the refractive index increment in eq. (10) proportional to the volume of a HSC,

$$\gamma_i = AR_i^{(3)}, \tag{31}$$

one obtains, using eq. (26), the following closed expression for the Rayleigh ratio:

$$R_{\theta=0} = 4\pi^2 n^2 \lambda_0^{-4} A^2 (1 - \phi)^2 \times \left(\xi^{(3,3)} + \frac{\xi^{(2,2)}(\xi^{(1,3)})^2 - 2(1 - \phi + \xi^{(1,2)})\xi^{(1,3)}\xi^{(2,3)} + (\xi^{(1,1)} - \xi^{(2)/4\pi})(\xi^{(2,3)})^2}{(1 - \phi + \xi^{(1,2)})^2 - (\xi^{(1,1)} - \xi^{(2)/4\pi})\xi^{(2,2)}} \right) \tag{32}$$

To get a feeling for the influence of polydispersity on the light scattering intensity, we evaluate the Rayleigh ratio (32) using a log-normal distribution for the length and diameter of HSC. The distribution for the HSC lengths and diameters can then be written as

$$P(x) = \frac{1}{x} (2\pi \ln z)^{-1/2} \exp\left(-\frac{\ln^2(xz^{1/2}/\langle x \rangle)}{2 \ln z}\right), \tag{33}$$

where

$$z = \frac{\langle x^2 \rangle}{\langle x \rangle^2} = 1 + \sigma_x^2, \tag{34}$$

and x refers to the length L or diameter D .

The normalized moments for a log-normal distribution can be expressed in terms of the average $\langle x \rangle$ and variance σ_x ,

$$\frac{\langle L^\nu \rangle}{\langle L \rangle^\nu} = (1 + \sigma_L^2)^{\nu(\nu-1)/2}, \tag{35}$$

$$\frac{\langle D^\nu \rangle}{\langle D \rangle^\nu} = (1 + \sigma_D^2)^{\nu(\nu-1)/2}. \tag{36}$$

The above expressions can be used to evaluate the quantities $\xi^{(n,m)}$ in terms of the averages $\langle L \rangle$ and $\langle D \rangle$ and variances σ_L and σ_D . This in turn allows one to calculate the Rayleigh ratio which will be expressed in terms of the dimensionless quantity,

$$\hat{R} = \frac{R_{\theta=0}}{4\pi^2 n^2 \lambda_0^{-4} A^2 \pi \langle D \rangle^3}. \tag{37}$$

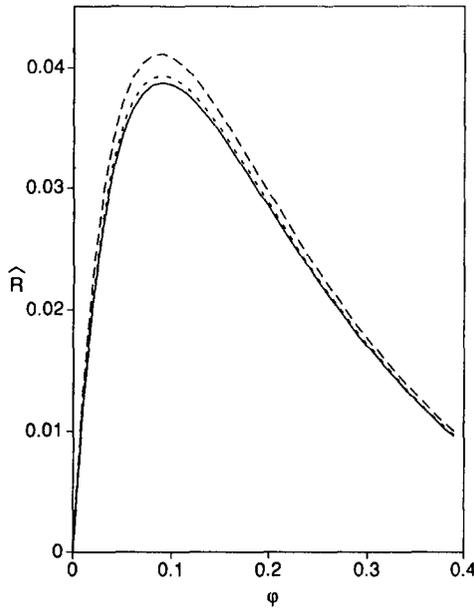


Fig. 1. Intensity of scattered light of a system of hard spherocylinders with diameter D and a log-normal distribution of the lengths with $\langle L \rangle/D = 5$ and relative standard deviation $\sigma_L = 0$ (—), 0.2 (---) and 0.4 (-·-·-) as a function of the total volume ϕ of the hard spherocylinders.

In figs. 1–3, representative results are given for the effect of polydispersity on the Rayleigh ratio. Notice that polydispersity in the diameter D has a far more pronounced effect than polydispersity in the length. Some insight in the effect of polydispersity on the light scattering intensity can be obtained by realizing that the concentration fluctuations of the colloidal species can be divided in two distinct contributions [30,31]. On the one hand, the concentration fluctuations are caused by overall density fluctuations which are accompanied by fluctuations in the osmotic pressure. Further, the exchange of different species at constant osmotic pressure also contributes to concentration fluctuations. The light scattering caused by these two kinds of fluctuations can be calculated quantitatively by adapting the fluctuation variables, introduced by Kirkwood and Goldberg [32], to a colloidal system [30,31]:

$$\lambda_j = \sum_{k=1}^n \left(\frac{\partial V}{\partial N_k} \right)_{\Pi, N_j} \delta \rho_k, \quad (38)$$

$$\lambda_j = \frac{\delta \rho_j}{\rho_j} - \frac{\delta \rho_1}{\rho_1}, \quad j = 2, 3, \dots, n.$$

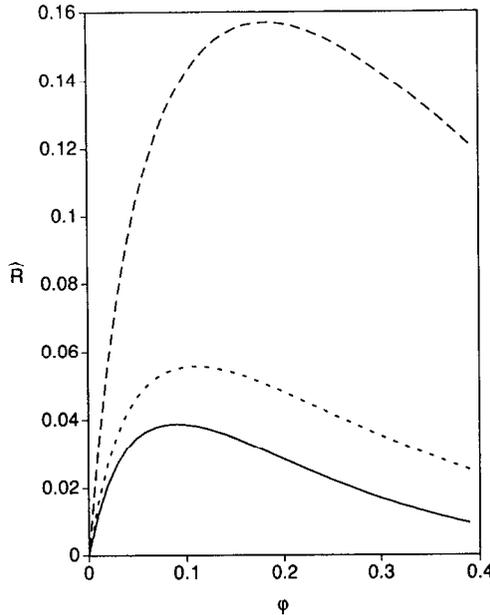


Fig. 2. Intensity of scattered light of a system of hard spherocylinders with diameter L and a log-normal distribution of the diameters with $\langle L \rangle / D = 5$ and relative standard deviation $\sigma_D = 0$ (—), 0.2 (---) and 0.4 (-·-·-) as a function of the total volume ϕ of the hard spherocylinders.

The mean square of the overall density fluctuations is related to the osmotic compressibility,

$$\langle \lambda_1^2 \rangle = \frac{k_B T}{V} \left[- \frac{1}{V} \left(\frac{\partial V}{\partial \Pi} \right)_T \right]. \tag{39}$$

Further it can be shown that the exchange fluctuations $\lambda_2, \lambda_3, \dots, \lambda_n$ are statistically independent from the overall density fluctuations λ_1 ,

$$\langle \lambda_1 \lambda_j \rangle = 0, \quad j = 2, 3, \dots, n. \tag{40}$$

This property makes it possible to write the light scattering intensity as a sum of the contribution of the overall density fluctuations R^+ and the exchange fluctuations R^- ,

$$R_{\theta=0} = R^+ + R^-. \tag{41}$$

Using eqs. (38) and (39) one obtains for R^+ the following result:

$$R^+ = \frac{4\pi^2 n^2 \lambda_0^{-4} A^2 \phi (1 - \phi)^4}{\xi^{(0)} (1 - \phi)^2 + 2\xi^{(1)} \xi^{(2)} (1 - \phi) + (\xi^{(2)})^3 / 4\pi}. \tag{42}$$

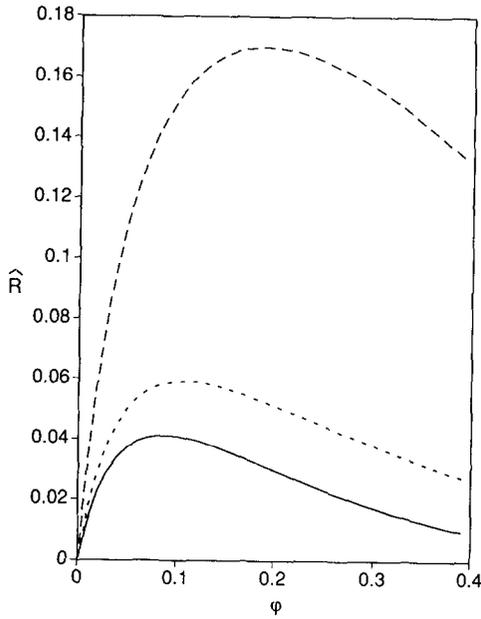


Fig. 3. Intensity of scattered light of a system of hard spherocylinders with independent log-normal distributions for the lengths and diameters with $\langle L \rangle / \langle D \rangle = 5$ and relative standard deviation $\sigma_L = 0.4, \sigma_D = 0$ (—), $\sigma_L = 0.4, \sigma_D = 0.2$ (---) and $\sigma_L = 0.4, \sigma_D = 0.4$ (-.-) as a function of the total volume ϕ of the hard spherocylinders.

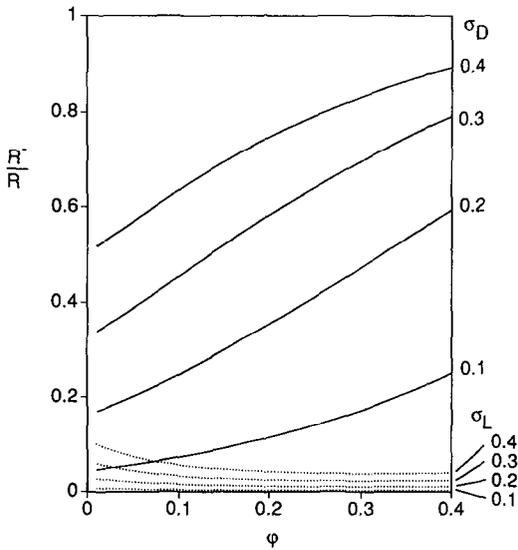


Fig. 4. Relative contribution of the exchange fluctuations to the total light scattering intensity as a function of the volume fraction ϕ of the hard spherocylinders for a log-normal distribution of the lengths with $\langle L \rangle / D = 5$ and relative standard deviation $\sigma_L = 0.1, 0.2, 0.3, 0.4$ and for a log-normal distribution of the diameters with $L / \langle D \rangle = 5$ and relative standard deviation $\sigma_D = 0.1, 0.2, 0.3, 0.4$.

Note that since the length of the particles only appears linearly in $\xi^{(\nu)}$ ($\nu = 0, 1, 2, 3$), the quantity R^+ only depends on the average length and not on the variance. In fig. 4 we present the contribution of the exchange fluctuations to the light scattering intensity, relative to the total light scattering intensity for a log-normal distribution for the length and diameter of HSC. Note that whereas for polydispersity in length the contribution of exchange fluctuations to the light scattering intensity is quite small, in case of polydispersity in diameter it is considerable. In fact, for a variance $\sigma_D \geq 0.3$ the contribution R^- becomes even larger than R^+ with increasing volume fractions. The completely different relative contributions of R^- in the case of length and diameter polydispersity, respectively, can be understood by the fact that the effect of length polydispersity only appears in the form of $\langle L^2 \rangle$, whereas for diameter polydispersity moments up to $\langle D^6 \rangle$ play a role.

6. Concluding remarks

Starting from the SPT results for the chemical potential, we have derived expressions for the light scattering and sedimentation equilibrium for an isotropic polydisperse solution of HSC. This requires the inversion of the matrix $(\partial\mu_k/\partial\rho_j)_{\rho_k}$ which, like in the case of polydisperse hard spheres, could be performed analytically. This inverse matrix can be expressed in terms of what Rosenfeld [33] refers to as fundamental measures and averages thereof. According to Rosenfeld the SPT results for the pressure and chemical potentials, expressed in terms of fundamental measures, are valid for all polydisperse convex hard body fluids. This would in turn imply that the results obtained here are also generally valid for polydisperse convex hard body fluids within the SPT.

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