Evaluation of Influence of Multiple Scattering Effect in Light-Scattering-Based Applications *

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The extinction cross sections of a system containing two particles are calculated by the T-matrix method, and the results are compared with those of two single particles with single-scattering approximation. The necessity of the correction of the refractive indices of water and polystyrene for different incident wavelengths is particularly addressed in the calculation. By this means, the volume fractions allowed for certain accuracy requirements of single-scattering approximation in the light scattering experiment can be evaluated. The volume fractions calculated with corrected refractive indices are compared with those obtained with fixed refractive indices which have been rather commonly used, showing that fixed refractive indices may cause significant error in evaluating multiple scattering effect. The results also give a simple criterion for selecting the incident wavelength and particle size to avoid the 'blind zone' in the turbidity measurement, where the turbidity change is insensitive to aggregation of two particles.

In colloidal physics, light scattering and turbidity measurement are widely used as the scattered light intensity contains some information concerning the characteristics of colloids, such as diffusion coefficient, the particle size and coagulation rate.[1−7] To simplify application of the light scattering techniques, the single-scattering approximation is used in many cases. In this approximation, the light scattering properties of single particle are expected to represent the behaviour of the entire ensemble. However, the single-scattering approximation is not always valid especially when the concentration of the particles is high, as single-scattering only occurs under the condition that the distances between particles in dispersion approach infinity. Therefore, the volume fraction should be carefully selected to ensure that the multiple scattering effect becomes negligible in light-scattering experiments. For studying the multiple scattering effect, it is useful to study the extinction cross sections of a system containing two particles (bisphere system) and to compare them with the results of two single particles with single-scattering approximation. Based on this, Quirantes *et al.*[8] developed a criterion that can be used to calculate the volume fraction needed for accuracy requirement of single scattering approximation. In this criterion, a ratio R is used to evaluate the effect of multiple scattering, which can be expressed as[8]

$$R(kr, \delta/r) = \frac{C_{\text{ext}}(kr, \delta)}{2C_{\text{ext}}(kr, Mie)}, \qquad (1)$$

where k is the wave number in medium, r is the particle radius, $C_{\text{ext}}(kr, \delta)$ is the extinction cross section of a bisphere system with distance δ between the relevant

two particles, and $C_{\text{ext}}(kr, \text{Mie})$ is the Mie extinction cross section for a single particle with size parameter $\alpha = kr$. When R is closer to 1, the multiple scattering effect is smaller.

In the turbidity measurement of coagulation process, the single-scattering approximation is also used for dilute dispersions. In this case the optical factor is $R(kr, \delta/r = 2) - 1$.[3,4,9] As shown in our previous paper,[3] the 'blind zone' that relates to the optical factor close to zero should be avoided. Therefore, to calculate R ratio is also desirable for selecting proper parameters such as the incident wavelength and particle size in turbidity measurement.

In this study, we use the same criterion as in Ref. [8] to study the multiple scattering effects with the T-matrix method. However, the corrected refractive indices of water and polystyrene for different incident wavelengths are used. To verify the necessity of the correction to the refractive indices, the results are compared with those in Ref. [8], which were calculated from the fixed (namely, uncorrected) relative refractive index $m = 1.2$. We also propose how to select the parameters to avoid the blind zone in turbidity measurement.

To obtain R in Eq. (1), $C_{\text{ext}}(kr, \text{Mie})$ should be calculated by Mie theory.[10] However, Mie theory is only applicable to spherical particles. Therefore, it cannot be used for evaluating $C_{\text{ext}}(kr, \delta)$, because two particles must be considered as a unit which is no longer spherical. The T-matrix method can solve complex scattering problems of irregular particles, including the system composed of many spherical particles. Therefore, the extinction cross sections of bisphere

particles $C_{\text{ext}}(kr, \delta)$ can be precisely calculated by the T-matrix method.

In the T-matrix method,[11−14] both incident and scattered electric fields are expanded in a series of vector spherical wavefunctions as follows:[12]

$$\boldsymbol{E}^{inc}(\boldsymbol{r}) = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} [a_{mn} Rg\boldsymbol{M}_{mn}(k\boldsymbol{r})$$
$$+ b_{mn} Rg\boldsymbol{N}_{mn}(k\boldsymbol{r})], \qquad (2)$$

$$\boldsymbol{E}^{sca}(\boldsymbol{r}) = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} [p_{mn} \boldsymbol{M}_{mn}(k\boldsymbol{r}) + q_{mn} \boldsymbol{N}_{mn}(k\boldsymbol{r})]. \qquad (3)$$

The harmonics $Rg\boldsymbol{M}_{mn}$ and $Rg\boldsymbol{N}_{mn}$ have a Bessel-function radial dependence and are regular (finite) at the origin, whereas the functions $\boldsymbol{M}_{mn}$ and $\boldsymbol{N}_{mn}$ have a Hankel-function radial dependence and vanish at infinity. Due to the linearity of Maxwell's equations, the scattered field coefficients $\boldsymbol{p} = [p_{mn}, q_{mn}]$ are related to the incident field coefficients $\boldsymbol{a} = [a_{mn}, b_{mn}]$ by means of the so-called transition matrix (or T-matrix):

$$p_{mn} = \sum_{n'=1}^{\infty} \sum_{m'=-n'}^{n'} [T_{mnm'n'}^{11} a_{m'n'} + T_{mnm'n'}^{12} b_{m'n'}], \qquad (4)$$

$$q_{mn} = \sum_{n'=1}^{\infty} \sum_{m'=-n'}^{n'} [T_{mnm'n'}^{21} a_{m'n'} + T_{mnm'n'}^{22} b_{m'n'}]. \qquad (5)$$

In compact matrix notation, Eqs. (4) and (5) can be rewritten as

$$\begin{bmatrix} \boldsymbol{p} \\ \boldsymbol{q} \end{bmatrix} = \boldsymbol{T} \begin{bmatrix} \boldsymbol{a} \\ \boldsymbol{b} \end{bmatrix} = \begin{bmatrix} \boldsymbol{T}^{11} & \boldsymbol{T}^{12} \\ \boldsymbol{T}^{21} & \boldsymbol{T}^{22} \end{bmatrix} \begin{bmatrix} \boldsymbol{a} \\ \boldsymbol{b} \end{bmatrix}, \qquad (6)$$

which means that the column vector of the expansion coefficients of the scattered field is obtained by multiplying the transition matrix $\boldsymbol{T}$ and the column vector of the expansion coefficients of the incident field.

For a spherical particle, the matrix $\boldsymbol{T}$ is diagonal, and its elements are simply the a_n and b_n coefficients in Mie theory.[10] Thus the T-matrix method converges with Mie theory for a single spherical particle. For a cluster consisting of N spheres, the total scattered electric field can be written as the sum of the fields scattered by all spheres:

$$\boldsymbol{E}^{sca}(\boldsymbol{r}) = \sum_{j=1}^{N} \boldsymbol{E}_j^{sca}(\boldsymbol{r}). \qquad (7)$$

Because of the electromagnetic interactions between the components, the total electric field exciting each particle can be written as the sum of the external incident field $\boldsymbol{E}_0^{inc}(\boldsymbol{r})$ and the partial fields scattered by all other particles:

$$\boldsymbol{E}_j^{inc}(\boldsymbol{r}) = \boldsymbol{E}_0^{inc}(\boldsymbol{r}) + \sum_{\substack{l=1 \\ l \neq j}}^{N} \boldsymbol{E}_l^{sca}(\boldsymbol{r}) \quad j = 1, 2, \ldots, N. \qquad (8)$$

By some deduction from Eqs. (7) and (8),[4,12] the T-matrix for system of N spheres $\boldsymbol{T}$ can be calculated from the T-matrix of single particle, which can be determined by Mie theory. For the bisphere system discussed in this study, N is equal to 2.

The T-matrix $\boldsymbol{T}$ as shown in Eq. (6) can be used directly in computing the orientationally averaged extinction cross section for the system containing two particles. The formula is expressed as[12]

$$\langle C_{\text{ext}} \rangle = -\frac{2\pi}{k^2} \text{Re} \sum_{n=1}^{\infty} \sum_{m=-n}^{n} [T_{mnmn}^{11} + T_{mnmn}^{22}]. \qquad (9)$$

By this means, the extinction cross sections $C_{\text{ext}}(kr, \delta)$ and $C_{\text{ext}}(kr, \text{Mie})$ and therefore the ratio R in Eq. (1) can be calculated by the T-matrix method.

The parameters needed in the calculation are the relative index of refraction m and the size parameter α. For the system of the polystyrene particle in water, a relative index of refraction $m = n_{\text{ps}}/n_{\text{water}} = 1.2$ is used in Ref. [8], where n_{ps} and n_{water} are refractive indices of polystyrene and water, respectively. Actually, this relative refractive index is rather commonly used in the studies for such a colloidal system, because it is close to the relative index of polystyrene in water. However, the refractive indices of water and polystyrene are dependent on different incident wavelengths, which will cause m to be different from 1.2. In our previous paper,[4] we have shown that tiny difference of refractive indices may cause large error in the calculation results of the so-called optical factor in turbidity measurement. Therefore, the refractive indices need to be as precise as possible for correctly calculating R in Eq. (1).

The dependence of the refractive indices of water and polystyrene on wavelength have already been studied.[15−18] In this study, we use the same formulas of the refractive indices as was used in our previous papers.[3,4] The refractive index of water for different wavelengths is given as[15]

$$\begin{aligned} n_{\text{water}}(\lambda) = &\, 1.447824 + 3.0110 \times 10^{-4} S \\ &- 1.8029 \times 10^{-5} T \\ &- 1.6916 \times 10^{-6} T^2 - 4.89040 \times 10^{-1} \lambda \\ &+ 7.28364 \times 10^{-1} \lambda^2 - 3.83745 \times 10^{-1} \lambda^3 \\ &- S(7.9362 \times 10^{-7} T - 8.0597 \times 10^{-9} T^2 \\ &+ 4.249 \times 10^{-4} \lambda - 5.847 \times 10^{-4} \lambda^2 \\ &+ 2.812 \times 10^{-4} \lambda^3), \end{aligned} \qquad (10)$$

where S is the salinity in ‰, T is the temperature in Celsius of degrees, and λ is wavelength in micrometres. The refractive index of polystyrene[18] is given as

$$n_{\text{ps}}(\lambda) = 1.56362 + 0.00884/\lambda^2 + 0.000255627/\lambda^4, \qquad (11)$$

where the unit for wavelength is micrometres.

By using Eqs. (10) and (11), we can obtain the corrected values for the refractive indices of water and polystyrene for different wavelengths to obtain the parameters α and m required in the calculation. In this study, $T = 25^\circ$C and $S = 28$ are used.

To study the multiple scattering effect, the critical values of particle distance δ_0 for given accuracy requirements of $\varepsilon = |R(kr, \delta_0/r) - 1|$ are calculated for different particle radii r and incident wavelengths, which is similar to Ref. [8]. Mathematically, this condition means that for any $\delta > \delta_0$, there will be $|R(kr, \delta/r) - 1| < \varepsilon$, because the effect of multiple scattering will tend to be smaller when the particle distance δ becomes larger. Apparently, the statement of Quirantes *et al.*,[8] 'for a given kr_0 value, find the value of δ/r_0 so that for any $r > r_0$ the condition $|R(kr, \delta/r) - 1| < \varepsilon$ holds' is incorrect or a typo, as the increase of particle radius will not result in smaller multiple scattering effect.

For bisphere particles, the distance δ will give the related volume fraction φ as

$$\varphi = \frac{4}{3}\pi \left(\frac{r}{\delta}\right)^3. \qquad (12)$$

Then we can obtain the volume fraction that fits $\varepsilon = |R(kr, \delta_0/r) - 1|$ for different incident wavelengths and particle radii, and compare the results calculated from corrected refractive indices and fixed indices.

Figures 1 and 2 show the calculated volume fractions with the corrected refractive indices for different sized particles with $\varepsilon = 0.01$ and $\varepsilon = 0.05$. The results are compared with those calculated with fixed refractive indices, which is compatible with the results for $m = 1.2$ in Ref. [8]. In these figures, the symbols are the calculated results for the corrected refractive indices, while the lines are the results for fixed refractive indices.

Since the same size parameter for corrected and uncorrected (fixed) refractive indices will correspond to different incident wavelengths in air even the particle radius r is the same, the abscissas in these figures are $2\pi r/(0.75\lambda)$ instead of the size parameter as in Ref. [8]. Here we choose $2\pi r/(0.75\lambda)$ as the abscissas in order to ensure that the calculated volume fraction from the same parameters in experiments (r and λ) can be compared for corrected and fixed refractive indices in the figures. Actually, $2\pi r/(0.75\lambda)$ is the size parameter for fixed refractive indices (n_{water} is 1.33). For distinguishing from size parameter α, $2\pi r/(0.75\lambda)$ will be denoted as α_f hereafter.

Since the range for the wavelengths used in the light scattering experiments cannot be infinite, we use wavelengths from 250 to 850 nm (UV–Visible), which is the range discussed in Refs. [3,4]. As the wavelength range is limited, the range of α_f for a given sized particle will also be limited. This is the reason why the value of α_f for small particles are smaller than those

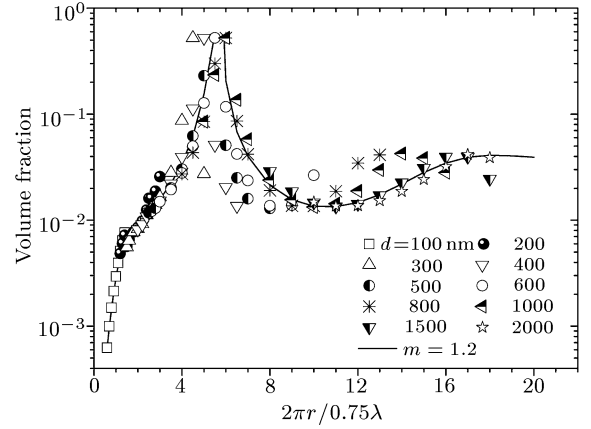for larger particles in Figs. 1 and 2.

Fig. 1. Comparison of the calculated volume fractions with the corrected refractive indices and fixed refractive indices for different sized particles with $\varepsilon = 0.01$. The symbols are the calculated results for the corrected refractive indices, while the line denotes the results for fixed refractive indices ($m = 1.2$).

Fig. 2. Comparison of the calculated volume fractions with the corrected refractive indices and fixed refractive indices for different sized particles for $\varepsilon = 0.05$. The symbols are the calculated results for the corrected refractive indices, while the line denotes the results for fixed refractive indices ($m = 1.2$).
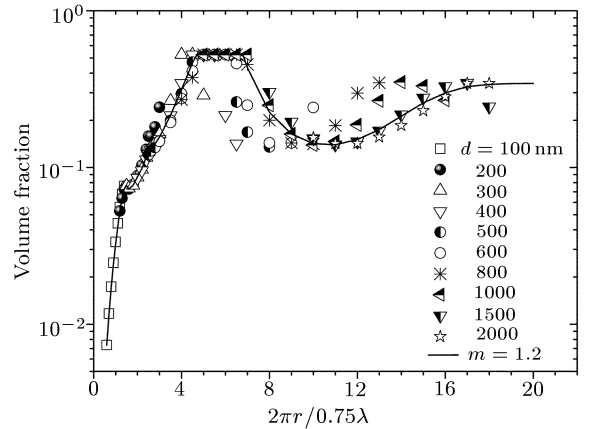
From these figures we can see that the calculated volume fractions for corrected refractive indices are different from those for fixed indices. The difference becomes remarkable for large sized particles (large size parameters). This result shows that the dependence of the multiple scattering effect on refractive indices is insignificant for small sized particles (small size parameters) so that the correction of the refractive indices is more crucial for large sized particles (large size parameters).

Comparing the two figures with each other, it can be seen that the difference becomes larger when ε is smaller. For $\varepsilon = 0.01$, the volume fraction calculated with fixed refractive indices reaches nearly 10 times different from that with corrected indices for some par-

ticle size, such as $d = 400$ nm particles at α_f around 6, where d is the diameter of the particles. For example, when $d = 400$ nm and $\alpha_f = 6$, the calculated volume fractions are 0.0205 and 0.2068, respectively, for corrected and fixed refractive indices. However, the differences for $\varepsilon = 0.05$ are not so significant although they are also obvious. This result indicates that accurate refractive indices are more necessary for higher accuracy requirements.

It can be seen from the figures that the calculated volume fractions at some α_f values reach a maximum. The maximal value of these volume fractions $V_{\max}$ in the figures is 0.524. This value corresponds to $\delta_0/r = 2$, which means that $|R(kr, \delta/r) - 1| < \varepsilon$ is satisfied for any $\delta > 2r$. As the distance of the two particles of the bisphere system cannot be smaller than $2r$, the calculated volume fraction will be set to 0.524 for this condition, which will be named the $V_{\max}$ condition hereafter.

It can then be concluded that the multiple scattering effect is not significant for the values of α_f that meet the $V_{\max}$ condition. Therefore, it seems that the related parameters (r and λ) for these values of α_f are good for light scattering experiments considering the above-mentioned criterion which is the same as discussed in Ref. [8]. However, α_f that meet the $V_{\max}$ condition for small ε should be avoided even for very small volume concentration in some experiments, such as studying of the coagulation process from turbidity measurements.

In the study of coagulation process by turbidity measurement, the optical factor is $R(kr, \delta/r = 2) - 1$[3,4,9] for dilute dispersions. If the $V_{\max}$ condition is satisfied for accuracy requirement ε, the absolute value of the optical factor will be smaller than ε. For the small ε discussed in this study, especially for $\varepsilon = 0.01$, the $V_{\max}$ condition means the optical factor is quite close to zero. As the turbidity change rate is proportional to the optical factor[3,4,9] for an aggregating colloidal system, the turbidity change will be insensitive to aggregation of two particles when the optical factor is close to zero. This will result in large error in measuring the coagulation rate constant by turbidity measurement. This condition is named the blind zone,[3] which should be avoided in turbidity measurement.

The ranges of α_f for the $V_{\max}$ condition for different sized particles are different when the refractive indices are corrected, although the ranges for fixed refractive indices are the same, as can be seen from the figures. For $d = 300$ nm particles, the α_f value that satisfies the $V_{\max}$ condition for $\varepsilon = 0.01$ is around 4.5, while for $d = 1000$ nm, the α_f value becomes around 6. Therefore, to avoid the blind zone in turbidity mea-

surement, the incident wavelength must be carefully chosen to make the α_f value far from the range 4.5–6.

In summary, we have discussed the multiple scattering effect by using the T-matrix method with the correction of refractive indices for different incident wavelengths. The results show that the refractive indices have great influence on the calculated results of the volume fraction for the given accuracy requirements. Therefore, a fixed refractive index will cause large error for studying the accuracy of single scattering approximation and the correction of refractive index is crucial, especially for large sized particles and higher accuracy requirements. By using the T-matrix method with corrected refractive indices, precise volume fractions for given ε can be calculated, which will be helpful for choosing volume fractions to satisfy the given accuracy requirements of single-scattering approximation in light scattering experiments.

However, it is important to avoid the blind zone in studying the coagulation process by turbidity measurement. Therefore, the α_f value that meets the $V_{\max}$ condition for $\varepsilon = 0.01$ should be avoided even for very small volume concentration. Considering this, we show that the incident wavelength should be carefully chosen to make the α_f value far from the range 4.5–6, which gives a simple criterion for avoiding the blind zone in the turbidity measurement.

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