Optical bistability of an aqueous aerosol particle detected through light scattering: theory and experiment


We present a catastrophe-based graphic model for understanding the optical bistability (OB) of an aqueous aerosol particle detected in light scattering. The model is shown to be in good agreement with hidden resonance experiments and indicates that OB in such particles can occur at an incident power level of \( <50 \times 10^{-9} \) W. This threshold is controlled principally by the quality factor of morphological resonances and thermophysical properties of the particle. A catastrophe scheme for the bistability of solid particles is anticipated.

1. Introduction

Recently Arnold et al.\(^1\) have shown that an aerosol particle can act as an optically bistable element by observing hysteresis in the wavelength spectrum of the scattered light. The mechanism for this effect was argued to be associated with the photothermal evaporation which accompanies visible absorption by structure resonances. Although a heuristic model was provided in Ref. 1 for explaining the observed effects based on an isolated morphological resonance of the particle, recent experimental work has revealed so-called hidden resonances which are not explained by such a model.\(^2\) We attempt in this paper to give a more complete description of the optical bistability of such a particle using a catastrophe-based graphic method in which all partial wave resonances are taken into account.

II. Physical Model

The absorption by an aerosol particle several wavelengths in diameter is properly described through Mie theory.\(^3\)\(^4\) Thus the absorption efficiency is given by

\[
Q_{a,\text{Mie}} = \frac{2}{(ka)^2} \sum_{n=1}^{\infty} (2n+1)[\text{Re}(a_n + b_n) - |a_n|^2 - |b_n|^2],
\]

where \( k \) is the angular wavenumber of the exciting light, \( a \) is the radius of the particle, \( a_n \) and \( b_n \) are the scattering coefficients associated with transverse magnetic (TM) and transverse electric (TE) partial waves of mode number \( n \) and are given by

\[
\begin{align*}
  a_n &= \frac{m \psi_n(mx)|\psi_n(x)'| - \psi_n(x)|\psi_n(mx)'|}{m \psi_n(mx)|\xi_n(x)'| - \xi_n(x)|\psi_n(mx)'|}, \\
  b_n &= \frac{\psi_n(mx)|\psi_n(x)'| - m \psi_n(x)|\psi_n(mx)'|}{\psi_n(mx)|\xi_n(x)'| - m \xi_n(x)|\psi_n(mx)'|},
\end{align*}
\]

where \( X = ka \), \( \xi_n \) and \( \psi_n \) are the Riccati-Bessel functions, and \( m \) is the complex index of refraction.\(^4\) Absorption at high intensities can lead to effects such as bleaching for which Eq. (1) will not apply since the dielectric function will have a spatial dependence. However, at lower intensities thermal effects will be of primary importance, and here the physical changes may be described to a good approximation using Eq. (1).

For a simple insulating liquid material, increased temperature will cause both thermal expansion and evaporation. The former leads to both a change in size and refractive index, while the latter will principally lead to a change in size. Since the latter mechanism is consistent with the relatively low laser intensity and relatively long switching time associated with the bistability of an aqueous particle,\(^1\) we deal almost exclusively with this mechanism in what follows.

We suppose that a particle is isolated and stabilized in size by suspending it in an appropriate concentration of the vapor of its solvent. This can be achieved for an aqueous particle by the addition of an ionic solute. In the presence of absorbing radiation the heat deposited causes the particle to evaporate until the vapor pressure returns to its original value due to an increase in the ionic solute concentration (i.e., following Raoult's law).\(^5\) This leads to a change in the optical size \( X = ka \) of the particle. A change in \( X \) will alter the absorption through the multiplicative factor \( 2/X^2 \) in Eq. (1) and also through changes in \( a_n \) and \( b_n \). Since
the coefficients $a_n$ and $b_n$ are functions of $m, X$ and the product of refractive index times $X, mX$, our assumption of constant refractive index means that both coefficients will be functions of $X$ alone; $Q_a, \text{Mie}$ is simply a function of $X$.

Arnold et al.\textsuperscript{5} have shown that when one turns on absorbing radiation of intensity $I$, a particle of radius $a_0$ and generalized absorption efficiency $Q_a$ will change its size to a new equilibrium size:

$$a = a_0 - \alpha Q_a I,$$

where $\alpha$ is a constant described in Ref. 5. Equation (3) can be written alternately as

$$X(X_0 I) = X_0 - \alpha' Q_a(X) I$$

by multiplying by the angular wavenumber $k$. Equation (4) has no current analytic solution. However, it may be solved numerically with $Q_a = Q_{a, \text{Mie}}$, and these calculations provide insight into the sort of physical behavior to be expected.

Figure 1 shows the basic scheme for solving Eq. (4). It is based on the rewriting of Eq. (4) in the form

$$Q_a(x) = {X_0 - X \over \alpha'I},$$

where $\alpha' = k\alpha$. The slope and horizontal intercept of the straight line (i.e., $Q_a$ vs $X$) described by Eq. (4) are sensitive to both wavelength and intensity. In particular, $X_0$ is only controlled by the wavelength of the incident radiation, while the slope of the line depends on wavelength and intensity. For most experiments the wavelength interval is across a narrow resonant mode, and consequently the influence of the wavelength on the slope of the straight line may be neglected.

The method of solution is to find intercepts between the straight line described by Eq. (5) and the relatively complicated function described by Eq. (1); find the values of $X$ for which $Q_a(x)$ as expressed by Eq. (5) is equal to $Q_{a, \text{Mie}}(x)$. Figure 1 illustrates this procedure for a particle having a refractive index of $1.38 + 10^{-5} i$ in the optical size range between 25.93 and 25.53. As one can see there is a pronounced feature at an optical size of 25.71. This is the first-order resonance of the thirtieth transverse magnetic partial wave coefficient $a_{30,1}$. (Perhaps a more physical characterization is to denote the resonance as TM$_{30,1}$.) It is seen to be nearly Lorentzian. Now suppose that the particle corresponding to Fig. 1 is 4.828 $\mu$m in diameter. For this size, and at low intensity, absorption corresponding to the $a_{30,1}$ resonance will occur at a wavelength of 590 nm. As the intensity is increased, however, the effects of Eq. (3) must be included in the analysis (i.e., Mie theory alone no longer applies). This is best illustrated in Fig. 2(a) by the straight line which terminates on the horizontal axis at $X_{1,0}$ corre-
sponding to a wavelength \( \lambda_1 = 587.5 \text{ nm} \). For the chosen intensity there are three possible solutions for the absorption. To understand which of these states can be equilibrium states of the system it is necessary to plot all solutions for absorption vs our experimental variable wavelength \( \lambda \). Figure 2(b) shows the result of doing this. To find the way in which the elastic scattering is affected, the optical sizes arrived at through the graphic scheme at a given wavelength are mapped onto the scattering response vs \( X \), Fig. 2(c). For the current calculation, the scattering response \( S_{so} \) [Fig. 2(c)] represents the average intensity through an f/6 aperture centered at 90° vs optical size for an incident plane wave polarized in the plane of scattering. The scattering vs wavelength is found by mapping these solutions onto a vertical line of constant wavelength [Fig. 2(d)]. All possible solutions for the chosen wavelength region are shown. The equilibrium states obtained in a wavelength scan are determined from Fig. 2(b) using conventions associated with catastrophe theory.

There are two extreme conventions associated with catastrophe theory. A system which can occupy several different states can be thought of as having potential barriers between the states. For example, a bistable system is associated with an effective double well potential. In such a nonlinear system the effect of changing external conditions (i.e., wavelength in our case) is to alter this potential. At \( g \) in Fig. 2(b) our system resides in state \( A \) separated by a barrier from the alternate state \( B \). As the wavelength is increased state \( B \) begins to move downward relative to \( A \), causing the barrier to become smaller. Finally, when \( h \) is reached the barrier has completely vanished and the system falls abruptly into state \( B \). The two extreme conventions are distinguished by the level of noise compared to the barrier height. In the so-called delay convention the noise level is considered to be much smaller than the barrier height, whereas for the so-called Maxwell convention the opposite is true. Consequently, based on the delay convention the system must be taken all the way to \( h \) before it will switch. However, for the Maxwell convention the system switches when state \( B \) goes just below \( A \) (i.e., the system switches to the state of lowest effective potential). Thus in accordance with the Maxwell convention the system would switch prematurely (i.e., between \( g \) and \( h \)).

For most nonlinear optical and mechanical systems, the delay convention has been found to be applicable; however, in systems which demonstrate phase transitions which are driven by intense noise such as a thermal bath the Maxwell convention is of somewhat greater importance. Because of its precedence for most optical phenomena, the scenario which follows is based on the delay convention.

The delay convention as it relates to Fig. 2 may be simply stated. The system will switch at points for which the response function [Fig. 2(b) in our case] has an infinite slope. As one can see from Fig. 2(b) this occurs at two positions. Thus as one performs a continuous wavelength scan upward from 585 nm (at constant intensity) our system will switch at 588.0 nm (point \( h \)) to a higher absorption. With further increase in wavelength toward \( p \) the system follows the upper trace. If the system is then scanned in reverse, it will retrace the upper curve to point \( j \). A further decrease in wavelength causes the system to continue moving along the upper path until point \( r \) is reached. At point \( r \) the infinite slope in Fig. 2(b) causes the system to switch back to state \( A \). Thus our simple model provides an alluring picture for the optical bistability of a cloud droplet. Further support comes from a comparison between the level of intensity used in affecting the optical bistability in Ref. 1 and the level of intensity needed to simulate the response curve calculated in Fig. 2(b). For the thermodynamic properties of the particles considered in Ref. 1 and for a particle 4.8 \( \mu \text{m} \) in diameter, \( \alpha' \) from Ref. 5 is 1.6 cm\(^2\)/W. Thus the slope of the straight line in Fig. 2(a) is produced for an intensity of 29.7 W/cm\(^2\), consistent with the levels of intensity used in Ref. 1. Experimental data are now presented for testing the model in more detail.

### III. Experiments

A single aqueous particle is levitated in an electrodynamic quadrupole trap just as in our IR absorption experiments. The particle is stabilized in size by ensuring that the concentration of the water vapor in the trap is equivalent to that at the particle surface. The particle is composed of 20% \((\text{NH}_4)_2\text{SO}_4\) (by mass) and crystal violet dye at a concentration of \(10^{-5} \text{ M}\). Figure 3(a) shows a wavelength spectrum of elastic scattering from the particle. The beam from a tunable dye laser irradiates the particle with a polarization in the plane of scattering and an intensity of 30 W/cm\(^2\). The intensity is measured at 590 nm; however, it was found to fall gradually to either side of this wavelength by as much as 30%. The scan is initially begun at 580 nm and proceeds toward a longer wavelength. One observes both narrow and broad features in the scan. In particular, small and narrow features are observed at \( a_1, a_2, a_3, \) and \( a_4 \), while relatively large and broad features appear at \( b_1, b_2, \) and \( b_3 \). The forward scan is carried out over a 1-min period (scan rate = 0.3 nm/s), as is the reverse scan. The reverse scan is considerably different from the forward scan. At position \( a_4 \) the light scattering becomes extremely noisy over more than 1 nm and then proceeds calmly until \( \gamma_2 \) is reached, at which point the light scattering maintains a relatively constant level until \( \beta_1 \) is reached. At \( \beta_2 \) the light scattering increases and then falls sharply. \( \beta_2 \) is not an equilibrium state; once the light scattering begins to increase, an irreversible and abrupt decrease always follows. This \( \alpha_4-\gamma_2-\beta_2 \) pattern is repeated again at \( \alpha_3-\gamma_1-\beta_1 \).

It should be noted that the spectra in Fig. 3(a) were not altered by lowering the scan rate below 0.3 nm/s; however, beyond 0.7 nm/s there was a substantial change in the spectra, and beyond 10 nm/s forward and reverse scans began to look similar. These observations are consistent with the slow response associated with the low intensity used in affecting the optical bistability.
resonances radiate perpendicular to the present scattering plane are transverse magnetic. Transverse electric polarization of the incident beam in the scattering resonances which should appear for 90° scattering with the assumptions on the basis of Mie theory. The principal resonances which should not be seen for our experimental conditions and, therefore, indirectly affects the scattering. To appreciate this effect more fully it is necessary to obtain solutions to Eq. (4) using the spectrum for $Q_{a Mie}$ which we have plotted in Fig. 3(c). Once this solution is arrived at using the method outlined in Fig. 2, the solutions for $X$ at a given wavelength may be used to determine the equilibrium scattering response.

A computer program was designed for solving Eq. (4) by the scheme outlined in Fig. 2. For a particle 8.03 μm in radius and composed of 20% (NH₄)₂SO₄ (by mass), $\alpha'$ is calculated from Ref. 5 to be 0.94 cm²/W. Using this value, the experimental value for the intensity $I$ of 30 W/cm², and taking $Q_{a Mie}(x)$ from Fig. 3(c), a solution is calculated for the absorption vs wavelength [Fig. 4(a)]. Bistability well beyond threshold is clearly indicated by noting that the narrow resonances in Fig. 3(c) are significantly tilted from the vertical, thereby allowing for multiple solutions at a given wavelength and bistable behavior similar to that indicated in Fig. 2(b). For some of the features the intensity is so far beyond threshold that the amount by which the resonances are tilted provides a good measure for the hysteretic width. In addition in a number of cases the predicted width is in good accord with experiment. For example, the TE₉₆.₃ hidden resonance is tilted by 1.8 nm, and the measured hysteretic width is essentially the same. It is interesting to note that the hysteretic effect associated with the TM₉₆.₃ resonance is not nearly in as good agreement. The measured width is 1.2 nm, whereas the predicted width is nearly twice as large. To compare the data in Fig. 3(a) [which is also redrawn in Fig. 4(b)] with the predicted behavior, the scattering level must be calculated at each wavelength for each of the solutions for $X$.

Figure 4(c) shows the predicted behavior of the scattering at 90° based on the delay convention. As one can see a number of the puzzling effects are explained. For example, the relatively constant scattering level in going from the $\gamma_n$ to $\delta_n$ in the data [Fig. 3(a)] comes directly out of the model. In addition the onset of the hysteretic behavior at the $\alpha$ points is also explained. However, as pointed out previously, it appears that the termination of the behavior beginning at the $\alpha$ point in the reversed scan is premature (i.e., not predicted by the model). In addition there is a clear correspon-

**Fig. 3.** (a) Wavelength spectrum of elastic scattering from a particle composed of 20% (NH₄)₂SO₄ (by mass) and a crystal violet dye at a concentration of 10⁻⁵ M. The particle was irradiated at 30 W/cm². (b) Best comparison between Mie theory ($a = 8.03$ μm, $m = 1.38 + 10^{-4} i$) for right angle in-plane scattering and the experimental scattering spectrum in (a) taken toward (a) longer wavelength. (c) Absorption corresponding to the Mie calculation in (b).

with the evaporative phase boundary relaxation mechanism. Although the hysteresis measured near the $\alpha$ points is not too surprising, since associated features are observed in the forward scan, the behavior observed starting at the $\gamma$ points in the reversed scan is a bit of a puzzle; there is no corresponding indication of features in this region in the forward scan. The $\gamma$ points, as we will show, indicate hidden resonances, resonances which should not be seen for our experimental conditions on the basis of Mie theory. The principal resonances which should appear for 90° scattering with the polarization of the incident beam in the scattering plane are transverse magnetic. Transverse electric resonances radiate perpendicular to the present scattering plane. As we see in Sec. IV, the so-called hidden resonances are transverse electric.

**IV. Analysis of Experimental Results**

In analyzing the data in Fig. 3(a) it is necessary to identify the partial waves which are associated with each of the features seen in the data. The most expedient way in which to do this is to compare Mie theory to data taken at an intensity at which no hysteresis exists. Although these low intensity data are not shown, the spectrum itself was found to be similar to the spectrum of elastic scattering recorded in the forward scan in Fig. 3(a). Figure 3(b) shows the calculated spectrum found to agree best with the spectrum in Fig. 3(a). The value taken for the refractive index, $m = 1.36 + 10^{-4} i$, was consistent with the known concentration of the solution. As one can see there is little difference between the high intensity forward scan and Mie theory. The corresponding absorption spectrum is plotted in Fig. 3(c). Here we clearly see the origin of the behavior occurring in the data at $\gamma_1, \gamma_2,$ and $\gamma_3$; the effects at $\gamma_1, \gamma_2,$ and $\gamma_3$ occur at essentially the same optical sizes at which TE₉₇.₃, TE₉₆.₃, and TE₉₅.₃ resonate, respectively. Although TE resonances should not appear in scattering for our optical configuration, stimulation of these resonances affects the particle size and, therefore, indirectly affects the scattering. To appreciate this effect more fully it is necessary to obtain solutions to Eq. (4) using the spectrum for $Q_{a Mie}$, which we have plotted in Fig. 3(c). Once this solution is arrived at using the method outlined in Fig. 2, the solutions for $X$ at a given wavelength may be used to determine the equilibrium scattering response.
V. Discussion and Conclusions

It is interesting to note that, although optical bistability is usually considered to be a high intensity effect, in the present case one has to go to a relatively low intensity before the effect can be eliminated. If we approximate our resonances as having a Lorentzian shape, one may use the recent work of Leung\(^7\) in addition to Ref. 1 to estimate the threshold intensity. In terms of the quality factor of the resonance \(Q_r\), and the maximum resonant absorption \(Q_{a,max}\), the threshold intensity is given by

\[
I_{th} = 1.54 \frac{X_0}{Q_r Q_{a,max}} \left[\alpha'\right]^{-1}. \tag{6}
\]

For our \(TE_{96,3}\) which is positioned at \(X_0 = 85.6\) a computed \(Q_r\) of \(5 \times 10^4\) and a maximum absorption efficiency for the current refractive index of 0.155, the estimated threshold intensity from Eq. (6) is 18 mW/cm\(^2\). When one considers that the cross section of the particle is only \(\approx 2 \times 10^{-6}\) cm\(^2\), this intensity represents a total power level of \(\approx 4 \times 10^{-8}\) W for which the volume averaged increase in temperature of the particle is calculated to be 2 mdeg Celsius! In part, this low threshold intensity is due to the extremely large value for \(\alpha'\) associated with the evaporative mechanism; for a \(2 \times 10^{-3}\) C change in temperature the evaporative mechanism allows the particle size to change by 50 ppm, whereas the refractive index changes by \(\approx 5 \times 10^{-3}\) ppm. An equally important parameter is the large feedback represented by the value of \(Q_r\). Although the current value of \(Q_r\) is large at \(5 \times 10^4\) it by no means represents the ultimate value. Recently Zhang et al.\(^8\) and Arnold and Folan\(^9\) have shown that the \(Q_r\) of a liquid particle can approach \(4 \times 10^6\). With such a large \(Q_r\) one can expect bistability at an intensity of \(\approx 10^{-9}\) W. Unfortunately our current experiments are limited by the dye laser linewidth which we have measured to have a resolution of \(\approx 10^{-5} \lambda_0\).

The foregoing suggests that particles composed of other isotropic materials which can support high \(Q\) morphological resonances should be candidates to demonstrate bistability. In this respect glass is a very good candidate since in it easily forms spheres and is available in many compositions. In the case of photothermal changes in refractive index one can fashion a model similar to that in Fig. 2. However, in this case the product of refractive index times optical size \(mX\) is
expected to be a more appropriate variable than optical size alone. Our preliminary calculations indicate that the $\alpha'$ values associated with such a mechanism are reduced by a factor of $10^4$--$10^5$ compared with the evaporative mechanism. However, the response time of such a system should be relatively fast (<100 ns) since it lacks the sluggishness associated with evaporation. The decrease in $\alpha'$ by 4--5 orders does not necessarily imply an increase in threshold intensity by $10^4$--$10^5$. Although Eq. (6) is still expected to be valid for a glass particle, one critical unknown needed for estimating the minimum threshold intensity is the optimum $Q_r$ value for a glass particle. It is now established that the longest measured photon lifetimes for liquid spheres are not successfully predicted from Mie theory.\(^{10}\) Apparently the stochastic fluctuations of the surface of the liquid microparticle, although only $\sim 0.1$ nm, limit $Q_r$ to $\sim 10^9$.\(^{11}\) Since the surface energy of most glasses is considerably greater than that of liquids, we might expect the surface fluctuation amplitude to be relatively small for a glass particle and the optimum $Q_r$ value to be relatively large. Therefore, the threshold intensity for a glass particle need not be 4--5 orders of magnitude larger compared to the threshold in this paper. Experiments concerning this question are currently a focus of our laboratories.

In summary, our model is in good agreement with the data. This model when extended to glass spheres suggests spherical photonic memories.

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