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On the link between particle size and deviations from the Beer–Lambert–Bouguer law for direct transmission

Michael L. Larsen [a,*], Aaron S. Clark [b]

[a] Department of Physics and Astronomy, College of Charleston, Charleston, SC 29424, USA
[b] Department of Mathematics, Southern Connecticut State University, New Haven, CT 06515, USA

A R T I C L E I N F O

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A B S T R A C T

Ballistic photon models of radiative transfer in discrete absorbing random media have demonstrated deviations from the Beer–Lambert–Bouguer law of exponential attenuation. A number of theoretical constructs to quantify the deviation from the Beer–Lambert–Bouguer law have appeared in the literature, several of which rely principally on a statistical measure related to the statistics of the absorber spatial positions alone. Here, we utilize a simple computational model to explore the interplay between the geometric size of the absorbing obstacles and the statistics governing the placement of the absorbers in the volume. We find that a description of the volume that depends on particle size and the spatial statistics of absorbers is not sufficient to fully characterize deviations from the Beer–Lambert–Bouguer law. Implications for future further theoretical and computational explorations of the problem are explored.

1. Introduction

Transmission of radiation through discrete correlated random media is a phenomenon of importance in atmospheric science (e.g. for transmission of electromagnetic radiation through a particle laden atmosphere [1]), and nuclear physics (e.g. for use in work associated with pebble-bed reactors [2]). For perfectly random (uncorrelated) discrete, perfectly absorbing obstacles dispersed in an otherwise optically transparent volume, the Beer–Lambert–Bouguer law (hereafter the BLB law) of exponential attenuation is well established. When the absorbing obstacles have some statistical departure from perfect spatial randomness (through "clustering" or the creation of "inhomogeneities"), the BLB law no longer applies in its traditional form [3,4].

A substantial number of studies exist that explore the detailed nature of how to interpret/modify/correct the BLB law for scenarios under which the perfect spatial randomness of the absorbers no longer applies. These studies have examined the problem from both a theoretical [1,3,5–7] and computational [4,8–10] perspective. Not all work on this topic has approached the question from the same basic theoretical framework; consequently there are some excellent studies recently published that have done an admirable job in relating the results from different studies under a single theoretical context [2,11]. In particular, the reader is advised to see the insightful investigation found in [12].

The computational study done by Shaw et al. [4] clearly demonstrated that, for perfectly absorbing discrete absorbers, there can be substantial deviations from the expected attenuation according to the BLB law. In particular, deviations from the BLB law can persist despite the absorber spatial structure that deviates only modestly from perfect spatial randomness – even when these spatial correlations are localized to scales far smaller than the characteristic lengths associated with transmission. (For an exploration of this seemingly paradoxical behavior, see the discussion that runs through Kostinski [5], Borovoi [6], and Kostinski

* Corresponding author. Tel.: +1 843 953 5593; fax: +1 843 953 4824.
E-mail address: LarsenML@cofc.edu (M.L. Larsen).

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[1]). The conclusion that is drawn in Matsuda et al. [10] from these studies is that the spatial scale associated with the correlations among obstacles is of central concern in determining whether or not the BLB is salvageable. This work then went on to investigate (using Stokes number as a proxy that ultimately governs correlation scale through particle dynamics) the interplay between the correlation scale and the size of the domain of interest.

A theoretical expression that could quantify deviations from the BLB law as a function of the spatial statistical properties of the absorbers would be of great use. Shaw et al. [4] conjectured that the effective optical depth of a medium could be expressed through a relationship directly related to the integral of the pair-correlation function (one measure of the deviation from perfect spatial randomness). The work in [1] develops a general theoretical framework that shows promise for relating statistical measures to departures from the BLB law, and the Matsuda et al. [10] study suggests that such a link may also be possible. Here, we use a computer simulation very similar to that used in [4] to explore the interplay between absorber cross-section, photon mean-free path, and length-scales associated with the geometric distribution of absorbers. (A future study including the effect of scattering to more closely mimic the study of Matsuda et al. [10] is forthcoming). Ultimately we find that, even in the very simplistic case of perfectly absorbing monodispersed spheres, the deviations from the BLB law are not easily characterized in terms of simple statistical measures alone. There seem to be at least *three* fundamental scales associated with the problem.

2. Brief theoretical overview

The basic framework used to describe attenuation in a random medium typically starts with the Beer–Lambert–Bouguer law of exponential attenuation:

$$I(z) = I_{\circ} \exp(-c\sigma z) \tag{1}$$

here $I(z)$ is a measure of the intensity of the beam of radiation some distance z from the edge of the absorber-laden volume, $I_{\circ}$ is the intensity of the beam prior to entering the volume that encloses the absorbers, c is the (number) concentration of absorbers per unit volume, σ is the effective cross-section of each absorber, and z is the distance traveled in the propagation direction through the absorbing medium. Often, this relationship is written as $I(z) = I_{\circ}\exp(-\tau)$ with $\tau = c\sigma z$ the so-called "optical depth" of the system.

In [4,10], this basic relationship is treated stochastically. In particular, for a discrete number of "ballistic photons" entering a volume, the fraction transmitted through at least a distance z into the volume can be written as

$$\frac{N_{tr}}{N_{inc}} = \exp(-c\sigma z) = \exp(-z/\lambda), \tag{2}$$

where N_{tr} is the number of transmitted "photons", N_{inc} is the number of "photons" incident on the volume, and $\lambda = (c\sigma)^{-1}$ corresponds to the mean free path for "photons" in the system. (Note that "photons" here are not meant to be conceived literally, but are just used as a ballistic model for EM wave propagation that are sufficient for the purpose of the simulation).

As carefully outlined elsewhere [1], the argument that ultimately leads to the BLB law relies on the statistical independence of the geometric placement of absorbers; when the actual absorbers are not perfectly spatially randomly distributed, attenuation both faster *and* slower than exponential is possible, depending on the nature of the correlations among the absorbing particles.

One proposed relationship [4] suggests that perhaps

$$\lambda^* \propto \lambda\left(1 + \alpha \int_0^x \eta(x')\,\mathrm{d}x'\right), \tag{3}$$

with $\eta(x')$ being the pair-correlation function evaluated at spatial scale x', α an undetermined constant that may have some functional dependence on other system parameters, and λ^* being the "effective" optical depth. Below, we simulate several different systems to try to develop further insight into the nature of how the pair-correlation function may be related to the effective optical depth of the system.

3. Simulation

The simulation we conducted was simple and constructed similar to that done in [4] to allow for easy comparison of results.

$\mathcal{N}$ particles were distributed in a rectangular parallelepiped of dimensions $1 \times 1 \times 4$. Each of the particles was a monodispersed sphere with absorbing radius $(\sigma/\pi)^{1/2}$. (Note that we are not using the traditional Mie scattering value of $r = (\sigma/2\pi)^{1/2}$; the value of $(\sigma/\pi)^{1/2}$ was chosen so that one can interpret the absorbing radius directly as a shadow. Since we do not tie our results to a physical size-scale, however, one may just re-scale σ if the chosen convention is difficult to interpret.) For each generated volume, 1×10^6 "ballistic photons" were injected, entering at $z=0$ and traveling in the $+z$ direction. These photons entered the distribution with uniformly random and independent x and y coordinates in the range $[(\sigma/\pi)^{1/2}, 1-(\sigma/\pi)^{1/2}]$. Wherever a "photon" intersected a particle, that photon was "absorbed" and removed from the propagating beam at the point of intersection. After noting the absorption points, the ratio $N_{tr}(z)/N_{inc}$ for different propagation distances z along the volume were tabulated.

To keep things as simple as possible, the product $c\sigma$ was constrained to unity for all simulations described below. Therefore, since the propagation distance was 4, all simulations would have had $\tau = 4$ for transmission through the entire volume if the classical BLB law holds.

To explore the influence of spatial structure, the $\mathcal{N}$ particles were distributed in several different ways.

1. Poisson distribution: First, in an effort to verify the code operation, a homogeneous Poisson distribution was simulated (i.e. each absorbing particle was distributed randomly inside the volume, independently of each other). For this system, the BLB law should faithfully hold, with some possible fluctuations due to sampling noise.
2. Clustered distribution: Following Shaw et al. [4], a correlated (or clustered) distribution of particles was

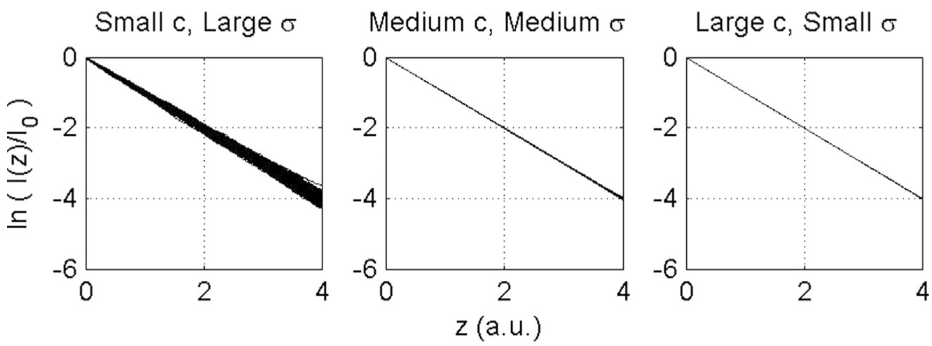

Fig. 1. A plot of the results from distributing the absorbers perfectly randomly in the $1\times1\times4$ rectangular parallelepiped. As expected, we see close adherence to the BLB law of exponential attenuation. (For all figures, a slope of -1 would indicate adherence to the BLB law.) The left panel shows all 500 runs for particles of size $\sigma=1/1000$ and $c=1000$. The middle panel shows all 10 runs for particles of size $\sigma=1/(5\times10^4)$ and $c=5\times10^4$. Finally, the right panel shows both runs for particles of size $\sigma=1/(5\times10^5)$ and $c=5\times10^5$. Except for some shot noise in the left panel, perfect agreement with the BLB law (as expected) is observed.

generated by simulating a random walk. An initial placement for the firsts particle was chosen at random from within the entire volume. After the first particle was placed, subsequent particles were placed via a random walk; the step-size for the random walk was chosen from an exponential probability density function (with a mean of 0.05), and the step was taken in a random direction. A particle was then placed at each location in the random walk. (This is similar, though not quite identical, to how the correlated distribution was generated in [4].) Periodic boundary conditions were used to ensure that all particles remained within the rectangular parallelepiped.

3. Superposition of fractal clumps: Following Soneira and Peebles [13], a clustered distribution of particles was generated by superposing fractal clumps. As described by Martinez and Saar [14], this system has a well characterized statistical structure with known fractal dimension and two-point correlation function. (This model was utilized as a convenient model that retains some scale-invariant properties, but still has low enough lacunarity to allow for substantial total absorption.) In this system, each fractal clump is built iteratively. Inside a randomly placed sphere of initial radius R, a set of ζ new spheres of radius R/k with $k>1$ are placed at random. Within each of these new spheres, ζnew spheres are placed, each of radius R/k^2. The process is repeated L times and the last generation of ζ^L centers are the positions of the particles. In the simulations used here, the adjustable parameters were set with $R=0.2$, $k=1.5$, $\zeta=2$, and $L=6$. (Where necessary, periodic boundary conditions were used to ensure all particles remain in the domain of interest.)

The Poisson and clustered distributions were both simulated 512 times. First, 500 different trials of each were run, setting $c=1000$ and $\sigma=1/1000$. An additional ten trials of each distribution were then run, with $c=5\times10^4$ and $\sigma=(5\times10^4)^{-1}$. Finally, 2 trials of each distribution were run with $c=5\times10^5$ and $\sigma=(5\times10^5)^{-1}$. Since each system was in a $1\times1\times4$ parallelepiped, this meant that $\mathcal{N}$ was 4×10^3, 2×10^5 and 2×10^6, respectively. As mentioned previously, all simulations should have optical depth equal to 4 if the classical BLB holds. The use of $c=1000$ for the low-$\mathcal{N}$ simulations was used to mimic [4], where 50 such realizations were averaged to obtain a statistically robust behavior.

The fractal clumps were simulated a total of 200 times. In the first 100 realizations, 125 separate clusters were placed, leading to a total of $\zeta^L\times125=4000$ particles (corresponding to $c=1000$), with each particle having $\sigma=\frac{1}{1000}$. In the second 100 realizations, 400 separate clusters were used, leading to a total of 12 800 particles (corresponding to $c=3200$), with each particle having $\sigma=\frac{1}{3200}$.

In addition to simulating a Poisson distribution (which is known to follow the BLB law), the simulation code was also verified with deterministic absorber alignments that have known attenuation relationships. (For example, one test was in setting a single giant particle in the middle of the volume. Another used a geometry known to give faster-than-exponential attenuation, described in [1].) All known cases were faithfully replicated with the simulation code. Additionally, we verified that particle overlaps were negligible. (In the very rare cases overlapping particles did occur, each of the two particles were allowed to act independently.)

(Although this study is designed to be purely computational in nature, we can tie our most dense simulation (with 2×10^6 particles) to some tangible spatial scales as an analog of a physical system that is approximately $1\ \mathrm{m}\times1\ \mathrm{m}\times4\ \mathrm{m}$ with cloud drops nominally $10\ \mu\mathrm{m}$ in diameter. The number density of droplets in this system is exceedingly low (nominally 0.5 drops/cc), but we are able to obtain the substantial amount of attenuation observed through this dilute medium because each of the drops is perfectly absorbing over its cross section).

4. Results

Results for the Poisson simulations are shown in Fig. 1. As expected, close adherence to the BLB law is observed.

Results for the clustered simulations (where absorber positions are placed at the vertices of a random walk with an exponentially distributed step size) are shown in Figs. 2 and 3. Fig. 2 shows the mean trace for each simulation type. We clearly see that even though the distributions have exactly the same underlying spatial statistics and the

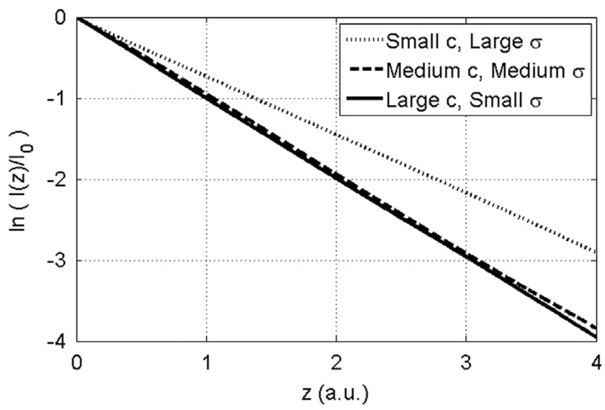

Fig. 2. A plot demonstrating the attenuation as a function of depth for the distributions of absorbers distributed via an "exponential random walk". We see clear deviation from the BLB expectation for the case where $c=1000$ and $\sigma=1/1000$. Deviations from the BLB are much less pronounced for larger c and smaller σ combinations.

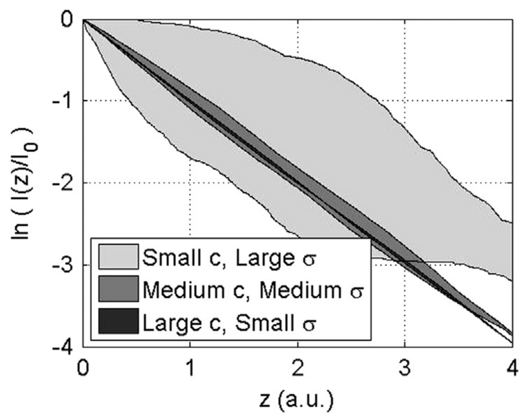

Fig. 3. This plot shows the entire range of values seen by all simulations for the distributions of absorbers distributed via an "exponential random walk". The shaded region indicates the boundaries between the largest and smallest attenuations seen among all simulations with the same distribution parameters. It is clear that at $z=4$ there is a clear difference between the attenuation in the large and medium c cases and the small c case. Since each of these three simulation types has exactly the same distribution parameters, one must conclude that the deviations from the BLB law are contingent on absorber size in addition to the statistics governing the distribution of absorbers.

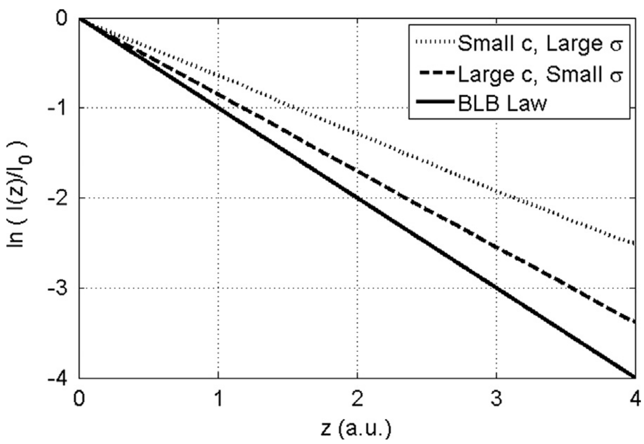

Fig. 4. This plot, similar in structure to Fig. 2, shows the attenuation as a function of depth for the distributions of absorbers distributed in the superposition of fractal clumps distributions as described in the text. Again a clear deviation from the BLB expectation is seen. Additionally, despite the same underlying spatial statistics, a difference is also seen between the large c/small σ and small c/large σ cases.

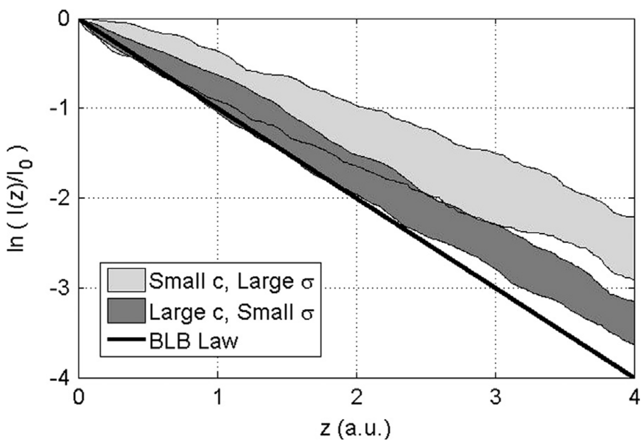

Fig. 5. This plot, similar in structure to Fig. 3, shows the entire range of values seen by all simulations run using the superposition of fractal clumps structure. Again, the shaded region indicates the boundaries between the largest and smallest attenuations seen among all simulations with the same distribution parameters. It is again clear that particle size must be necessary to fully characterize/describe the deviations from the classical BLB behavior.

same classical BLB attenuation expectation, a different amount of absorption occurs in the three cases. This result was surprising, and resulted in some concern that the observed result was due to improper/unphysical averaging between realizations. To ensure this is not the case, Fig. 3 shows the range of the different extinction curves observed in the three different simulation types. Clearly, the phenomenon we are seeing is not due to averaging, but a more complicated interplay between the particle size and the attenuation curve.

Results for the fractal clump simulations are shown in Figs. 4 and 5. Fig. 4 shows the mean traces for the two different simulations; once again, note that despite the same underlying spatial statistics for both simulations (e.g. same pair-correlation function, same fractal dimension, etc.), a clear difference in deviation from the classical BLB law is observed. This difference is further explored in Fig. 5 where, once again, a clear difference between the observed attenuations for systems with few (but large) particles and many (but small) particles is evident.

To further explore this relationship, an additional fractal clump simulation was run. In this simulation, three separate realizations of the fractal distribution used above were utilized. In this system, 12 800 particles were generated in the $1\times1\times4$ volume. Like previously, the parameters were set with $R=0.2$, $k=1.5$, $\zeta=2$, and $L=6$ and 400 clusters were used per realization. For particle size, however, four different values of σ which corresponded to BLB optical depths of $2, 4, 6$ and 8 were used. Thus, 12 volumes were created – the same volume that was used to generate a classical optical depth of 2 was also used to generate classical optical depths of 4, 6, and 8 – just by altering the absorber size. The effective optical depth through the entire volume for each of these simulations was then compared to the BLB expectation. Results are summarized in Fig. 6.

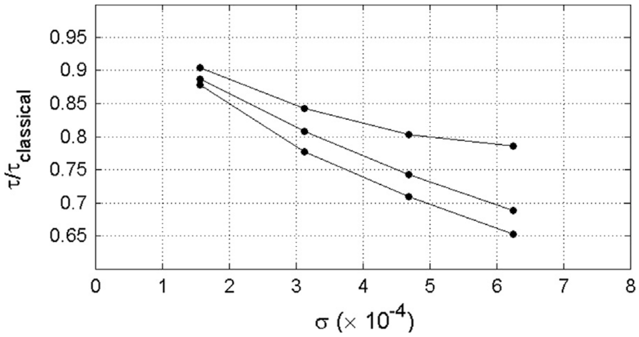

Fig. 6. This plot shows the ratio of the actual optical depth to the predicted optical depth as a function of absorber size for the superposition of fractal clumps distributions as described in the text. As the particle size gets larger, it is clear that the deviation between the actual optical depth and the BLB prediction increases. However, the rate of change for the top trace and the bottom two traces appear to be different, suggesting that perhaps a simple relationship between the deviation from the classical expectation, statistical properties of the underlying distribution, and the size of the particles may not be very simple.

5. Discussion

Previous studies (e.g. [4,5]) argued that the actual effective optical depth through a random correlated medium should depend on both the classically expected optical depth from the BLB law as well as some statistical measure of the correlations among absorbers – perhaps characterized by the pair-correlation function. The study of Matsuda et al. [10] went on further to note that there seemed to be a dependence of this deviation from the BLB law on the domain size and Stokes number (which, in that study, was a proxy to describe absorber dynamics and, hence, the statistical measure of the correlations among absorbers). Neither of these studies noted that a third length-scale is integral to the problem – the size of the absorbers themselves. (*Note*: although the Stokes number does include particle size, the DNS conducted in [10] kept the particle size constant and merely varied the Stokes number by changing the intensity of the turbulence and, hence, the spatial scale associated with the correlation of obstacles. Using the Stokes number as a dimensionless measure of the properties of a system, though normally a feature, here ends up being unhelpful since two separate – but independently relevant – spatial scales are tied together in this single number.)

We have clearly found that systems that have the same physical domain *and* the same underlying statistical structure among absorbers can have markedly *different* deviations from the BLB law. In short, knowledge of the pair-correlation function (or some other measure of the distribution of absorbers) is not enough to characterize deviations from the BLB law.

The speculative relationship given in [4], summarized in Eq. (3), may be salvageable. In the original paper, it was noted that α could depend on other system parameters; if one of those parameters is absorber size, it may be possible to write the relationship in the way proposed. However, Fig. 6 suggests that this may not be easily done. From only three simulations, it is hard to make any general conclusions – but the fact that the three curves have different first derivatives, despite identical statistical structure, implies that the relationship might be more complex than initially hoped. (It is possible that the differing behavior of the three curves is governed by sampling variability. Exploring this in more detail, however, is beyond the scope of this work.)

The central observation is that the simulations suggest that absorber size does matter in a non-trivial way. In fact, this result does make sense. The argument given in [5,1] was essentially an argument from geometry. In the case of pure absorption, we can view the absorbing particles as casting a “shadow” on the area behind the particle from the propagating photon's point of view. If a second absorber is in the “shadow” of another absorber, it contributes less to the beam attenuation since some of its absorbing surface area is “wasted”. The BLB law depends on the amount of “wasted” or “shadowed” area of a random absorber being exactly equal to the amount of shadowed area in the entire plane.

However, as outlined in [5,1], if absorbers are distributed in a clumpy (or correlated) fashion, then there is a larger-than-random chance that absorbers are near each other. If absorbers are near each other, there is also a larger-than-random chance they align in the direction of propagation and thus one of the two aligned absorbers ends up partially in the shadow of the other absorber. This “extra shadowing” from the nearest neighbors leads to slower-than-exponential attenuation and, therefore, the larger transmissions seen in the clustered distributions in the previous sections.

The key observation that needs to be made, however, is that “greater than random shadowing” – although generated by characterizing the statistical spatial structure of the absorbers – is influenced also by the size of the absorbers. For our case of monodispersed spherical absorbing regions, we note that the larger the particle, the larger the solid angle shadowed behind the particle. Therefore the deviations from the BLB law expectation become more pronounced as the absorber size increases (which is consistent with all of the figures in this paper).

6. Conclusions and further work

In various fields, an easy to parameterize relationship that connects the statistical properties of discrete absorbers in a random medium to the deviation from the classical BLB law is desired. Several recent studies suggested that perhaps this relationship could be determined by using the pair-correlation function (or fractal dimension, or the Stokes number, or some other proxy) along with the size of the volume and the classical optical depth. Our simple numerical simulation reveals that there is likely at least one more spatial scale of relevance to the problem – absorber size. It is possible that this is why some investigators have argued that deviations from the classical BLB law should be negligible (e.g. [6,7]) whereas others have seen substantial deviations from exponential behavior in computational studies (e.g. [4,10]). Further investigations examining whether or not the deviation from the BLB law can be tied to the three spatial scales of correlation distance, absorbing domain, and particle size should be conducted to determine whether or not a simple parametrization can be found. Additionally, a similar study to this one that investigates any influence of obstacle size on bulk extinction properties in a primarily scattering medium should be conducted.

Acknowledgments

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