

Ambiguity of Polystyrene Aerosol Beads Properties Found with Mie Spectra Analysis

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Abstract Broadband Mie scattering is used to determine the parameters of polystyrene aerosol beads in air, such as size and wavelength dependence of refractive index. This method consists in the selection of such parameters of the scattering object, which reproduce observed spectrum properties. That is why it is very sensitive and hence very precise. We found that there is an ambiguity of polystyrene aerosol beads properties, determined with this method. Different combinations of polystyrene particle size and its refractive index can give the same position of Mie resonances. This ambiguity leads to an increase in the error in determining the size and refractive index of the particle. The refined errors are calculated and the way of their reduction is indicated.

Keywords Nanomaterials; Mie theory; Polystyrene beads; Size; Refractive index

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Introduction

Aerosol is defined as a suspension of small solid or liquid particles in a gaseous medium. These particles in the Earth's atmosphere have a significant influence on many areas of human existence, ranging from astronomical observations to the Earth's energy balance and climate change^[1-2]. The main influence of these particles is through the absorption and scattering of the incident electromagnetic radiation. Particles contained in the air scatter light in different ways, depending on their size and chemical composition. That is why the study of such parameters of atmospheric aerosols, as the size and spectral dependence of their refractive index, is a rather important and highly relevant task.

A prominent role among atmospheric aerosols is played by polystyrene beads. Polystyrene is widely used as food containers and packaging and is generated from both industrial and municipal polymers sources. It has becoming a major environmental concern due to large quantities disposed to landfills and its non-biodegradable in nature^[3]. Polystyrene

beads, due to their features, such as the spherical shape, are often used by researchers as a test aerosol. Polystyrene beads are commonly used for characterization and calibration of instruments, which remotely sensing the atmosphere aerosol's particles^[4]. These challenges require a careful characterization of test aerosol particles.

1 Polystyrene beads parameters

There are a lot of methods to study the polystyrene beads particles. One of them is the measurements of scattering spectra of small spherical particles and their interpretation with the help of Mie theory^[5-7]. The same approach was used to polystyrene beads study^[8-9]. This way allows determining the radius and wavelength dependence of refractive index. Details for application of Mie theory are given in^[10] and references therein.

Most precise measurements of polystyrene beads spectra were carried out by Jones and colleagues^[9]. They measured the scattering spectra of polystyrene beads samples in the range 480~700 nm with a resolution of 0.028 nm. They used

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a fitting procedure to select the values of radius and refractive indices, which provide best coincidence between measurements and theoretical calculations of Mie resonances positions. It was found, that polystyrene beads have size $r=1\ 227\ \text{nm}$ and the dispersion of refractive index is described by equation:

$$n = 1.571\ 8 + \frac{8\ 412}{\lambda^2} + \frac{(2.35 \times 10^8)}{\lambda^4} + 0.000\ 3i \quad (1)$$

where n is complex refractive index and λ is the wavelength of incident light. Eqn. (1) is valid for λ expressed in nanometers and in spectral range $480 \sim 700\ \text{nm}$. From fitting

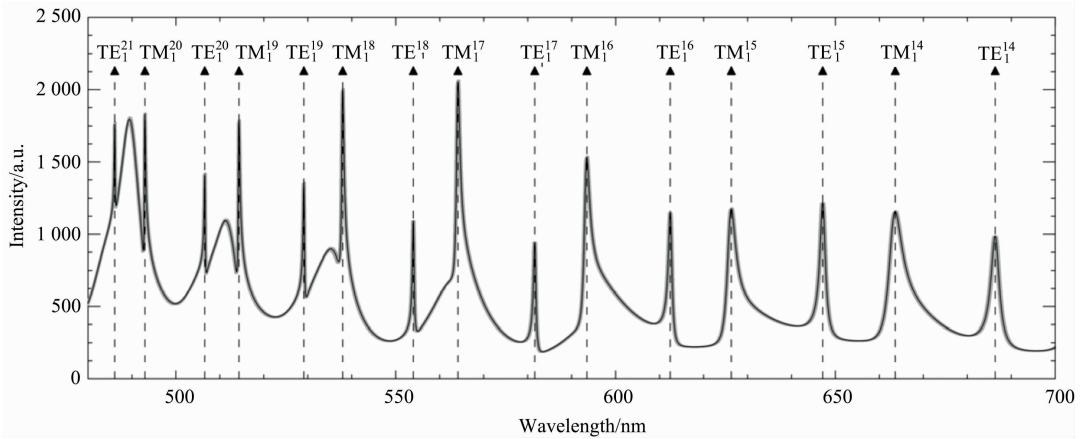


Fig. 1 Mie spectra, calculated for spherical polystyrene bead with size $r=1\ 227\ \text{nm}$ and refractive index, described by Eqn. (1) Solid line corresponds to exact calculation and gray shadow shows the area of uncertainty obtained by both radius variation $\pm 0.4\ \text{nm}$ and refractive index variation $\pm 0.000\ 5$. Dotted vertical lines show the positions of Mie resonances

2 Mie spectra calculations

The fundamental theory of electromagnetic scattering by a sphere developed by Gustav Mie has been used in great number of publications (see, e. g., [11-20] and references therein). There are numerous codes available to calculate Mie scattering. We developed our own code, which allow making enough precise calculations of intensity and polarization of spherical particles, and using it to studying the polarization behavior with size and refractive index changing.

The interesting question arises—are the particle parameters determined by fitting the Mie resonances uniquely determined?

To answer on this question, we change the size of polystyrene bead Δr and looking for the corresponding change of refractive index Δn , which makes minimal the difference between Mie resonances positions in changed and initial cases. Following^[9], to determine the best fit for particle size, we minimize the average difference per resonance χ_r ,

$$\chi_r = \frac{1}{N} \sum_i \sqrt{(\lambda_i^0 - \lambda_i^{\text{var}})^2} \quad (2)$$

where N is the resonances quantity (in this case $N=15$), λ_i^0

process the single polystyrene bead radius was determined with an uncertainty of $\pm 0.4\ \text{nm}$ and refractive index dispersion with an uncertainty of $\pm 0.000\ 5$.

Figure 1 shows the Mie spectra, calculated for spherical polystyrene bead with size $r=1\ 227\ \text{nm}$ and refractive index, described by Eqn. (1). Solid line corresponds to exact calculation and gray shadow shows the area of uncertainty obtained by both radius variation $\pm 0.4\ \text{nm}$ and refractive index variation $\pm 0.000\ 5$. Dotted vertical lines show the positions of Mie resonances, which was used to fitting process.

is the position of i -th resonance of initial spectra (where $r=1\ 227\ \text{nm}$ and n is described by Eqn. (1)), and λ_i^{var} is the position of i -th resonance of varied spectra.

Figure 2 shows the part of polystyrene bead spectra in the range $480 \sim 500\ \text{nm}$, containing two resonances. Solid curve and gray shadow is the same, as on Fig. 1. Dotted curve corresponds to variation of radius value $\Delta r=1\ \text{nm}$ (so the radius become $r=1\ 228\ \text{nm}$) and corresponding change of refractive index $\Delta n=-0.001\ 47$. Note, that although this

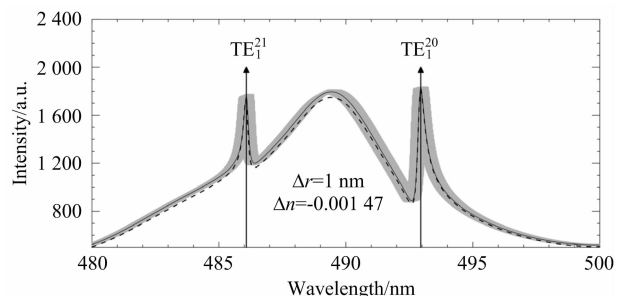


Fig. 2 Polystyrene bead spectra in the range $480 \sim 500\ \text{nm}$. Solid curve corresponds to particle radius $r=1\ 227\ \text{nm}$ and refractive index $n(\lambda)$, described by Eqn. (1)

Gray shadow corresponds to area, obtained by radius variation $\pm 0.4\ \text{nm}$ and refractive index variation $\pm 0.000\ 5$. Dotted curve corresponds to the radius $r=1\ 228\ \text{nm}$ and refractive index $n(\lambda)$

-0.001 47

figure show only narrow spectral part, value $\Delta n = -0.001 47$ found for all 15 Mie resonances in spectral range 480 ~ 700 nm. Negative value of Δn means that increasing of radius can be compensated by decreasing of refractive index.

You can see, that despite the fact that solid and dotted curves quite different and in some spectral ranges is out of the gray area of uncertainty, difference between resonances position is rather small. Wherein average difference per resonance $\chi_r = 0.019$ nm in this case, that is smaller than not only typical values of χ_r , determined in [9], but also smaller than spectral resolution of measured spectra (0.028 nm).

After that, we began to change the Δr and calculate the corresponding values of Δn and χ_r . This dependence is shown on Figure 3 and due to small changes of values is approximately linear. Values of Δr plotted on the axis X, χ_r - left axis Y and Δn - right axis Y. Horizontal dotted line corresponds to spectral resolution of measurements 0.028 nm. Because it is impossible to determine resonances position precisely that spectral resolution, this line defines the uncertainty of polystyrene bead refractive index $\pm 0.002 2$. Vertical dotted line passes through the intersection of solid curve and horizontal dotted line, and defines the uncertainty of polystyrene bead size ± 1.48 nm.

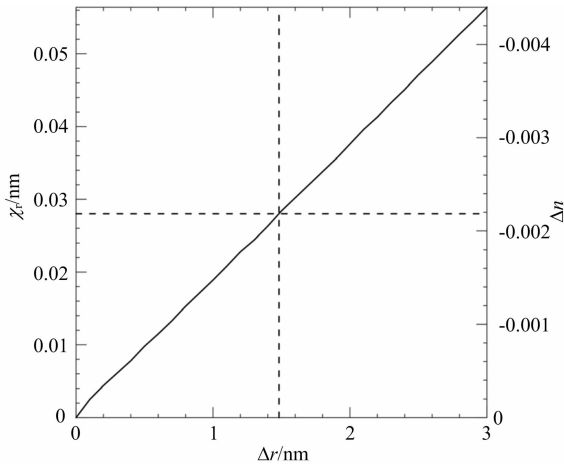


Fig. 3 Average difference of resonances positions χ_r and variation of refractive index Δn as a functions of radius variation Δr

Horizontal dotted line corresponds to spectral resolution of measurements 0.028 nm and defined real uncertainty of polystyrene bead refractive index $\pm 0.002 2$. Vertical dotted line passes through the intersection of solid curve and horizontal dotted line, and defines the uncertainty of polystyrene bead size ± 1.48 nm

So, the uncertainties turn out to be much larger, than thinking before. Is there a way to reduce them? To investigate this, we calculated not only average difference per reso-

nance, but also the position differences for each resonance separately. It turned out that different resonances have different sensitivity to changes of Δr and Δn . We chose four resonances for which the change in position with changes in the radius and the refractive index seems to be maximal.

Figure 4 shows the average difference per resonance of most sensitive Mie resonances - TM_1^{14} , TM_1^{15} , TM_1^{16} and TM_1^{21} (solid lines). Line with points corresponds to calculations of average difference per resonance χ_r only for this four resonances ($N=4$ in Eqn. 2). In this case, the uncertainty of polystyrene bead size is only ± 0.85 nm (left vertical dotted line). Consequently, using only these sensitive resonances can improve the precision of polystyrene beads size determination.

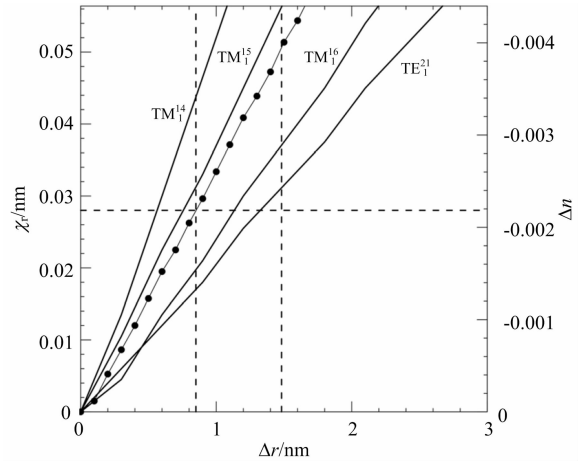


Fig. 4 Average difference of resonances positions χ_r and variation of refractive index Δn as a functions of radius variation Δr for most sensitive Mie resonances- TM_1^{14} , TM_1^{15} , TM_1^{16} and TE_1^{21} (solid lines)

Line with points corresponds to calculations of average difference per resonance χ_r only for the sefour resonances. Horizontal dotted line and gight vertical dotted line are the same as on figure 3. Left vertical dotted line defines the uncertainty of polystyrene bead size ± 0.85 nm

3 Conclusion

We investigated the determination of the size and spectral dependence of the refractive index of polystyrene beads by interpreting their spectrum. It has been established that different combinations of the refractive index can lead to almost identical positions of Mie resonances differing less than the spectral sensitivity of the instrument. This ambiguity leads to an increase in the uncertainties in determining the size and refractive index compared to the previously defined ones. It has been established that Mie resonances have different sensitivity to variations of size and refractive index. We suggest to use the four most sensitive resonances TM_1^{14} , TM_1^{15} , TM_1^{16} and TM_1^{21} to reduce uncertainty in determining the size of polysty-

rene beads.

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