Evidence for Nanoparticles in Microwave-Generated Fireballs Observed by Synchrotron X-Ray Scattering

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The small-angle x-ray scattering method has been applied to study fireballs ejected into the air from molten hot spots in borosilicate glass by localized microwaves [V. Dikhtyar and E. Jerby, Phys. Rev. Lett. **96** 045002 (2006)]. The fireball's particle size distribution, density, and decay rate in atmospheric pressure were measured. The results show that the fireballs contain particles with a mean size of ~50 nm with average number densities on the order of $\sim 10^9$. Hence, fireballs can be considered as a dusty plasma which consists of an ensemble of charged nanoparticles in the plasma volume. This finding is likened to the ball-lightning phenomenon explained by the formation of an oxidizing particle network liberated by lightning striking the ground [J. Abrahamson and J. Dinniss, Nature (London) **403**, 519 (2000)].

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The ball-lightning enigma has attracted scientists for more than a century. This apparently rare natural phenomenon has been observed accidentally by eyewitnesses, mostly during electrical storms, as glowing luminous objects floating in the air and lasting for up to several seconds [1–3]. In the 1950s, Kapitza was able to produce fireballs using high-power microwaves [4] and suggested accordingly that an external-energy mechanism is responsible for the production of ball lightning in nature. In other experiments, Ohtsuki and Ofuruton *et al.* obtained fireballs using microwaves in air-filled cavities and demonstrated fireball motions similar to those observed in nature [5,6].

A self-sustaining mechanism for ball lightning has been proposed by Abrahamson and Dinniss [7] involving the formation of a glowing ball when a lightning strike to the ground ejects a plume of silicon nanoparticles whose oxidation generates the heat that sustains the reaction. The oxide layer on the particles' surfaces slows the oxidation rate in the interior owing to the higher melting point of the oxide, hence yielding the delayed time structure of the phenomenon (thus the ball lightning seems to be a hybrid effect between plasma and the combustion phenomenon).

Dikhtyar and Jerby [8] have recently demonstrated experimentally the ejection of fireballs from molten hot spots induced by electrode-localized microwaves in solid substrates. These fireballs float in the air, hence demonstrating the buoyancy feature of ball lightning. These fireballs can be sustained for minutes in the microwave field. After the microwave supply is turned off, the fireball lasts for another ~30 ms. Stable atmospheric-pressure fireballs in air without the use of vaporized solids were demonstrated by Stephan [9]. Processes of plasma self-organization and formation of plasma structures at reduced pressures in electrode microwave discharges were studied intensively by Lebedev *et al.* [10]. Recently, Paiva *et al.* [11] have demonstrated an electrode-based mechanism operated at 50 Hz to ignite ball-lightning-like objects from silicon. The lifetime of these luminous objects exceeded 8 s, but they did not demonstrate yet the ball-lightning buoyancy feature. Thus various characteristics of ball lightning have been generated in various experiments; however, a definitive demonstration of a long-lived, floating object has yet to be achieved.

A key factor in the ball-lightning modeling, theoretically and experimentally, is the size distribution of the particles involved. The Abrahamson and Dinniss theory [7] predicts, for instance, a significant content of nanoparticles, and thus one may consider the ball lightning to be a form of dusty or complex plasma [12] subjected to an inner oxidation process.

In this Letter, we report results obtained using the small-angle x-ray scattering (SAXS) method for measuring the size distribution of particles contained in fireballs generated from molten hot spots by localized microwaves [8]. SAXS is a well established experimental technique that has been used to study nanoscale structures in solid, liquid, and gaseous phases. Here we describe a novel application of this method to the examination of the fourth state of matter: the plasma (actually, a dusty plasma such as that believed to be manifested in the phenomenon of ball lightning). The results obtained may help to elucidate the relevance of these laboratory fireballs to the natural ball-lightning phenomenon.

The application of SAXS to dilute systems in extreme environments has been demonstrated previously in measurements of particle size distributions in diffusion flames [13–16]. The density of particles in the fireball was assumed to be similar to that of soot particles in a hydrocarbon flame, and hence the contrast in x-ray scattering intensity signals compared to background air scattering was expected to be measurable similarly.

The microwave part of the experimental setup is similar to that described in Ref. [8] and is illustrated schematically in Fig. 1. It consists of a microwave cavity fed by a 0.6-kW magnetron. The microwave energy is concentrated by the movable electrode into the substrate material (e.g., borosilicate glass) to form a molten hot spot on the surface, from which the fireball evolves. A mirror made of vanes under cutoff conditions allows a direct optical view into the cavity for visual observation and video recording, while preventing microwave energy from leaking out. The fireball is formed when the electrode, made of tungsten or copper, is brought into contact with the dielectric substrate placed on the floor of the waveguide. An initial hot spot is created by the microwave-drill mechanism [17] in a thermal-runaway process [18]. A molten drop can be detached from the substrate, evaporated, and blown up to form a confined glowing fireball floating in air [19] by retracting the electrode. Figure 2 shows an optical image of such a fireball created from a substrate of borosilicate glass. The fireball may last for several minutes, as long as it is irradiated by the microwave power. Reference [20] presents more experimental results including optical spectroscopy and microwave measurements of fireballs generated from various materials (e.g., salt solution).

The microwave fireball apparatus was installed in the ID02 beam line at the European Synchrotron Radiation Facility (ESRF). The x-ray beam crossed the fireball through metallic tubes in the cavity walls as shown in Fig. 1 (these tubes are narrower than the microwave cutoff and therefore do not transfer microwaves). By illuminating the fireball with 12.5-keV x rays ($\lambda \approx 1$ Å), we performed x-ray scattering experiments using a high brilliance pinhole SAXS instrument [21]. The distance between the microwave cavity and the SAXS detector (FReLoN CCD) was 5 m. The fireballs in these experiments were ignited by a copper electrode from borosilicate glass substrates.

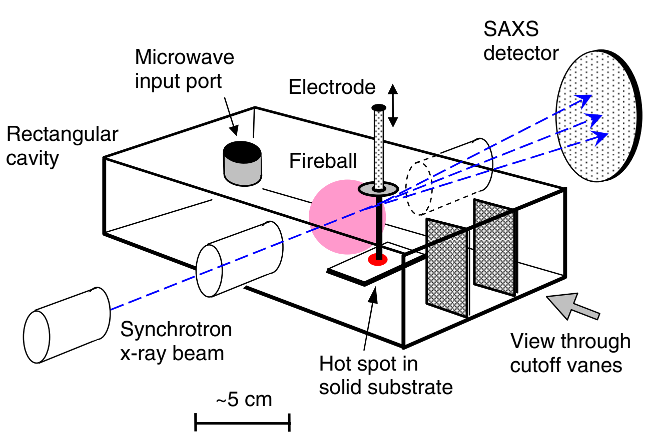

FIG. 1 (color online). The experimental setup including the microwave cavity in which the fireball is created [8] adapted for the synchrotron scattering experiment. The distance between the microwave cavity and the SAXS detector was 5 m with an evacuated flight tube after the cavity.

The background subtracted normalized scattered x-ray intensity is shown in Fig. 3 as a function of the scattering vector, $q = (4\pi/\lambda)\sin(\theta/2)$, where λ and θ are the wavelength of the incident x-ray radiation and the scattering angle, respectively. The results can be very well fitted using a single level unified scattering function [22]:

$$I(q) = G\exp(-q^2R_g^2/3) + B(q^*)^{-d}. \quad (1)$$

The first term on the right-hand side of Eq. (1) is the Guinier function [23] for scattering from particles with average volume and radius of gyration V and R_g, respectively. The prefactor G is given by $G = N\Delta\rho_e^2V^2$ with N being the particle number density, and $\Delta\rho_e$ is the scattering length density, $\Delta\rho_e = n_eDN_Ar_e/M_W$, where n_e is the number of electrons per molecule, D is the mass density (2×10^3 kg/m^3 for colloidal silica), N_A is Avogadro's number, M_w is the molar mass, and r_e is the classical electron radius (2.818×10^{-15} m). The second term in the right-hand side of Eq. (1) is a power-law decay that reflects the morphology of the underlying particle structure. The prefactor B is given by $B = 2\pi N\Delta\rho_e^2S$ with S being the average surface area of the particles, and $q^* = q[\mathrm{erf}(qR_g/\sqrt{6})]^{-3}$ defines the lower cutoff of the region defined by a power-law exponent, d, and erf is the error function. For compact objects with a sharp interface $d = 4$ (Porod behavior), while $3 \le d \le 4$ indicates the surface roughness of the particles characterized by a fractal dimension, $D_s = 6 - d$. In addition, the value of S then corresponds to a rough surface.

For Porod behavior ($d = 4$), the size distribution of the particles can be characterized by the polydispersity index $\mathrm{PDI} = BR_g^4/1.62G$, where $\mathrm{PDI} = 1$ for monodisperse spheres. For polydisperse spheres with a log-normal distribution with a standard deviation σ, the mean radius of the spheres is given by $\langle R\rangle = \sqrt{5/3}R_g\exp(-13\sigma^2/2)$, where $\sigma = (\ln \mathrm{PDI}/12)^{1/2}$ [24]. With glass as the initial substrate, we can assume that the particles are predominantly silicon dioxide and thus $\Delta\rho_e = 1.7 \times 10^{-3}$ nm^{-2}.

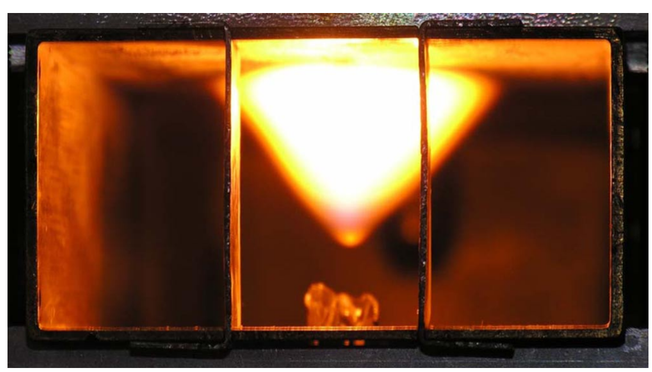

FIG. 2 (color online). An optical image of a stable fireball generated in the setup shown in Fig. 1. The nipple at the bottom of the fireball demonstrates its origin from a molten drop of liquid detached from a hot spot in the solid substrate.

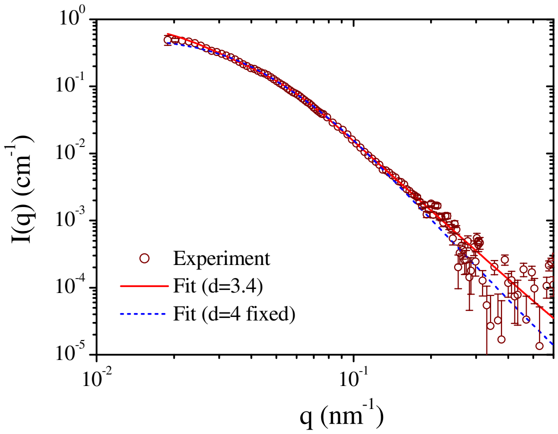

FIG. 3 (color online). Normalized SAXS intensity, $I(q)$, as a function of momentum transfer, q, for a typical fireball in our experiment. The continuous line corresponds to a fit to Eq. (1) with $R_g = 690 \pm 13$ Å, $G = 1.05 \pm 0.025$, $B = (2.08 \pm 0.43) \times 10^{-9}$, and $d = 3.4 \pm 0.04$. The dotted line represents a fit with $d = 4$ fixed.

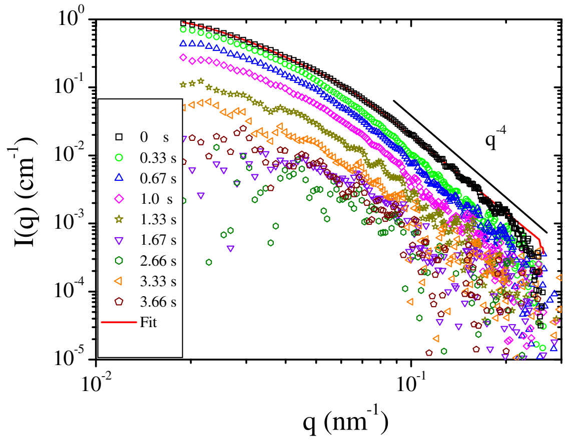

FIG. 4 (color online). Decay of the normalized SAXS intensity $I(q)$ after the microwave energy has been turned off. The signal level reaches the background scattering levels after about 4 s. The continuous line for the upper curve corresponds to a fit to Eq. (1) with $R_g = 622$ Å, $G = 1.53$, $B = 5.16 \times 10^{-10}$, and $d = 3.8$.

Using the absolute SAXS intensity, it is possible to estimate the number density of particles in our target plasma from the G prefactor.

The data from 29 separate synchrotron measurements of fireballs similar to those shown in Fig. 3 were fitted using Eq. (1). The averaged values of parameters for the fireballs generated by copper electrodes from borosilicate glass are $R_g = 60.3 \pm 4.6$ nm with $d \approx 3.4$. The precise value of R_g is sensitive to the d value in Eq. (1). For the representative data in Fig. 3, fixing d at a value of 4 allows us to estimate the PDI factor. The dotted line in Fig. 3 indicates the corresponding fit with $d = 4$, $G = 0.59$, $R_g = 47$ nm, and $B = 1.66 \times 10^{-6}$. The resulting PDI ≈ 8.4 or $\sigma = 0.42$ is well above the log-normal self-preserving limit of aerosol growth presumably indicating the rapid process involved in their formation [25]. The analysis of PDI, averaged over the 29 runs, leads to an estimate of $\langle R \rangle \approx 25$ nm and $N \approx 10^9$ cm^{-3}, and thus the volume fraction of particles in the fireball is of the order of 10^{-7}.

Once the microwaves are shut down and the fireball disappears, the SAXS data show that the particle number density falls to background levels after a few seconds (note that the visible fireball's lifetime was measured as ~30 ms [8]). Figure 4 shows the typical decay of scattered intensity at several time intervals after the microwave energy is turned off. During the initial drop in the intensity, the scattering curves appear to shift downward parallel to the initial level. From Eq. (1), this is an indication of the decrease of particle number density while their size distribution remains nearly the same. Presumably during this period particles diffuse out of the scattering volume primarily by convective flow as the system cools down. The local temperature is indicated by the background scattering level at high q values (data not shown). Further work is planned to investigate quantitatively this decay behavior including the effect of temperature change.

The observed decay period is shorter than expected from the Abrahamson and Dinniss model [7] and from the observations of Paiva *et al.* [11], and it is also shorter than the typical neutral particle Brownian diffusion rates (our lifetime results are closer though to Boichenko's model [26] and to Kapitza's estimates [4] for ball-lightning lifetimes). It has to be noted, however, that the ball-lightning's lifetime is attributed to the slow oxidation process [7]. In our experiment, the oxidation effect may occur also during the microwave illumination period and hence the remaining lifetime of the fireball afterward is shortened accordingly. Furthermore, unlike the Abrahamson and Dinniss model [7] in which the silica is reduced by carbon and subsequently oxidized, the nanoparticles contained in the fireballs studied here are likely to remain oxidized during the entire process; hence, these fireballs are not self-sustaining. The ball's lifetime could be affected also by its volume and mass, noting the similar $\sim 10^2$ ratios between both the volumes and lifetimes of the natural ball lightning reported (~0.3 m$^{\varnothing}$, 3 s) and our fireball (~0.05 m$^{\varnothing}$, 0.03 s), respectively. The average silica mass density of the latter is found here to be $\sim 6.6 \times 10^{-4}$ mg/cm^3, which is ~150 times smaller than estimated for ball lightning [7].

Given the intense light emission seen during the fireball, and in view of our previous analyses [8,20], it is reasonable to suppose that the particles' temperature is in the order of $\sim 10^3$ K, and therefore they emit electrons due to thermionic emission (as do soot particles in a flame). The free electrons will also be interacting with the microwaves, and thus these luminous objects containing ~50-nm macroparticle networks could be considered as a dusty plasma

[12]. Similar experiments could be conducted also with other substrate materials, such as germanium and alumina, for the sake of comparison with silica. The experimental results may contribute to the comprehension of the ball-lightning enigma, as well as to the development of practical applications of fireballs (e.g., [27]), and, in particular, to the direct production of nanoparticles from solid materials.

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