Aerosol Science 40 (2009) 790 – 801

Contents lists available at ScienceDirect

Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci

Directional dependence of thermal emission from nonspherical carbon particles

Nobuhiro Moteki[a,*], Yutaka Kondo[a], Nobuyuki Takegawa[a], Shin-ichi Nakamura[b]

[a]*Research Center of Advanced Science and Technology, University of Tokyo, Room-414 Bldg.-3, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8904, Japan*
[b]*Center for Instrumental Analysis, College of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara-shi, Kanagawa 229-8558, Japan*

ARTICLE INFO

Article history:
Received 21 March 2009
Received in revised form
9 May 2009
Accepted 11 May 2009

Keywords:
Particle shape
Thermal emission
Light scattering
Laser-induced incandescence
Single-particle

ABSTRACT

The directional intensity distribution of thermal emission from nonspherical particles can be predicted in the geometric optics limit using the Kirchhoff's law, or, in general case, using the Rytov's theory based on the fluctuation–dissipation theorem. This study demonstrates the first experimental evidence of the directional variation of thermal emission from nonspherical particles of a size smaller than the geometric optics limit. We used a method of laser-induced incandescence with multi-angle detectors to observe the directional dependences of thermal emission from individual carbon particles. For laboratory carbon particles with various shapes, the measured directional dependences of thermal emission were consistent with theoretical calculations for model nonspherical particles. This study provides a new physical principle for measuring the shape of aerosols according to the directional dependence of their thermal emission and is especially useful for online, in situ shape classification of carbon particles.

1. Introduction

Online, in situ measurement of aerosol particle shape is important for detecting hazardous particles (e.g., asbestos) in a working environment. In addition, a priori information regarding particle shape is necessary for data interpretation in aerodynamic and mobility-based particle sizing, and in the remote sensing of aerosols. Validation of lidar remote sensing of aerosol properties (e.g., Sassen, 2000, chapter 14) requires in situ, online observation of particle shapes in atmospheric aerosols. The angular dependence of light scattering has been used as a principle for on-line, in situ measurements of the nonsphericity of aerosol particles (Barton, Hirst, Kaye, & Clark, 2000; Sachweh, Barthel, Polke, Umhauer, & Büttner, 1999). No other physical principle, other than this angular light-scattering method, has been used for online and in situ classification of individual particle shapes. To compensate for the inherent ambiguities of the angular light-scattering method, a new independent physical principle for online, in situ measurement of particle shape is desired.

This paper demonstrates evidence of the directional dependence of thermal emission from nonspherical carbon particles with sizes comparable to the wavelength, using a method of single particle measurement of laser-induced incandescence (Moteki & Kondo, 2007; Stephens, Turner, & Sandberg, 2003). A priori information regarding the shape of the carbon particles is obtained based on transmission electron microscope images of bulk samples and the mass-to-mobility relationship of the aerosolized carbon samples. Theoretical predictions of the directional dependence of the thermal emission from model nonspherical carbon particles were found to be consistent with measurements of laboratory carbon particles with various shapes. In addition to the thermal emission, light-scattering properties of the carbon particles were simultaneously measured as independent data supporting the validity of the model calculations. This study demonstrates that the degree of directional dependence of thermal

* Corresponding author. Fax: +81 3 5452 5148.
E-mail address: moteki@atmos.rcast.u-tokyo.ac.jp (N. Moteki).

0021-8502/$ - see front matter
doi:10.1016/j.jaerosci.2009.05.003

emission varies substantially with particle shape, demonstrating that multi-directional detection of thermal emission is a new physical principle that can be applied to single-particle measurement of particle shape, especially of carbon particles.

2. Physical basis

Kirchhoff's law states the equality between radiative emissivity and absorptivity for each direction, wavelength, and polarization. The original form of Kirchhoff's law was derived from the geometric optics limit (i.e., any curvature of the body is much larger than the wavelength), under which any effects of diffraction can be neglected (Planck, 1914). Because of the manifestation of diffraction, the applicability of Kirchhoff's law is nontrivial for bodies of a size comparable to or smaller than the wavelength, as is the case for atmospheric aerosols or any other small particles not much larger than the wavelength under consideration. For spherical particles, Kirchhoff's law has been extended beyond the geometric optics limit. For spherical particles of arbitrary size compared to the wavelength, the equivalence of emissivity to absorption efficiency (i.e., the ratio of absorption cross-section to geometric cross-section) has been predicted from the principle of detailed balance while considering radiative equilibrium in an opaque cavity (Bohren & Huffman, 1983; Landau & Lifshitz, 1980). Laboratory experiments by Egan and Hilgeman (1984) demonstrated the validity of the prediction for di-2-ethylhexyl sebacate droplets. In recent papers using physical modeling of the thermal emission from small particles, spherical particle shape was commonly assumed because of the validated formula of emissivity (e.g., Filippov, Markus, & Roth, 1999; Hansen & Campbell, 1998; Melton, 1984; Moteki & Kondo, 2007). Although past studies on laser-induced incandescence (LII) have used a model of fractal aggregates to calculate emissivity of a volume containing many soot particles (Farias, Carvalho, & Köylü, 1998; Köylü, 1996; Schulz et al., 2006), these studies did not consider the emissivity of single particles.

In contrast to spherical particles, it is impossible to deduce the directionality of thermal emission from nonspherical particles of a size comparable to the wavelength by the conventional argument that considers radiative equilibrium in an opaque cavity (Landau & Lifshitz, 1980). Rytov (1953) was the first to theoretically deduce the directionality of thermal emission from a nonspherical body with arbitrary size: he used the fluctuation–dissipation theorem (e.g., Bekefi, 1966; Callen & Welton, 1951; Landau & Lifshitz, 1980) to calculate the thermal radiation originating from micro-scale fluctuating electric currents inside a body under boundary conditions associated with shape. In addition, Tsang (1984) derived succinct formulas for thermal emission from arbitrary particles on the basis of a similar physical idea. Notably, the conventional Kirchhoff's law is correct only under the geometric optics limit, and the law's extension to spherical particles with arbitrary size can be regarded as special cases of Rytov's theory. In spite of these theoretical developments, no experimental evidence has been reported regarding Rytov's theory for nonspherical particles of a size smaller than the range of the geometric optics limit.

3. Methods

3.1. Single-particle detection of thermal emission and light scattering

A single-particle soot photometer (Baumgardner, Kok, & Raga, 2004; Gao et al., 2007; Moteki & Kondo, 2007; Moteki & Kondo, 2008; Schwarz et al., 2006; Stephens et al., 2003) was slightly modified to measure the directional dependences of thermal emission and light scattering from individual particles (Fig. 1). Particles are introduced to the laser beam through an aerosol jet directed orthogonal to the plane parallel to the detectors. Individual particles pass though a Gaussian laser beam (i.e., TEM_{00} mode) of ~1 mm diameter within ~30 μs, with the transit velocity determined solely by the velocity of the sheath flow of the aerosol jet. Four optical detectors are mounted in the horizontal plane at mutually orthogonal positions. A light-collection lens in front of each detector collects either thermal emission or scattered light within a cone of 30° half angle (i.e., solid angle $\Delta\Omega_1$ and $\Delta\Omega_2$ shown in Fig. 1). Two identical photo-multiplier tubes (PMT model H6779, Hamamatsu Photonics, Inc., Japan) for visible thermal emission ($\lambda = 350$–550 nm) detection are placed on one side of the intra-cavity laser beam (upper side in Fig. 1), whereas two Si-avalanche photodiodes (Si-APD; Model C30916E and C30927E, Perkin Elmer, Inc., USA) for light-scattering ($\lambda = 1064$ nm) detection are mounted on the other side of the laser beam (under side in Fig. 1). In this paper, we refer to the differential scattering cross-section of a particle integrated over the solid angle of light collection of the photometer (i.e., $\Delta\Omega_1$ or $\Delta\Omega_2$ in Fig. 1) as the partial scattering cross-section. Following the notation of Moteki and Kondo (2008), the position of a particle inside the laser beam is measured as the distance from the center of the Gaussian, in units of the standard deviation (σ) of the Gaussian function. The C30927E light-scattering detector is a position-sensitive detector (direction-2 in Fig. 1) that can estimate the position of a particle inside the laser beam from the signal waveform (Gao et al., 2007; Schwarz et al., 2008; Shiraiwa et al., 2008). If the position of the particle inside the laser beam is known, the partial scattering cross-section can be estimated from the scattering waveforms at arbitrary positions in the laser beam (Gao et al., 2007; Moteki & Kondo, 2008). For the thermal emission channels, interference from the 1064-nm intra-cavity Nd:YAG laser or 808-nm pumping diode laser is negligible because the sensitivity of the detector at a wavelength of 808 nm or longer is zero. For each light-scattering channel, a long-pass optical filter RG-850 (Schott, Inc.) is placed in the lens system to block stray light from the 808-nm pumping laser. For carbon particles, only the time domain of the light-scattering signals before onset of visible thermal emission is used for analysis of the scattering properties to avoid interference from thermal emission. The cutoff frequency of the low-pass filter of the electronic amplifiers was adjusted to be 5 MHz, which is equal to the data acquisition frequency (i.e., every 0.2 μs) of the analog-to-digital converter to obtain maximum information from the signal waveforms.