Journal of Colloid and Interface Science **240,** 78–82 (2001)
doi:10.1006/jcis.2001.7641, available online at http://www.idealibrary.com on IDEAL®

Multiple Light Scattering by Spherical Particle Systems and Its Dependence on Concentration: A T-Matrix Study

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Received October 17, 2000; accepted April 13, 2001

The T-matrix method has been used to calculate scattering cross-sections of two spherical particles close to each other. By comparing our results with those expected for infinite distance, we can determine the maximum distance required to produce interparticle light-scattering interactions. As a result, we can determine the degree of dilution needed in a particle suspension to remain within the single-scattering approximation. Cross sections have been calculated for a relative refractive index $m = 1.2$ and a range of particle sizes and separations. Since the approach in this paper assumes double scattering as the first mechanism for beginning multiple scattering, our results will be compared with those arising from the condition that the optical depth is less than unity, $\tau < 1$. It is shown that this condition, widely used in transfer theory, is more restrictive than ours except for the smallest particles, where double scattering becomes the main agent for multiple scattering. © 2001 Academic Press

Key Words: **multiple scattering in colloidal suspensions; T-matrix; dilute suspensions.**

INTRODUCTION

Light-scattering (LS) techniques are widely used in colloidal physics to infer information from a particle suspension. The dependence of the scattered radiation on particle size, shape, and composition makes it suitable for applications such as particle sizing and aggregation/stability studies (1–3). In many cases the single-scattering approximation (SSA) is used: LS properties are calculated for a single particle and expected to represent the behavior of the entire ensemble.

However, the SSA is not applicable in some cases. Turbidity measuremens demand that coherence effects be taken into account (4). For nonzero angles, the effects of multiple-scattered light have to be dealt with. Hartel's 1940 theory (5) was developed to calculate the effect of double-, triple-, and quadruple-scattered light, and several authors (6, 7) used it to try to quantify multiple scattering on latex solutions. Hartel's one-flux theory itself fails for large values of the optical depth (8), making it necessary to resort to many-flux theories (9, 10) to solve the radiative transfer equation (11).

While this is a very active and rewarding field, a colloidal scientist might not be willing to face RTE-like problems just to know how dilute his concentration should be to work within the SSA regime. Trial-and-error methods like checking the linear relationship between incident and scattered light at several concentrations, spanning orders of magnitude, are used.

In the present paper, we intend to establish upper limits for concentration values such that the SSA holds. A T-matrix (12) method is used to calculate extinction efficiencies for bispherical particles at several interparticle distances, including touching spheres. From their comparison with infinite-distance calculations, some conclusions about which volume concentrations allow the SSA simplification to hold can be drawn. Such concentrations will depend on both particle size and composition, so an index of refraction $m = 1.2$ (close to the relative index of polystyrene in water) has been set. The reason to choose the extinction efficiency is to allow an easy comparison of LS behavior between finite-distance and infinite-distance particles; otherwise, the amount of LS data derived from T-matrix calculations (angle-dependent phase function and degree of linear and circular polarization, among others) would make comparisons unsuitable in practice. However, the coherent behavior of zero-angle scattering does not allow our results to be used in turbidity measurements.

THEORY

For the calculation of light-scattering properties, the T-matrix method (12) is used. Both incident and scattered electric fields are expanded in a series of vector spherical harmonics (13) $\mathbf{M}_{mn}(kr)$, $\mathbf{N}_{mn}(kr)$ as

$$\mathbf{E}_i(\mathbf{r}) = \sum_{n=1}^{\infty}\sum_{m=-n}^{n}[a_{mn}Rg\mathbf{M}_{mn}(kr) + b_{mn}Rg\mathbf{N}_{mn}(kr)]$$
$$\mathbf{E}_s(\mathbf{r}) = \sum_{n=1}^{\infty}\sum_{m=-n}^{n}[p_{mn}\mathbf{M}_{mn}(k\mathbf{r}) + q_{mn}\mathbf{N}_{mn}(k\mathbf{r})] \quad [1]$$

where $k = 2\pi/\lambda$, and λ is the free-space wavelength. Due to the linearity of Maxwell's equations, the scattered field coefficients $\mathbf{p} = [p_{mn},\ q_{mn}]$ are related to the incident field

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0021-9797/01 $35.00

coefficients $\mathbf{a} = [a_{mn},\ b_{mn}]$ by means of a transition matrix

$$p_{mn} = \sum_{n'=1}^{\infty} \sum_{m'=-n'}^{n'} \left[T^{11}_{mm'nn'} a_{m'n'} + T^{12}_{mm'nn'} b_{m'n'}\right]$$
$$q_{mn} = \sum_{n'=1}^{\infty} \sum_{m'=-n'}^{n'} \left[T^{12}_{mm'nn'} a_{m'n'} + T^{22}_{mm'nn'} b_{m'n'}\right] \quad [2]$$

or $\mathbf{p} = \mathbf{T} \cdot \mathbf{a}$ in compact notation. The T-matrix, which depends on the particle (size, shape, composition, and orientation) but not on the incident field, can then be used to calculate the light-scattering properties of nonspherical particles in random orientation, following Mishchenko's analytical averaging scheme (14).

For a spherical particle, the simpler Mie theory is preferred (in fact, the T-matrix for a spherical particle is diagonal, with $T^{11}_{mm'nn'} = -\delta_{mm'}\delta_{nn'} b_n$ and $T^{22}_{mm'nn'} = -\delta_{mm'}\delta_{nn'} a_n$). The reason for using the more complex T-matrix approach is that it allows the study of a pair of spherical particles as a single scatterer. Let us assume a system of N spheres. The scattered electric field can be written as the sum of the fields scattered by all spheres: $\mathbf{E}_s = \Sigma\ \mathbf{E}^i_s$. To apply the boundary conditions that will ultimately lead to a relationship between the field coefficients $\mathbf{a}^i = [a^i_{mn}, b^i_{mn}]$ and $\mathbf{p}^i = [p^i_{mn}, q^i_{mn}]$ for sphere i, it is necessary to write the spherical harmonics about sphere j into harmonics about sphere i by means of addition theorems,

$$\mathbf{M}_{mn}(k\mathbf{r}^j) = \sum_{l=1}^{\infty} \sum_{k=-1}^{l} \left[A^{mn}_{kl}(k\mathbf{r}^{ji}) Rg\mathbf{M}_{kl}(k\mathbf{r}^i) + B^{mn}_{kl}(k\mathbf{r}^{ji}) Rg\mathbf{N}_{kl}(k\mathbf{r}^i)\right]$$
$$\mathbf{N}_{mn}(k\mathbf{r}^j) = \sum_{l=1}^{\infty} \sum_{k=-1}^{l} \left[A^{mn}_{kl}(k\mathbf{r}^{ji}) Rg\mathbf{N}_{kl}(k\mathbf{r}^i) + B^{mn}_{kl}(k\mathbf{r}^{ji}) Rg\mathbf{M}_{kl}(k\mathbf{r}^i)\right], \quad [3]$$

where $\mathbf{r}^{ji} = \mathbf{r}^j - \mathbf{r}^i$. Explicit expressions for the addition coefficients $\mathbf{A}^{ji} = [A^{mn}_{kl}\ (k\mathbf{r}^{ji}), B^{mn}_{kl}(k\mathbf{r}^{ji})]$ can be found in Ref. 15. We then derive in matrix notation (16, 17)

$$\mathbf{p}^j = \mathbf{T}^j\left(\mathbf{a}^i + \sum_{i \neq j} \mathbf{A}^{ji}\mathbf{p}^i\right), \quad [4]$$

where $\mathbf{T}^j$ represent the T-matrix for the particle j, when isolated, ($\mathbf{p}^j = \mathbf{T}^j\mathbf{a}^i$). The $\mathbf{A}^{ji}$ matrices account for the electromagnetic interaction between particles i and j and depend on the distance and orientation between them. Inversion of Eq. [4] gives sphere-centered transition matrices that transform the expansion coefficients of the incident field into expansion coefficients of the individual scattered fields:

$$\mathbf{p}^j = \sum_i \mathbf{T}^{ji}\mathbf{p}^i. \quad [5]$$

Finally, the scattered field expansions from the individual spheres will be transformed into a single expansion based on a single origin of the particle system. The incident and scattered coefficients $\mathbf{a}$, $\mathbf{p}$ for the system will be derived as

$$\mathbf{p} = \sum_j \mathbf{p}^j = \sum_{j,i} \mathbf{B}^j\mathbf{T}^{ji}\mathbf{a}^i = \sum_{j,i} \mathbf{B}^j\mathbf{T}^{ji}\mathbf{B}^i\mathbf{a} = \mathbf{Ta}, \quad [6]$$

where the $\mathbf{B}$ matrices are similar to the $\mathbf{A}$ matrices of Eq. [4]. The matrix $\mathbf{T}$ so defined is the one that we seek to obtain to make calculations of light-scattering properties of the particle system. In our case study, $N = 2$.

Several computing advantages derive from the fact that a two-particle system can be considered single particle with rotational symmetry. Using spheres also allows us to disregard an important limitation, namely, the fact that the circumscribing spheres to both particles cannot overlap; that is, for spheres, simply state that particles cannot interpenetrate each other. Though many choices for the origin of the expansion in Eq. [6] can be chosen, we will take the midpoint of the line joining both spheres as such origin. As we will also assume that both particles are identical, $\mathbf{T}^1 = \mathbf{T}^2$.

The application to the study of multiple scattering follows from the fact that two particles separated long enough will behave as essentially independent scatterers: $\mathbf{T} = \mathbf{T}^1 = \mathbf{T}^2$. As particles come closer to each other, however, the two-sphere T-matrix $\mathbf{T}$ (and any light-scattering property that can be derived from it) will differ. We can then use light scattering as a measure of how far particles should be on average to make multiple scattering negligible. Once this distance δ is found, its relationship with the particle radius r will give us the single-scattering-limit volume fraction ϕ:

$$\phi = \frac{4}{3}\pi\left(\frac{r}{\delta}\right)^3. \quad [7]$$

RESULTS

Calculations have been carried out for a particle relative refractive index $m = 1.2$, close to that of polystyrene in water at visible wavelengths. Since many light-scattering properties can be computed, cross sections alone will be considered. To illustrate the differences between the extinction cross-section of a bisphere system $C_{\text{ext}}(kr, \delta)$ and that of an isolated sphere, the R ratio given as

$$R = \frac{C_{\text{ext}}(kr, \delta)}{2C_{\text{ext}}(kr, \text{Mie})}, \quad [8]$$

has been plotted; $C_{\text{ext}}(kr, \text{Mie})$ is the Mie extinction cross section for a single particle with size parameter kr. When both particles behave as independent scatterers, $R = 1$. Figure 1 shows a three-dimensional plot of R as a function of both monosphere size parameter kr and separation-to-radius ratio δ/r. The reason to choose the latter, instead of the interparticle separation δ, is that,

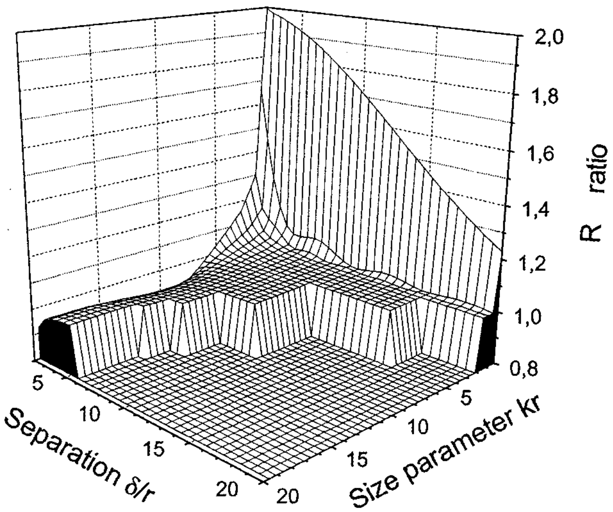

FIG. 1. Plot of $R = C_{\mathrm{ext}}$ (bisphere)$/2C_{\mathrm{ext}}$(Mie) as a function of particle size kr, and separation-to-radius ratio δ/r.

as seen above, the volume concentration of a particle system depends on δ/r.

The first conclusion that can be drawn is that finite-distance effects become more noticeable as particle size gets smaller. In the Rayleigh limit it is found that $R = 2$. This is to be expected, since in that limit cross sections are proportional to the square volume of the scattering particle. A two-particle system, therefore, has four times the scattering power of a single particle, or twice that of two isolated particles. For $kr = 0.1$, particles with a volume concentration $\phi = 10^{-5}$ still show a 2–2.5% difference respect to the infinite-dilution value.

As the sphere size increases, R goes to unity more rapidly for a given separation, which means that particle suspensions can get closer without showing the effects of near-particle interactions. In particular, particles with a size parameter equal to 5.7 show a difference in scattering cross sections (respective to infinite separation) no larger than 0.4% for any interparticle separation. Double aggregation could then be neglected in the range $kr =$ 5.5–6, as far as multiple scattering is concerned, provided that dimers are separated by a distance large enough.

Larger particles show a decrease in scattering cross sections. The single-scattering regime is reached for values of δ/r around 5–7. It can be seen that close particles in the 6–15 size range have lower cross sections than infinitely separated bisphere systems; this is specially seen for touching spheres. For large particles, R is expected to reach the geometrical optics limiting value of 0.924. This can be seen in Fig. 2.

IMPLICATIONS FOR MULTIPLE SCATTERING

In usual work in the field of light scattering, one will simply need to know how dilute a particle system (e.g., a colloidal suspension) should be to work in the single-scattering approximation (SSA). This question can be addressed by finding out how far particles must be separated in average so that R is sufficiently close to unity. Mathematically, this condition can be described as follows: for a given kr_o value, find the value of δ/r_o so that for any $r > r_o$ the condition $|R(kr, \delta/r) - 1| < \varepsilon$ holds. The value of ε will depend on the user's accuracy requirements. As an example, Fig. 3 shows the phase function and degree of linear polarization for spheres with $kr = 4$ and varying separations, in agreement with calculations by Mishchenko *et al.* (18).

Figure 4 shows the maximum volume concentration of scatterers ϕ^{R} as a function of sphere size parameter for $\varepsilon = 0.01$ and 0.05. It can be seen that ϕ^{R} increases with particle size up to $kr = 5.5$. It then decreases to a minimum at kr around 11 and again goes up. Unfortunately, computing time limitations do not allow us to go to kr values that are high enough to determine whether ϕ^{R} increases monothonically or oscillates. As a rule of thumb, concentrations of 0.01 or lower will fall under the SSA for size parameters larger than 2.5. In the $kr = 1$–2.5 region, concentrations lower than 0.001 become necessary. Smaller particles require even lower concentrations, which draws a warning for those dealing with particles in the Rayleigh approximation.

The concentration requirements to ensure single scattering on wavelength-sized particles compare with the results of Ref. 18. The authors conclude that essentially independent scattering is achieved for an interparticle distance equal to four times their radii ($\phi = 0.065$). For size parameters in the range 2.5–20, our data indicate that the value of ε always falls below 0.03. The fact that ref. 18 considered a different refractive index ($m = 1.5 + \mathrm{i}0.005$) is an indication that the four-radii separation rule might be of more general application, although we are cautious until the validity for other values of m is properly addressed. Further studies in that direction are currently in progress.

It must be stressed that the figures in the present paper, along with the theory that supports it, refer to incoherent light scattering. The possibility of coherent scattering must also be addressed. Typically, orientation averaging tends to cancel the coherent scattering effect, so that incoherent multiple scattering

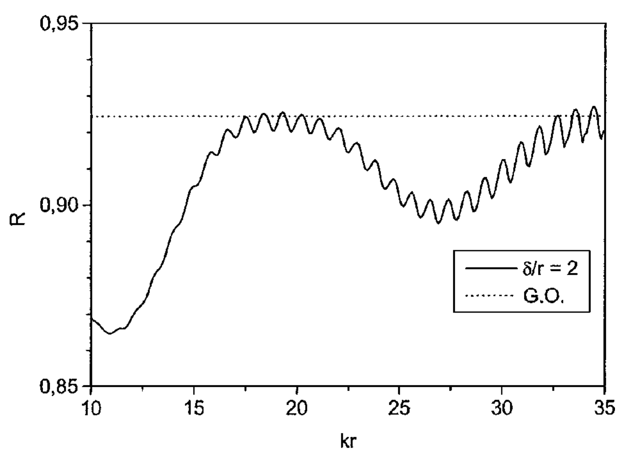

FIG. 2. Value of R for touching spheres ($\delta/r = 2$) and comparison to the geometrical optics (G.O.) value 0.9244.

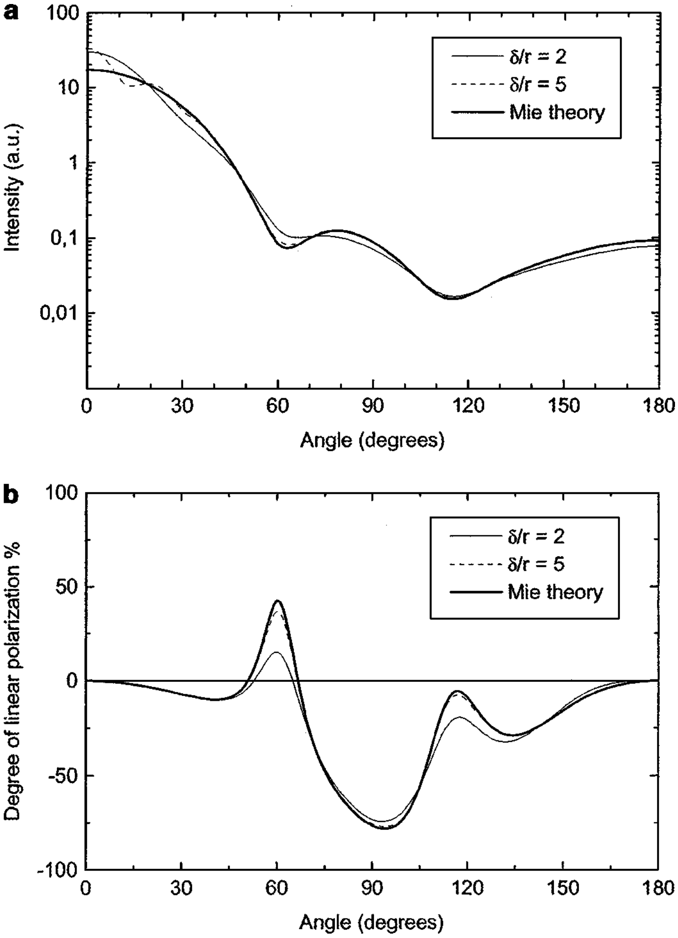

FIG. 3. (a) Phase function and (b) degree of linear polarization for the light scattered by randomly oriented bispheres with monosphere size parameter $kr = 4$ and separations equal to 2 (touching spheres) and 5 sphere radii. The values of R for these separations are 1.082 and 1.01, respectively. Mie theory results are also displayed for comparison (thick line). The particle refractive index is $m = 1.2$.

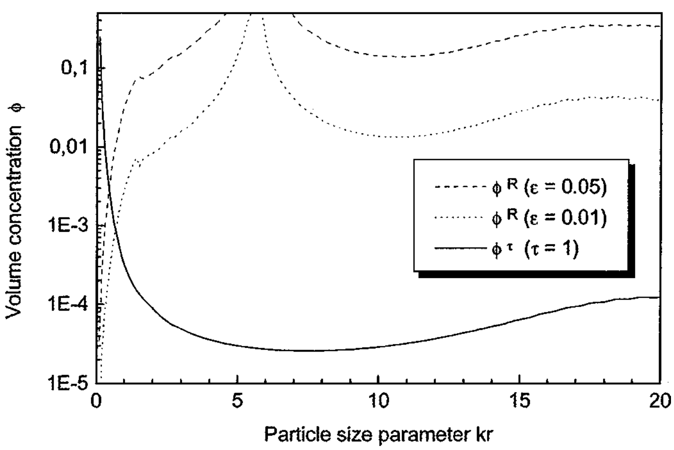

FIG. 4. Maximum allowable volume concentration of particles, ϕ^{R}, as a function of particle size kr. Curves refer to values of the accuracy parameter ε equal to 0.01 and 0.05. As a comparison, the concentration holding the condition $\tau = 1$, for a path length of 10 mm, is also shown (ϕ^{τ}).

becomes effective at lower concentrations that coherent interference effects (19). An exception to the above is the well-known case of forward scattering, where the interference of light is always constructive (4). The effect of coherent scattering has been studied in relation to the applicability of the Beer law, for which a beam radiation extinction follows an exponential law given by

$$I(z) = I_0 \exp(-NC_{\mathrm{ext}}z), \qquad [9]$$

where N is the number density of the particles. This law is in fact a steady-state solution to the radiative transfer equation (RTE) when scattering is negligible, though it can be successfully applied to nonzero scattering if the detector's acceptance angle is small enough (20). It has been found in both experimental data and calculations that addressing the problem of coherent scattering by means of approximations such as the QCA (quasi-crystalline approximation) gives better agreement to experimental data than trying to calculate multiple incoherent scatterings. Furthermore, our results show that the incoherent multiple scattering calculations give corrections which, with few exceptions, have signs different from those yielded by the QCA (21–23).

This makes our approach somewhat useless in turbidity measurements, where incoherent scattering is supposed to be null and, in practical terms, is reduced to nearly zero by a careful selection of both scattering volume element and detector aperture (21). It is interesting to note, however, that maximum concentration vs size curves under the incoherent approximation (Eq. [9]) have a similar behavior for large particle size, as Fig. 4 shows, though a comparison of both curves shows that the noncoherent approximation stands valid at lower values of concentration than single incoherent scattering for all but the smallest particles.

As stated above, light scattered at angles different than zero is mostly incoherent. If the particle concentration is low enough so that single scattering can be assumed, theories for single-particle scattering (Mie for spheres) can be used. Higher concentrations require other, more complex approaches incorporating interparticle interactions. Such an approach is outlined in the present paper. However, a basic assumption is made, namely, that only double-scattering is taken into account. While assuming double scattering as the first mechanism for beginning multiple scattering sounds reasonable, it is not always the case. Hartel's theory on multiple scattering (5) describes the angular distribution of light scattered as a number of contributions from light scattered after m encounters. Calculations made for latex particles at $kr = 15$ under Hartel's theory show (6) that the contribution of double-scattered light ($p = 2$) equals that of single scattering for volume concentrations larger than about 0.003, a whole order of magnitude lower than those predicted by us.

It must be pointed out, however, that the transition between single and multiple scattering in Hartel's theory depends on the optical depth $\tau = NC_{\mathrm{ext}}z$. If the path length z is large enough, multiple scattering will be detected even in cases where neighboring particles seem not to interact. In the Hartel theory, the contribution of the m-scattered light is larger than any other when $m = \tau$. Experimental data (6, 7) show that the transition between single and multiple scattering takes place for values of τ close to unity. Hartel's theory itself is found to fail for optical depths larger than about 3, thus calling for less simple models (two-, four-, and six-flux models in radiative transfer theory), but $\tau = 1$ has been long regarded as a rule of thumb for single-scattering approximations in radiative transfer theory.

To make sure that multiple scattering is not present, the usual procedure is to reduce either the concentration (N) or the path length (l). Since low N values, in turn, mean a longer average interparticle distance, $|R - 1| < \varepsilon$ is also implicitly sought. However, for low path lengths, concentration can reach values so high that this condition is not met and C_{ext} deviates from the infinite-dilution value, even as optical depth is kept to a value lower than unity. Therefore, low optical depth (τ) does not guarantee single scattering in such cases.

Figure 4 compares the results from T-matrix calculations and the values of concentration for which $\tau = 1$ applies for a path length of 10 mm. As it can be seen, at most size values the condition $\tau \leq 1$ is more restrictive than $|R - 1| < \varepsilon$ in the meaning that it is violated for a smaller concentration value. Only for small particles the maximum concentration value for which $\tau \leq 1$, (ϕ^{τ}), is higher than the maximum concentration for which $|R - 1| < \varepsilon$, (ϕ^{R}). For other path lengths, the maximum particle size for which $\phi^{\tau} > \phi^{\text{R}}$ changes. When particles are larger than this limiting value (about $kr = 0.6$ for path length $z = 10$ mm, or $kr = 1.0$ for $z = 1$ mm), the experimenter needs only to check that the optical depth value falls below unity. Only for smaller particles are double-scattering effects so high that the $\tau = 1$ condition does not suffice to ensure that the single-scattering regime is present.

ACKNOWLEDGMENT

Financial support from the Spanish Ministry of Education and Culture, Project MAT98-0940, is gratefully acknowledged.

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