Computational Evaluation of Approximate Rayleigh–Debye–Gans/Fractal-Aggregate Theory for the Absorption and Scattering Properties of Soot

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A computational evaluation of an approximate theory for the optical properties of soot is described, emphasizing the small-angle (Guinier) regime. The approximate theory (denoted RDG-FA theory) is based on the Rayleigh–Debye–Gans scattering approximation while treating soot as mass-fractal aggregates of spherical primary particles that have constant diameters and refractive indices. The approximate theory was evaluated by more exact predictions from the solution of the volume integral equation formulation of the governing equations, using the method of moments, and based on the ICP algorithm of Iskander et al. (1989). Numerical simulations were used to construct statistically significant populations of soot aggregates having appropriate fractal properties and prescribed numbers of primary particles per aggregate. Optical properties considered included absorption, differential scattering, and total scattering cross sections for conditions typical of soot within flame environments at wavelengths in the visible and the infrared. Specific ranges of aggregate properties were as follows: primary particle optical size parameters up to 0.4, numbers of primary particles per aggregate up to 512, mean fractal dimensions of 1.75, mean fractal prefactors of 8.0, and refractive indices typical of soot. Over the range of the evaluation, ICP and RDG-FA predictions generally agreed within numerical uncertainties (ca. 10 percent) within the Guinier regime, complementing similar performance of RDG-FA theory in the power-law regime based on recent experiments. Thus, the use of approximate RDG-FA theory to estimate the optical properties of soot appears to be acceptable—particularly in view of the significant uncertainties about soot optical properties due to current uncertainties about soot refractive indices.

Introduction

Soot is present within most practical nonpremixed hydrocarbon-fueled flames, which affects their structure, radiation, and pollutant emission properties (Köylü and Faeth, 1993). Thus, the absorption and scattering (optical) properties of soot are needed to predict the continuum radiation properties of soot and to interpret nonintrusive optical measurements to find soot concentrations and structure. Soot optical properties are a challenging problem, however, due to the complexity of soot structure. For example, while soot generally consists of small spherical primary particles that individually satisfy the Rayleigh scattering approximation, these primary particles combine into branched aggregates that exhibit neither Rayleigh nor Mie scattering behavior (Dalzell et al., 1970; Jullien and Botet, 1987; Köylü and Faeth, 1993). However, a potentially useful approximate theory for soot optical properties (denoted RDG-FA theory in the following) recently has been developed, based on the Rayleigh–Debye–Gans (RDG) scattering approximation while assuming that soot aggregates are mass-fractal objects (Jullien and Botet, 1987; Martin and Hurd, 1987; Dobbins and Megaridis, 1991; Köylü and Faeth, 1994a). In particular, the approximate RDG-FA theory provides a computationally tractable way of treating complex populations of soot aggregates having widely varying numbers of primary particles per aggregate that must be considered for practical applications (Köylü and Faeth, 1993, 1994a). Nevertheless, past theoretical and experimental evaluations of RDG-FA theory have not been definitive due to computational and experimental limitations (Köylü and Faeth, 1993, 1994a, b). Thus, the objective of the present investigation was to complete an additional theoretical evaluation of RDG-FA theory for soot, based on computations using a more exact theory (that unfortunately is not tractable for estimates of the optical properties of practical soot aggregates) for populations of mass-fractal aggregates having prescribed properties.

Although RDG-FA theories have been applied to estimate soot scattering properties and to interpret scattering measurements in order to find soot structure properties (Dobbins et al., 1990; Puri et al., 1993; Sorensen et al., 1992), there are significant uncertainties about some of the approximations of the theory for soot aggregates. In particular use of the RDG approximation requires that both $|m - 1| \ll 1$ and $2x_p|m - 1| \ll 1$ (Bohren and Huffman, 1983; Kerker, 1969; van de Hulst, 1957), which is questionable due to the large refractive indices of soot. Additionally, Berry and Percival (1986) argue that RDG theory should be effective for mass-fractal objects having $D_f < 2$, which is true for soot aggregates, when

$$N \ll x_p^{-D_f} \tag{1}$$

or if this criterion is not satisfied, when

$$x_p \ll \left[\frac{|m^2 - 1|2^{1-D_f}(D_f(D_f + 1))^{D_f/2}}{3(D_f - 1)(2 - D_f)}\right]^{1/(D_f - 3)} \tag{2}$$

The first criterion is rarely satisfied for soot aggregates. The second criterion generally requires $x_p \ll 0.15$, which also is not sat-

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isfied for a very wide range of soot properties, particularly in the visible portion of the spectrum, which usually is used for optical measurements of soot structure. Finally, recent computational studies suggest significant effects of multiple scattering for large soot aggregates, which is ignored when the RDG approximation is used (Berry and Percival, 1986; Chen et al., 1990; Ku and Shim, 1992a, b; Nelson, 1989). Thus, additional evaluation of RDG-FA theory is required before it can be recommended for predictions of soot optical properties.

In spite of these concerns about RDG-FA theory, however, recent experimental evaluations of the approach have been encouraging. These evaluations involved comparing RDG-FA scattering predictions, based on measured soot structure properties from thermophoretic sampling and analysis by transmission electron microscopy, with in situ scattering measurements for the same soot aggregate population. This work involved both large soot aggregates in the fuel-lean (overfire) region of buoyant turbulent diffusion flames, which emphasized the large-angle (power-law) scattering regime (Köylü and Faeth, 1994a), and small soot aggregates in the fuel-rich (underfire) region of laminar diffusion flames, which emphasized the small-angle (Guinier) scattering regime (Köylü and Faeth, 1994b). The predictions and measurements agreed within experimental uncertainties for both the power-law and Guinier regimes. This finding was reasonably definitive within the power-law regime, where the soot aggregate fractal properties that dominate aggregate scattering properties could be found accurately from structure measurements. The evaluation was less definitive in the Guinier regime, however, due to difficulties of accurately measuring both scattering properties at small angles and the higher moments of the aggregate size distribution function (e.g., $\overline{N^2}$) that dominate scattering properties at small angles (Köylü and Faeth, 1994a, b). This limitation is unfortunate because multiple-scattering effects that could compromise the use of RDG-FA theory are most significant in the Guinier regime (Nelson, 1989).

Existing computer simulations of the optical properties of soot also do not provide an adequate basis for evaluating RDG-FA scattering theory. In particular, problems of computational tractability for past computer simulations imply that they either involve fundamentally accurate solutions for small nonfractal aggregates where effects of multiple and self-induced scattering are small, or approximate solutions having uncertain accuracy for the large soot aggregates of interest for practical flames (Köylü and Faeth, 1993). Additionally, existing computations have been limited to relatively small samples of both orientations of given aggregates and aggregate configurations, raising questions about the statistical significance of the results (Köylü and Faeth, 1993).

To summarize, while the approximate RDG-FA approach offers a promising treatment of the optical properties of practical soot aggregates, past experimental and theoretical evaluations have not provided a definitive assessment of the approach over the full range of interest. In particular, although acceptable performance of RDG-FA theory has been established in the power-law regime, comparable assessment in the Guinier regime has not been achieved. Thus, the objective of the present investigation was to undertake a theoretical evaluation of RDG-FA theory, emphasizing the Guinier regime. The evaluation was based on computations using the ICP approach of Iskander et al. (1989), which provides a more exact treatment of aggregate scattering in the Guinier regime than RDG-FA theory, by including effects of multiple and self-induced scattering. Problems of defining the higher moments of the size distribution functions of polydisperse aggregates during experiments were avoided by using numerical simulations to generate aggregates having prescribed sizes and mass-fractal properties.

Theoretical Methods

RDG-FA Scattering Theory. The RDG-FA scattering theory is based on methods described by Freltoft et al. (1986), Jullien and Botet (1987), Lin et al. (1989), Martin and Hurd (1987), and Dobbins and Megaridis (1991). Present considerations, however, will be limited to the extended version due to Köylü and Faeth (1994a), which allows for the presence of the power-law regime when finding total scattering cross sections because this regime is important for large aggregates. The major assumptions of this approach with respect to soot aggregate physical properties are as follows: spherical primary particles have constant diameters, primary particles have uniform refractive indices, primary particles just touch one another, and the aggregates are mass-fractal objects. Justifications of these assumptions for soot aggregates are discussed by Köylü and Faeth (1993, 1994a).

The mass fractal approximation for aggregates of constant-diameter spherical primary particles implies the following relationship between the number of primary particles in an aggregate, N, and the radius of gyration of the aggregate, R_g (Jullien and Botet, 1987):

$$N = k_f(R_g/d_p)^{D_f} \tag{3}$$

The fractal dimension and prefactor in Eq. (3), D_f and k_f, appear to be relatively universal properties of soot aggregates, e.g., recent measurements for a variety of soot in flame environments indicate $D_f = 1.77$ and $k_f = 8.1$, with standard deviations of 2 and 10 percent, respectively (Köylü and Faeth, 1993, 1994a, b). Thus, Eq. (3) provides a critical relationship between N, a quantity that is readily measured, and R_g, an important parameter required by RDG scattering theory.

Nomenclature

C = optical cross section
d_e = equivalent sphere diameter
d_i = diameter of object i
d_p = primary particle diameter
D_f = mass fractal dimension, Eq. (3)
$E(m)$ = refractive index function $= \mathrm{Im}((m^2 - 1)/(m^2 + 2))$
$f(qR_g)$ = aggregate form factor, Eq. (5)
$F(m)$ = refractive index function $= |(m^2 - 1)/(m^2 + 2)|^2$
$g(\lambda, R_g, D_f)$ = aggregate total scattering factor, Eq. (8)
i = $(-1)^{1/2}$
k = wave number $= 2\pi/\lambda$
k_f = fractal prefactor, Eq. (3)
m = refractive index of object $= n + i\kappa$
n = real part of refractive index of object
N = number of primary particles in an aggregate
q = modulus of scattering vector $= (4\pi/\lambda)\sin(\theta/2)$
R_g = radius of gyration of an object
x_i = optical size parameter based on d_i; $x_i = \pi d_i/\lambda$
θ = angle of scattering from forward direction
κ = imaginary part of refractive index of object
λ = wavelength of radiation
ρ_v^a = depolarization ratio

Subscripts

a = absorption
e = optically equivalent object
h = horizontal polarization
i = property of primary particle i
ij = incident (i) and scattered (j) polarization directions
s = total scattering
v = vertical polarization

Superscripts

a = aggregate property
p = primary particle property
$(\bar{\ })$ = mean value over aggregate size distribution

In addition to the RDG approximation, it is also assumed that the primary particles are small enough to satisfy the Rayleigh scattering approximation as individual particles. This is reasonable because primary particle optical size parameters generally are less than 0.4 for soot in the visible and infrared wavelength ranges, which implies that the total scattering and absorption cross sections of individual primary particles are within 1 and 5 percent, respectively, of estimates based on the Rayleigh scattering approximation for refractive indices typical of soot (Köylü and Faeth, 1993). This yields the following expressions for the absorption and scattering cross sections of individual primary particles (Bohren and Huffman, 1983; Kerker, 1969):

$$C_a^p = 4\pi x_p^3 E(m)/k^2,$$

$$C_s^p = 8\pi x_p^6 F(m)/(3k^2), \quad C_{vv}^p = x_p^6 F(m)/k^2 \quad (4)$$

In Eq. (4), and the following equations, subscripts for differential scattering cross sections denote the direction of polarization vectors with respect to the scattering plane defined by the light source, the aggregate and the observer: v and h designate polarization vectors normal and parallel to this plane while the first and second subscripts designate incident and scattered light.

Under the RDG approximation, differential scattering cross sections for aggregates of a given size (after averaging over all orientations of each aggregate within a statistically significant monodisperse aggregate population) satisfy the following formulas (Kerker, 1969):

$$C_{vv}^a(\theta) = C_{hh}^a(\theta)/\cos^2\theta = N^2 C_{vv}^p f(qR_g) \quad (5)$$

The form factor, $f(qR_g)$, is expressed as follows in the Guinier and power-law regimes (Freltoft et al., 1986; Jullien and Botet, 1987; Lin et al., 1989; Martin and Hurd, 1987):

$$f(qR_g) = \exp(-(qR_g)^2/3), \quad \text{Guinier regime} \quad (6)$$

$$f(qR_g) = (qR_g)^{-D_f}, \quad \text{power-law regime} \quad (7)$$

Adopting the proposal of Dobbins and Megaridis (1991), the boundary between the Guinier and power-law regimes is taken to be $(qR_g)^2 = 3D_f/2$, which is chosen to match the value and the derivative of $f(qR_g)$ where the two regimes meet. The total scattering cross section then becomes:

$$C_s^a = N^2 C_s^p g(\lambda, R_g, D_f) \quad (8)$$

where $g(\lambda, R_g, D_f)$ has different forms if the power-law regime is reached for $\theta \le 180$ deg, or not; see Köylü and Faeth (1994a) for these expressions. It also is assumed that absorption is not affected by aggregation, while the extinction cross section is the sum of the absorption and scattering cross sections by definition, i.e.,

$$C_a^a = NC_a^p, \quad C_e^a = C_a^a + C_s^a \quad (9)$$

The corresponding formulation for a polydisperse aggregate population, which is not needed here, can be found from Köylü and Faeth (1994a).

ICP Scattering Theory. Ku and Shim (1992a, b) review theories of aggregate optical properties more accurate than the RDG approximation. Various methods are considered but those of Borghese et al. (1984), Jones (1979a, b), Purcell and Pennypacker (1973), and Iskander et al. (1989) are emphasized. Borghese et al. (1984) developed an exact solution for the optical properties of clusters of spheres but this approach is computationally intensive and its practical accuracy is limited by the truncation of series expansions. The popular Jones (1979a, b) formulation, after correction of errors found by Kumar and Tien (1989) and Ku (1991), only includes multiple-scattering terms up to second order (based on the reciprocal of the distance between primary particles) and it was found to be less reliable than the rest. The Iskander et al. (1989) and Purcell and Pennypacker (1973) formulations both include multiple-scattering terms up to third order in the reciprocal distance between primary particles; however, the latter formulation omits a self-interaction term that can be significant for practical aggregates. Based on these considerations, Ku and Shim (1992b) conclude that the ICP formulation of Iskander et al. (1989) was superior to the rest; therefore, this approach was adopted for the present calculations.

The soot aggregate structure approximations of the ICP and RDG-FA calculations were the same. In addition, each primary particle constituted an ICP computational cell, which implies that individual primary particles satisfy the Rayleigh scattering approximation, i.e., the internal electrical fields of primary particles are assumed to be uniform. This approximation is reasonable because errors are less than 10 percent for cross sections and near-forward scattering when $x_p < 0.8|(m^2 + 5)/(2m^2 + 1)|$, taking individual primary particles to be ICP computational cells (Ku and Shim, 1992b). The refractive index factor in this expression is roughly unity for soot, so that present calculations satisfied the criterion with a significant margin for $x_p \le 0.4$.

The ICP approach involves first determining the internal field of each primary particle, and then finding the optical cross sections resulting from these fields. The formulation for these calculations is lengthy and Iskander et al. (1989) and Ku and Shim (1992b) should be consulted for details. Present results were obtained as averages obtained over various orientations of individual aggregates with respect to the direction of the incident field (in equally spaced spherical coordinate angles) and over populations of fractal aggregates of specified size, N, unless otherwise noted.

Simulation of Aggregates. Mountain and Mulholland (1988) generated aggregates using a simulation of cluster/cluster aggregation based on solution of the Langevin equations. This approach yields fractal aggregates that satisfy the power-law relationship of Eq. (3) with $1.7 < D_f < 1.9$ and k_f circa 5.5, for $N > 10$. These sample aggregates subsequently were used by Chen et al. (1990) for ICP calculations of aggregate scattering properties. However, a larger sample of aggregates was required for the present work, and it was desired to have $1.7 < D_f < 1.8$ and k_f circa 8.0 in order to correspond to recent observations of the fractal properties of soot aggregates (Köylü and Faeth, 1992, 1994a, b). As a result, an alternative aggregate simulation was used during the present investigation. The present numerical simulations of aggregates sought to create populations of aggregates by cluster/cluster aggregation, following Jullien and Botet (1987). The process started with individual and pairs of primary particles, which then were attached to each other randomly, assuming uniform distributions of the point and orientation of attachment but rejecting configurations where primary particles intersected. This procedure was continued in order to form progressively larger aggregates, but with the additional restriction that the aggregates should have $1.7 < D_f < 1.8$ and k_f circa 8 for $N > 8$. It was observed that D_f fell naturally in the range 1.6–1.9 for $N > 48$ during these simulations; therefore, few cluster/cluster combinations were rejected for inappropriate fractal properties when larger aggregates were constructed. Similarly, for D_f in the range 1.7–1.8, the value of k_f fell naturally near k_f = 8.0 for statistically significant populations of aggregates.

Projected images of typical aggregates constructed using the present simulation are illustrated in Fig. 1 for N = 16, 64, and 256, which cover the range of mean aggregate sizes observed in nonpremixed flames (Köylü and Faeth, 1992, 1993, 1994a, b). The appearance of the aggregates varies considerably with the direction of projection, and from aggregate to aggregate within a population of given size. Nevertheless, the simulated aggregates are qualitatively similar to both past experimental observations of soot aggregates (Dalzell et al., 1970; Jullien and Botet, 1987; Köylü and Faeth, 1992, 1994a, b) and other numerical simulations of soot aggregates (Chen et al., 1990; Jullien and Botet, 1987; Mountain and Mulholland, 1988; Nelson, 1989). Combined with their prescribed fractal properties, this suggests

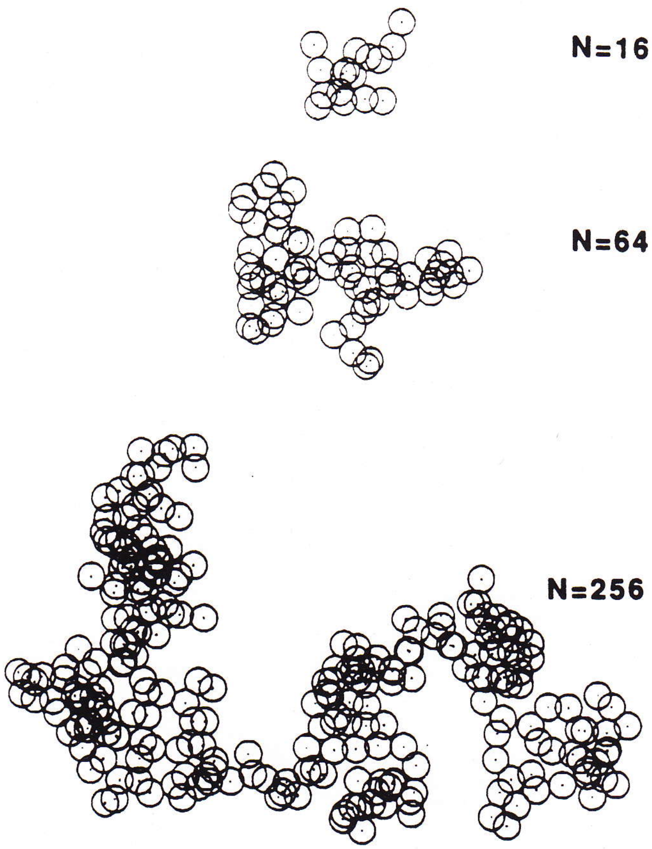

Fig. 1 Projected images of typical aggregates used in the computations for N = 16, 64, and 256

that the present simulated aggregate populations are reasonably representative of the structure of the soot aggregates found in flame environments.

Results and Discussion

Evaluation of ICP Predictions

Spherelike Aggregate. The ICP algorithm was checked by computing the scattering properties of spherelike aggregates, and comparing these results with Mie scattering predictions for an optically equivalent sphere. The configuration of the spherelike aggregate was similar to the arrangement considered by Purcell and Pennypacker (1973) and Ku and Shim (1992b), involving 136 spherical primary particles in a cubical lattice with the aggregate having a spherical outer boundary. For this arrangement, each primary sphere is bounded by a cube having an edge length of d_p, so that the diameter of the equivalent sphere is given by $d_e = (6N/\pi)^{1/3}d_p$, or $d_e = 6.38d_p$ for $N = 136$. In order to apply Mie scattering predictions to this aggregate, the following Maxwell–Garnett relationship was used to find the effective refractive indices for the equivalent sphere, m_e, noting that the volume fraction of the primary particle within its surrounding cubical volume is $\pi/6$ (Ku and Shim, 1992b):

$$(m_e^2 - 1)/(m_e^2 + 2) = (\pi/6)(m^2 - 1)/(m^2 + 2) \quad (10)$$

The present calculations were carried out for various values of x_p with $m = 1.60 + 0.60i$, which is a typical value of the complex refractive index of soot (Charalampopoulos, 1992). This implies $m_e = 1.33 + 0.25i$ from Eq. (10).

Predictions of normalized differential scattering patterns, $k^2C_{vv}^a(\theta)$, as a function of θ and x_p, are illustrated in Fig. 2 for the spherelike aggregate. The results include Mie scattering predictions for an equivalent sphere, as well as ICP predictions for both a single orientation and averaged over 128 orientations of the aggregate. At small angles, within the Guinier regime, effects of orientation averaging are small and the agreement between the Mie and ICP predictions is excellent for the full range of x_p considered ($x_p \le 0.5$). This behavior agrees with the small-angle criterion for ICP cell sizes of Ku and Shim (1992b), discussed earlier, and helps to justify the use of ICP predictions to evaluate RDG-FA theory in the Guinier regime. ICP also yields similar performance for the complete range of scattering angles for $x_p \le 0.25$. At large angles for $x_p = 0.5$, however, effects of orientation averaging become more important, as discussed subsequently, and there are considerable discrepancies between ICP and Mie scattering predictions, which are caused by truncation errors due to excessively large ICP cell sizes. Thus, the use of ICP to estimate the differential scattering properties of aggregates having large x_p is questionable at large angles.

Fractal Aggregates. The next issues to be established are the number of orientations (in spherical coordinate angles, as noted earlier) of individual aggregates, and the number of individual aggregates, that should be averaged in order to obtain statistically significant ICP predictions. The required numbers of realizations increased with increasing N, m, and x_p; therefore, effects of averaging are illustrated in Fig. 3 for $N = 256$, $m = 1.57 + 0.57i$, and $x_p = 0.4$, which represents a conservative condition for present calculations and a typical refractive index of soot (Charalampopoulos, 1992). The results shown include vv scattering patterns for a single realization (a particular aggregate and orientation) as well as average values and standard deviations for 128 orientations of one aggregate and single orientations (each) of a population of 128 aggregates. The results for a single realization exhibit a complex scattering pattern, particularly at larger scat-

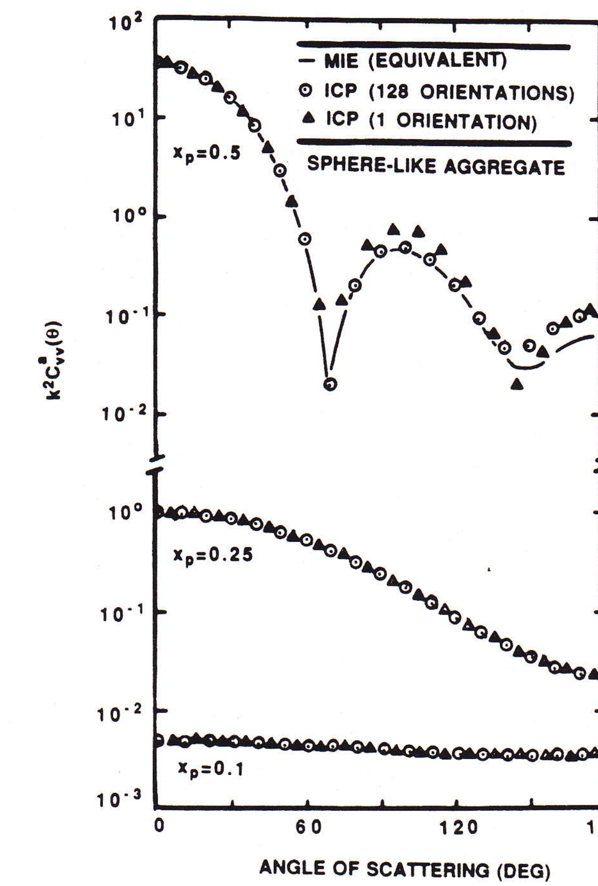

Fig. 2 Normalized vv scattering patterns for a spherelike aggregate, computed using ICP and Mie scattering for an equivalent sphere (N = 136, m = 1.60 + 0.60i, m_e = 1.33 + 0.25i, x_e = 6.38x_p)

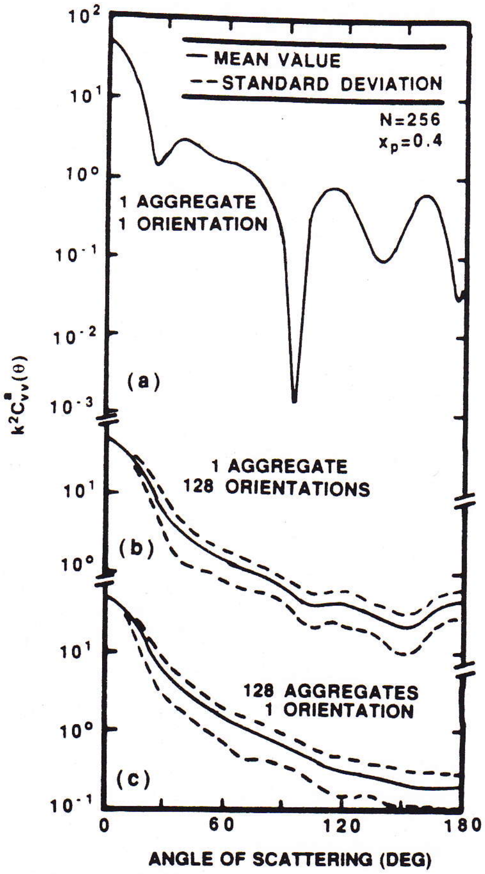

Fig. 3 Normalized vv scattering patterns for fractal aggregates computed using ICP (N = 256, D_f = 1.72, k_f = 8.0, λ = 514.5 nm, m = 1.57 + 0.57i and x_p = 0.4): (a) results for a single aggregate and orientation, (b) results for a single aggregate averaged over 128 orientations, (c) results for a single orientation averaged over 128 aggregates

tering angles, due to interference effects for this particular aggregate array and incident wave propagation direction. Naturally, such patterns are not observed for scattering from practical soot aggregates because aggregate orientations are random and scattering patterns involve averages over very large aggregate populations.

The smoothing of scattering patterns due to averaging is evident from the results considering orientation and aggregate averaging in Fig. 3. Thus, the scattering patterns based on averages decay smoothly, and optical properties are relatively independent of the method of averaging, at small and moderate angles ($\theta <$ 30 deg), which is critical for present evaluation of RDG-FA theory. Oscillations begin to appear with increasing angle, particularly when only one aggregate is considered; nevertheless, the performance of ICP for $x_p = 0.4$ is suspect at these conditions in any event, based on the results discussed in connection with Fig. 2. Similarly, the standard deviations of the cross sections over the sample populations progressively increase with increasing scattering angle. This latter behavior is similar to results found by Mountain and Mulholland (1988) for RDG scattering calculations using numerically simulated populations of aggregates, and reflects the increasing importance of the aggregate arrangement as the scattering angle increases. For example, under the RDG scattering approximation, the form factor is nearly unity in the small-angle (Guinier) scattering regime and scattering mainly depends upon the number of primary particles in the aggregates, see Eq. (6). In contrast, the form factor depends strongly on the aggregate arrangement through the values of R_g and D_f in the large-angle (power-law) scattering regime; see Eq. (7). Thus, the largest angle controls the requirements for sampling to achieve statistically significant ICP predictions of differential scattering patterns.

Based on the previous considerations, 64 aggregates, each sampled at 16 orientations, were used to obtain a numerical uncertainty (95 percent confidence) less than 10 percent for ICP predictions of differential scattering cross sections at 180 deg. Fewer realizations were required to obtain statistically significant absorption and total scattering cross sections. Thus, using as few as four orientations of eight aggregates still yielded numerical uncertainties (95 percent confidence) less than 5 percent for ICP predictions of these two cross sections. Naturally, these estimates do not include effects of deficiencies of ICP predictions at large angles and x_p, noted earlier.

Evaluation of RDG-FA Predictions

Differential Scattering Cross Sections. Figure 4 is an illustration of RDG-FA and ICP predictions of $C^a_{vv}(\theta)/(NC^p_{vv})$ as a function of the radiation momentum, qd_p, for aggregates having $D_f = 1.75$, $k_f = 8.0$, $m = 1.57 + 0.57i$, and x_p up to 0.4 for λ = 514.5 nm. The results for large x_p represent severe conditions: rather large primary particles, refractive indices typical of soot, and a wavelength provided by argon-ion lasers that frequently is used for nonintrusive measurements of soot properties. Results are plotted for aggregates of various size, considering N = 16, 64, and 256—the last representing a reasonable limit for ICP calculations in view of current computer capabilities and the sampling requirements needed to achieve the computational uncertainties stated earlier, and representative of maximum mean aggregate sizes observed in nonpremixed flames (Köylü and Faeth, 1992, 1993, 1994a, b). The predictions are terminated at values of qd_p that correspond to θ = 180 deg.

The RDG-FA results illustrated in Fig. 4 exhibit extended Guinier regimes for the range of aggregate properties considered, reaching $C^a_{vv}(\theta)/(NC^p_{vv}) = N$ at small values of qd_p, as anticipated from Eqs. (5) and (6). It is seen that there are progressively larger regions of power-law behavior, where the slopes of the RDG-FA plots approach $-D_f$ according to Eqs. (5) and (7), as both x_p and N increase. This can be explained by noting that the maximum value of $qd_p = 4x_p$ at θ = 180 deg, which implies a greater range of qd_p as x_p increases, while the boundary between the Guinier and power-law regimes can be represented as $qd_p = (3D_f/2)^{1/2}(k_f/N)^{1/D_f}$, which implies smaller values of qd_p at the onset of the power-law regime as N increases for given aggregate fractal properties. Another feature of the normalization used in Fig. 4 is that the RDG-FA results become universal in the power-law regime for given aggregate fractal properties. This can be seen by eliminating R_g from Eqs. (5) and (7), using Eq. (3), to yield the following relationship for the power-law regime:

$$C^a_{vv}(\theta)/(NC^p_{vv}) = k_f(qd_p)^{-D_f} \tag{11}$$

Thus, RDG-FA predictions only depend on the values of the fractal properties and qd_p within the power-law regime, and reach an intercept of $k_f = 8.0$ at $qd_p = 1$ if this value of qd_p is within the power-law regime.

For the conditions considered in Fig. 4, the comparison between ICP and RDG-FA predictions is excellent throughout the Guinier regime. For example, the maximum discrepancy between the two predictions within the Guinier regime is roughly 15 percent for forward scattering at x_p = 0.4 and N = 256 (see Fig. 4c). Additionally, discrepancies at other conditions within the Guinier regime generally are less than 10 percent, with comparable agreement over the entire available range of scattering angles for $x_p \le 0.2$ (see Figs. 4a, b). Thus, for the range of conditions where ICP predictions are reliable, in view of the results discussed in connection with Fig. 2, RDG-FA predictions seem generally satisfactory based on agreement with ICP predictions.

The comparison between RDG-FA and ICP predictions is less satisfactory in the power-law regime for x_p = 0.4 (see Fig. 4c); however, this behavior does not imply a deficiency of RDG-FA

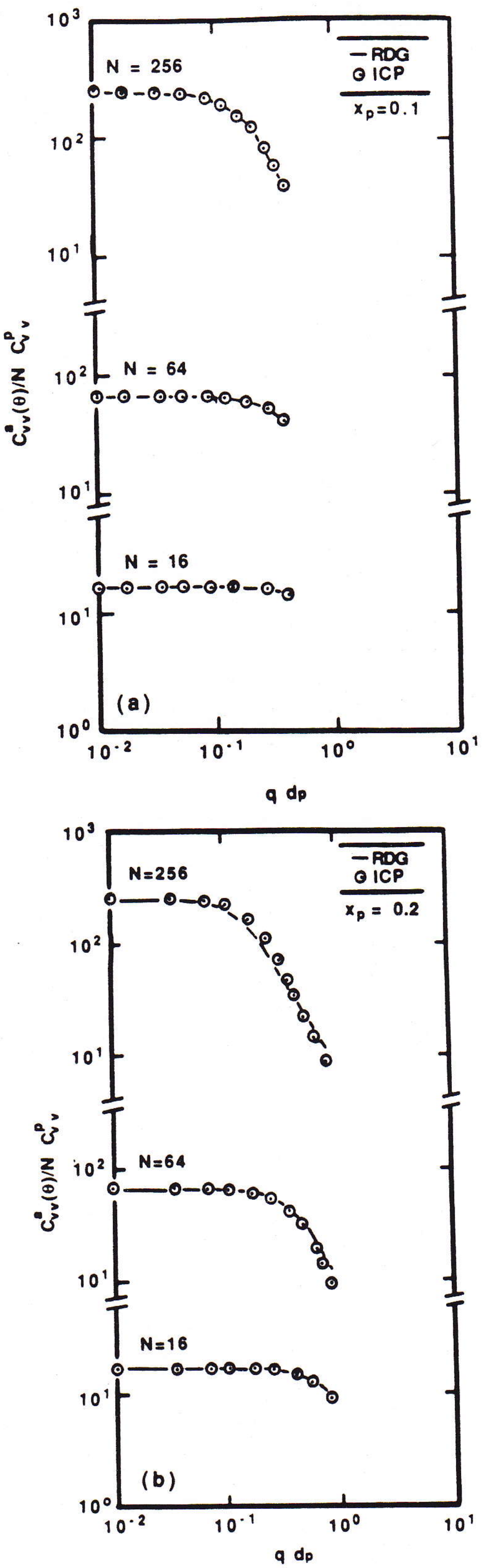

Fig. 4 Normalized vv scattering cross sections as a function of the radiation momentum for fractal aggregates of various size, computed using the ICP and RDG-FA methods (D_f = 1.75, k_f = 8.0, λ = 514.5 nm, m = 1.57 + 0.57i): (a) x_p = 0.1, (b) x_p = 0.2, (c) x_p = 0.4

theory. In particular, past experimental evaluations in the power-law regime are reasonably definitive and indicate satisfactory performance for RDG-FA theory (Köylü and Faeth, 1994a, b), as noted earlier. In contrast, ICP predictions are not very satisfactory at large angles and x_p due to truncation errors, as discussed in connection with Fig. 2. The main problem is that ICP overestimates the rate of decrease of $C^a_{vv}(\theta)$ with increasing qd_p for soot aggregates in the power-law regime. This behavior yields slopes of the ICP plots in Fig. 4(c) that are greater than $-D_f$ from Eq. (11), which contradicts a well-established property of soot aggregates having an extended power-law regime (Köylü and Faeth, 1993, 1994a, b).

Normalized differential scattering patterns found from both the ICP and RDG-FA theories are illustrated in Fig. 5. The results are plotted as $k^2C^a_{vv}(\theta)$ in order to highlight effects of aggregate size on differential scattering patterns. The aggregate properties for these calculations are the same as Fig. 4, except that only the worst-case condition, x_p = 0.4, has been illustrated. For the properties used to construct Fig. 5, scattering is in the power-law regime at 90 deg for the RDG-FA predictions. Then evaluating $C^a_{vv}(\theta)$ at 0 and 90 deg from Eqs. (5)–(7) yields:

$$C^a_{vv}(0\ \mathrm{deg})/C^a_{vv}(90\ \mathrm{deg}) = C^a_{hh}(0\ \mathrm{deg})/C^a_{vv}(90\ \mathrm{deg}) = N(2\sqrt{2}x_p)^{D_f}/k_f \quad (12)$$

Thus, Eq. (12) explains the increase of the normalized vv and hh scattering cross sections in the forward-scattering direction seen in Fig. 5 as N is increased, as well as a corresponding increase when x_p is increased, which is not illustrated in the figure. Similarly, within the power-law regime, Eqs. (5) and (7) yield:

$$C^a_{vv}(\theta)/C^a_{vv}(90\ \mathrm{deg}) = C^a_{hh}(\theta)/(\cos^2\theta C^a_{vv}(90\ \mathrm{deg})) = (\sqrt{2}\sin(\theta/2))^{-D_f} \quad (13)$$

Thus, Eq. (13) implies that variations of vv and hh differential scattering cross sections with scattering angle are controlled by D_f in the power law regime.

The RDG-FA predictions of $C^a_{hh}(\theta)$ in Fig. 5 were corrected for effects of depolarization ratios by analogy to Rayleigh scattering theory (Rudder and Bach, 1968) using the approach of

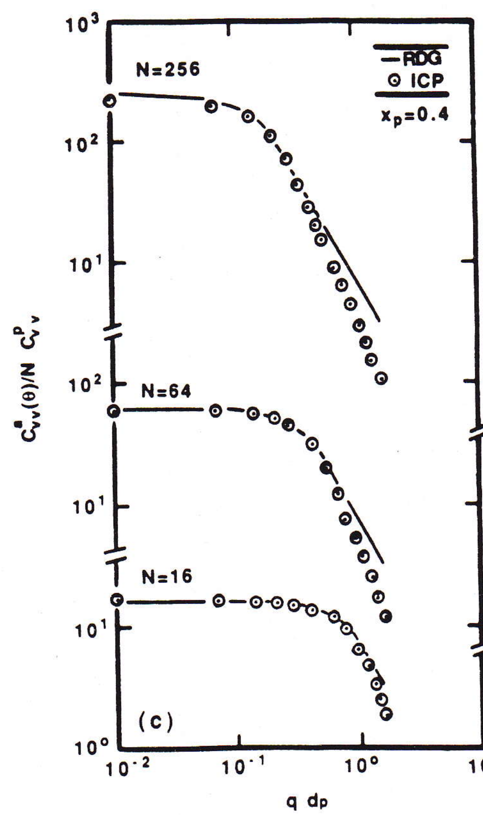

Fig. 4. (Continued)

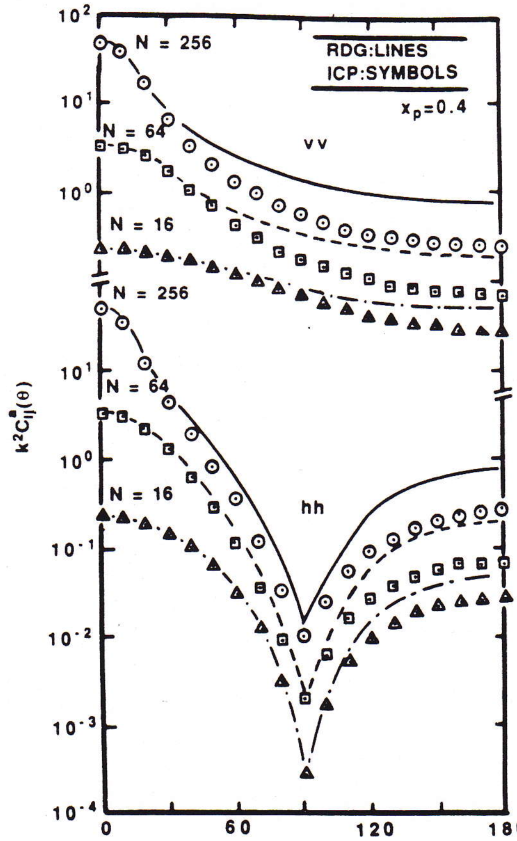

Fig. 5 Normalized scattering patterns for fractal aggregates of various size, computed using the ICP and RDG-FA methods (D_f = 1.75, k_f = 8.0, λ = 514.5 nm, m = 1.57 + 0.57i, and x_p = 0.4)

Köylü and Faeth (1994a). These corrections were based on depolarization ratios, ρ_v^a = 0.0035, 0.0071, 0.0113, for N = 16, 64, and 256, respectively, from the ICP predictions. After correcting $C^a_{hh}(\theta)$ for RDG-FA predictions in this manner, the agreement between RDG-FA and ICP predictions in Fig. 5 is within numerical uncertainties throughout the Guinier regime (roughly θ < 20, 40, and 90 deg for N = 256, 64, and 16, respectively). As discussed earlier, ICP predictions underestimate scattering levels at larger angles due to truncation errors at large x_p, accounting for the discrepancies between the two predictions in this region. However, results similar to Fig. 5 indicated good agreement between the two theories at all angles for $x_p \leq 0.2$, similar to the findings illustrated in Fig. 4.

Effects of refractive indices on the comparison between ICP and RDG-FA predictions also were considered. The variations of m were carried out by taking $n = 1 + \kappa$ and $|m - 1|$ = 0.2, 0.4, and 0.8. This procedure yields progressively increasing refractive indices with the largest values corresponding to typical values for soot in the visible wavelength range (Charalampopoulos, 1992). Other properties of these calculations were similar to the results illustrated in Figs. 4 and 5. The comparison between ICP and RDG-FA predictions of the differential scattering cross sections as refractive indices varied was similar to results discussed in connection with Figs. 4 and 5. In particular, the agreement between the two predictions was within numerical accuracies at small and moderate angles (roughly θ < 30 deg), while ICP predictions tended to underestimate scattering levels at large angles where they are less reliable.

Absorption and Total Scattering. The last phase of the present evaluation of RDG-FA theory was to consider absorption and total scattering cross sections. Figure 6 is an illustration of normalized absorption and total scattering cross sections from the ICP and RDG-FA predictions plotted as a function of N for various values of x_p. The other parameters of these calculations were similar to Figs. 4 and 5; that is, D_f = 1.75, k_f = 8.0, λ = 514.5 nm and m = 1.57 + 0.57i. As noted earlier, reduced sampling requirements to obtain statistically significant values of these cross sections allowed maximum values of N up to 512 to be considered for the ICP predictions.

The ICP predictions of normalized absorption cross sections, $C^a_a/(NC^p_a)$, remain within 10 percent of unity for the conditions illustrated in Fig. 6, even including questionable values for x_p = 0.4 at large N. This is in good agreement with RDG-FA predictions where this ratio is unity from Eq. (9), i.e., the absorption of primary particles in aggregates is identical to the absorption of individual primary particles. In contrast, both predictions of $C^a_s/(NC^p_s)$ increase with increasing N, with the rate of increase gradually decreasing as N increases. This latter effect is observed because fractal aggregate scattering becomes saturated at large N for $D_f < 2$; in contrast, for $D_f > 2$, $C^a_s/(NC^p_s)$ continues to increase without bound as N increases (Berry and Percival, 1986; Dobbins and Megaridis, 1991). In particular, RDG-FA theory yields the following expression for $C^a_s/(NC^p_s)$ at large N (Köylü and Faeth, 1994a):

$$C^a_s/(NC^p_s) = k_f(4x_p)^{-D_f}(3/(2 - D_f) - 12/((6 - D_f)(4 - D_f))) \quad (14)$$

Thus, for given fractal properties, $C^a_s/(NC^p_s)$ is independent of N for large N, with this plateau value tending to decrease as x_p increases. Present predictions in Fig. 6 do not extend to large enough values of N to reach the plateau condition; however, both predictions are in good agreement over the range of conditions that are illustrated for $x_p \leq 0.2$. In contrast, problems with ICP predictions at large angles for x_p = 0.4 (see Fig. 5) cause greater discrepancies between the two theories for large N. Similar calculations over the range of refractive indices considered yielded the same general behavior.

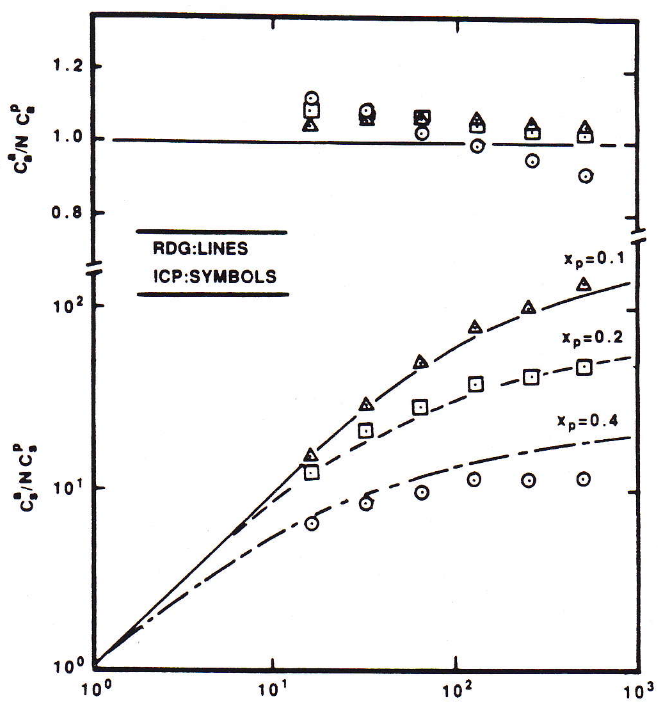

Fig. 6 Normalized absorption and total scattering cross sections as a function of aggregate size for fractal aggregates having various x_p, computed using the ICP and RDG-FA methods (D_f = 1.75, k_f = 8.0, λ = 514.5 nm, m = 1.57 + 0.57i)

Conclusions

An evaluation of an approximate RDG-FA theory for the optical properties of soot aggregates, emphasizing the Guinier regime, was completed based on predictions using the more precise ICP theoretical approach due to Iskander et al. (1989). Conditions considered during the evaluation were selected to approximate the properties of soot aggregates in the visible and near-infrared portions of the spectrum, as follows: x_p up to 0.4, N up to 512, $D_f = 1.75$, $k_f = 8.0$ and refractive indices typical of soot. The main conclusions of the study are as follows:

1 RDG-FA and ICP predictions of absorption cross sections, and of differential scattering cross sections within the Guinier regime, generally agreed within numerical uncertainties (ca. 10 percent) over the range of the evaluation. Combined with reasonable performance of RDG-FA predictions during recent experimental evaluations (Köylü and Faeth, 1994a, b), these results suggest that RDG-FA theory should replace other approximate theories of soot optical properties, such as Rayleigh scattering and Mie scattering for an equivalent sphere, which have not been very effective during recent experimental and computational evaluations (Köylü and Faeth, 1993, 1994a, b).

2 Present calculations using the ICP approach were not satisfactory at large scattering angles for aggregates having $x_p > 0.25$, based on evaluations using Mie scattering predictions for a spherelike aggregate and well-established RDG-FA predictions in the power-law regime for soot aggregates. This difficulty is due to the truncation errors caused by excessively large ICP cell sizes and might be avoided by dividing each primary particle in an aggregate into several ICP cells. This approach, and other methods of treating large aggregates having large x_p, merit further study.

3 Effects of aggregate size mainly dominate scattering properties in the Guinier regime, while the power-law regime exhibits nearly universal behavior independent of aggregate size. Thus, forward-scattering properties, rather than dissymmetry ratios, provide the most reliable indication of aggregate size for large aggregates where scattering properties are dominated by the power-law regime.

4 Variations of refractive indices over the range typical of current uncertainties about these properties yielded far greater variations of optical cross sections than uncertainties concerning RDG-FA predictions for the aggregate properties considered during the present investigation. Thus, current uncertainties about soot refractive indices are the main limitation for accurate estimates of the continuum radiation properties of soot, and the application of nonintrusive optical diagnostics to measure soot concentrations and structure.

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