A COMPUTATIONAL STUDY OF THE ABSORPTION AND SCATTERING PROPERTIES OF SOOT

by

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Introduction

Soot is present within most nonpremixed hydrocarbon-fueled flames, which affects their structure, radiation and pollutant emission properties. Thus, the absorption and scattering properties of soot are of interest in order to estimate continuum radiation from soot and to interpret nonintrusive optical measurements of soot concentrations and structure. Soot optical properties are challenging, however, due to the complexity of soot structure. For example, while soot consists of small primary particles that individually satisfy the small particle (Rayleigh) scattering approximation, these particles form branched aggregates that exhibit neither Rayleigh nor Mie scattering behavior [1-3]. Nevertheless, a potentially useful approximate theory of soot optical properties (denoted RDG-FA theory in the following) has been developed recently, based on the Rayleigh-Debye-Gans (RDG) scattering approximation while assuming that soot aggregates are mass-fractal objects [2,4-7]. Past theoretical and experimental evaluations of RDG-FA theory, however, have not been definitive due to computational and experimental limitations [3]. Thus, the objective of the present investigation was to complete an additional theoretical evaluation of RDG-FA theory for soot, based on computations using more exact theory for populations of mass-fractal aggregates having prescribed properties.

Although RDG-FA theories have been applied to estimate soot scattering properties [8-10], there are significant uncertainties about the approximations of the theory for soot aggregates. In particular, use of the RDG approximation requires that both $|m-1|$ and $2x_p|m-1| << 1$, where m is the complex refractive index for soot and x_p is the optical size parameter, $\pi d_p/\lambda$, for the given primary particles diameter, d_p, and wavelength, λ. Both these requirements are problematical due to the large refractive indices of soot. Berry and Percival [11] have found more specific requirements for mass-fractal aggregates but this still requires $x_p << 0.15$ which is not satisfied for a very wide range of soot properties in the visible portion of the spectrum. Finally, recent computational studies suggest significant effects of multiple scattering for large soot aggregates which is ignored using the RDG approximation [11-14]. Thus, additional evaluation of RDG-FA theory is needed before it can be used with any confidence to estimate soot optical properties.

Prompted by these questions concerning the RDG scattering approximation, RDG-FA theory has been evaluated experimentally, based on direct measurements of soot structure and scattering properties [6,7]. The evaluation involved both large soot aggregates emitted from turbulent diffusion flames, which emphasized the large-angle (power-law) scattering regime [6], and small soot aggregates in the fuel-rich portion of laminar diffusion flames, which emphasized the small-angle (Guinier) scattering regime [7]. Predictions and measurements agreed within experimental uncertainties, however, experimental uncertainties of finding critical higher moments of the aggregate size distribution function for these polydisperse aggregate populations were rather large, which compromised evaluation of the theory to some extent.

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Existing computer simulations of the optical properties of soot also do not provide an adequate basis for evaluating RDG-FA scattering theory. In particular, they either involve fundamentally accurate solutions for small non-fractal aggregates where effects of multiple and self-induced scattering are small, or approximate solutions having uncertain accuracy for the large soot aggregates of practical interest [3]. Furthermore, existing computations have been limited to relatively small samples of orientations for given aggregates, and aggregate configurations, introducing uncertainties about the statistical significance of the results [3].

In order to help fill this gap in the literature, the objective of the present investigation was to complete a new theoretical evaluation of RDG-FA theory, based on computations using the ICP approach of Iskander et al. [15], which treats both 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 in Refs. [4-6] and references cited therein. Present considerations, however, were limited to the extended approach of Köylü and. Faeth [6], which allows for the presence of the power-law regime when finding total scattering cross sections because this regime is important for large soot aggregates. The major assumptions of the theory with respect to soot aggregate physical properties are as follows: spherical primary particles having constant diameters, primary particles have uniform refractive indices, primary particles just touch one another, and the aggregates are mass-fractal objects. Justifications for these assumptions are discussed elsewhere [3,6].

In addition to the RDG approximation, it also is 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 total scattering and absorption cross sections are within 1 and 5 percent, respectively, of estimates based on the Rayleigh scattering approximation for refractive indices typical of soot [3]. Finally, the proposal of Dobbins and Megaridis [5] was adopted to fix the crossover condition between the Guinier and power-law regimes, based on matching the value and the derivative of the form factor that appears in the expression for differential scattering cross sections, as noted earlier. The complete formulation, for both monodisperse and polydisperse aggregate populations, can be found in Ref. [6].

ICP Scattering Theory. Ku and Shim [13] review theories of aggregate optical properties more accurate than the RDG approximation, including Borghese et al. [16], Jones [17], Purcell and Pennypacker [18] and Iskander et al. [15]. Ku and Shim [13] concluded that the ICP formulation of Iskander et al. [15] was superior to the rest; therefore, it was adopted for present calculations.

The soot aggregate structure approximations of the ICP and RDG-FA calculations were the same. In addition, each primary particle comprised an ICP computational cell which implies that primary particles individually satisfy the Rayleigh scattering approximation similar to the RDG-FA approach. This approximation was reasonable because errors are less than 10% for cross sections and near-forward scattering for refractive indices typical of soot and $x_p < 0.8$ based on a criterion given in Ref. [13], while present calculations were limited to $x_p \leq 0.4$. The formulation of ICP is extensive, see Refs. [13] and [15] for the details.

Simulation of Aggregates. Mountain and Mulholland [19] have simulated soot aggregates by cluster/cluster aggregation while solving Langevin equations. This yields fractal aggregates with $1.7 < D_f < 1.9$ and k_f ca. 5.5 for $N > 10$. However, larger samples of aggregates were needed for present work while it was desired to have $1.7 < D_f < 1.8$ and k_f ca. 8 in order to correspond with recent observations of soot aggregate fractal properties [3,5,6]. Thus, a new aggregate simulation was carried out by cluster/cluster aggregation of equal-sized aggregates following a suggestion of Jullien and Botet [2]. The process began with pairs of primary particles which then were attached to each other randomly, assuming uniform distributions of the point and orientation of attachment while excluding configurations where primary particles intersected. This procedure was continued in order to create progressively larger aggregates, but with the additional restriction that the aggregates should have $1.7 < D_f < 1.8$ and k_f ca. 8 for $N > 8$. It was observed that D_f fell naturally in the range 1.65-1.85 for $N > 32$ during these simulations; therefore, very few cluster/cluster combinations were rejected for inappropriate fractal properties when larger aggregates were constructed.

Results and Discussion

Evaluation of ICP Predictions. The present calculations using the ICP algorithm were checked by computing the scattering properties for sphere-like aggregates and comparing these results with Mie scattering predictions for an optically-equivalent sphere. The configuration involved 136 spherical primary particles in a cubical lattice with the aggregate having a spherical outer boundary, similar to Refs. [13] and [18]. The diameter of the equivalent sphere was taken to be $d_e = (6N/\pi)^{1/3}d_p$. The following Maxwell-Garnett relationship was used to find the effective refractive indices, m_e, of the optically equivalent sphere, noting that the volume fraction of a primary particle within its surrounding cubical volume is $\pi/6$ [13]:

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

Present calculations were carried out for various values of x_p with $m = 1.60 + 0.6i$, which is a typical value for soot, and with 128 orientations of the spherical aggregate. Absorption and total scattering cross sections from ICP were in excellent agreement with Mie scattering predictions for $x_p \leq 1$. Differential scattering cross sections yielded similar results for $x_p \leq 0.25$ but differences between ICP and Mie scattering predictions were significant for scattering angles, θ, greater than 140° and $x_p = 0.5$. This behavior, however, was largely due to interference effects for a finite array of scattering centers within ICP calculations that can not be treated using the Maxwell-Garnett approach. Thus, the discrepancies were not evidence of a failure of ICP, and could be removed by increasing the number of primary particles in the sphere-like aggregate.

The next evaluation of ICP involved finding the number of orientations of individual aggregates, and the numbers of individual aggregates that were needed to obtain statistically-significant results. These requirements became more stringent as N, m and x_p were increased; therefore, the evaluation focused on $N = 256$, $m = 1.57+0.57i$ and $x_p = 0.4$. Separate series of calculations were carried out for one aggregate and 256 orientations and a single orientation (each) for a population of 256 aggregates. Differential scattering cross sections for single orientations of a given aggregate were complex due to interference effects for a particular primary particle array, except at small angles where the scattering cross section mainly depends on the number of primary particles in an aggregate rather than their arrangement. Thus, the variance of differential scattering cross sections over a particular population progressively increased, becoming comparable to the mean value itself as θ approach 180°. The scattering patterns were somewhat more sensitive to variations of aggregates than of orientation angles; therefore, 16 orientations of 64 aggregates were used during final calculations to achieve a determination of the mean differential scattering cross section at 180° (95% confidence) within 10%. Sampling requirements for absorption and total scattering cross sections were less stringent, with 4 orientations of 16 aggregates sufficient to achieve a numerical uncertainty (95% confidence) of 10%.

Evaluation of RDG-FA Predictions. The evaluation of RDG-FA predictions involved absorption, differential and total scattering cross sections for N up to 516, x_p up to 0.4, $D_f = 1.75$, $k_f = 8.0$ and refractive indices typical of soot. Over this range, ICP and RDG-FA predictions generally agreed within 10%, which is comparable to the fundamental and sampling limitations of ICP itself. However, discrepancies between the two theories progressively increased as N, x_p and m were increased so that use of RDG-FA theory outside the present range of evaluation may incur larger errors. Combined with the reasonable performance of RDG-FA predictions during recent experimental evaluations [6,7], these results suggest that RDG-FA theory should replace other approximate theories, such as Rayleigh and particularly Mie scattering for an equivalent sphere, which have not been effective during recent computational and experimental evaluations [3,6,7].

The predictions also showed that 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 for N > ca. 100. Thus, forward-scattering properties, rather than dissymmetry ratios, provide the most reliable indication of aggregate size for conditions where aggregates can be large. Finally, variations of refractive indices over ranges typical of current uncertainties about soot refractive indices yielded greater variations of optical cross sections than differences between ICP and RDG-FA predictions over the present range of aggregate properties. Thus, current uncertainties about soot refractive indices are the main limitation for accurate estimates of soot radiation properties, and the use of optical diagnostics to measure soot concentrations and structure.

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