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Packing density effects on the fluctuations of the emission lines in laser-induced breakdown spectroscopy ☆

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ABSTRACT

In an earlier publication, we reported the results of a nanosecond-laser-induced breakdown spectroscopy (LIBS) analysis of pellets of Iron and Carbon and have shown that the shot-to-shot variations of the intensities of iron emission lines measured in iron to be much stronger than those measured in carbon. Here, we present a numerical model based on two-dimensional random close packing of disks in a confined geometry that shows that the fluctuation effects observed in C and Fe are essentially due to the packing density of the samples interrogated.

1. Introduction

Over the past few years, laser induced breakdown spectroscopy (LIBS) has experienced a rich and a relatively strong growth in many and diverse areas of research and to some extent in industrial applications. This growth is in part due to the fact that LIBS is an all-optical, relatively rapid spectrochemical analytical technique that can be used essentially without any sample preparation. Another important feature of LIBS is that the samples of interest can not only be of any type but also may be interrogated even in challenging environments [1,2]. As a result, LIBS has been used in fields as diverse as protein characterization [3] and remote sensing of the planet Mars [4] to name a few. In addition, LIBS has been the subject of intense theoretical studies focused on better understanding the various fundamental and complex processes that take place before, during and immediately following laser ablation [5–7]. Often the accuracy of the analysis is limited by shot-to-shot spectral fluctuations of the intensities of the various emission lines. These fluctuations, which vary tremendously depending on the type of target and laser used limit the domain of applications of LIBS. This drawback has been addressed by few researchers who have investigated the source of the intensity fluctuations in LIBS spectra [8,9] and proposed methods to correct for them [8,10–12]. Thus, the sources of fluctuations are sometimes attributed to the characteristics of the laser pulses used to induce breakdown in targets that are not necessarily spatially uniform on the scale of the laser beam. Furthermore, the environment in which the laser–target interaction takes place is not always reproducible from one pulse to the next. Typically, these effects as well as instrument used for the detection of LIBS signals contribute to the generation of non-uniform and thus fluctuating LIBS plasmas. Some researchers have focused their work on overcoming the extensive spectral fluctuations observed on a laser shot-to-shot basis through the use of classical ensemble averaging of spectra or statistical analysis of single-shot spectral data [13,14]. Others have investigated the effects of sample properties such as micro-hardness or particle size on the fluctuations of LIBS spectra [15,16]. In a recent publication, using a binary carbon–iron mixture as a test sample, we reported stronger shot-to-shot variations of the intensities of iron emission lines than those from carbon [17]. In addition, we suggested that the morphology, and more specifically the packing density of the binary carbon–iron mixture greatly affect the relative standard deviation (RSD) of the laser-induced plasma emission lines. In this letter, we provide the theoretical framework for this suggestion by simulating the laser–target interaction using a two dimensional (2D) random close packing (rcp) model of disks distributed in a confined geometry.

Packing density of powder mixtures is an empirical parameter that describes the density of solid particles obtained when they are packed closely. In powder processing operations and especially in powder compaction by dry pressing [18], this effect has been the subject of theoretical and experimental investigations which led to the calculation of the packing density from known characteristics of particulate mixture [19–22]. Often the proposed approaches resort to simplified or semi-empirical models of the experimental packing situations [23]. Yet, the theoretical approaches used often fail to identify the mechanisms involved in the distortion of the packing of individual components when they interact in the mixture, and fail to account for the effect of mixture inhomogeneity. However, these models can provide insights into the surface and volume structures of binary compacted powder mixtures.

☆ This paper is dedicated to the memory of our colleague Mr. Tahar Kerdja, *Allah Yerahmou*, who passed away recently.

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2. Experimental

In Ref. [17], we described the experimental setup as well as the method of preparation of the $C_{1-x}Fe_x$ composites using powdered graphite (Spectrum, USA) and iron (99% Powder, 325 Mesh, Acros Organics) as sources. These were hand ground in an Agate mortar for approximately 6 min then fitted in a 15 mm bore non magnetic stainless steel (300 series) and pressed at (4500 ± 500) psi (Benchtop Shop Press, Big Red). A laser-induced micro plasma was generated by focusing laser pulse on the surface of the target material via a 60 mm focal length fused silica Bi-Convex lens, from a 10 ns Q-switched Nd: YAG laser (B.M. Industries Thomson-CSF Series 5000) operating at the 1064 nm. The focused laser spot diameter at the sample surface was measured using a knife-edge approach and estimated using a knife-edge technique to be (450 ± 45) μm, which yields an irradiance of (5 ± 1) GW/cm^2. An energy meter (FieldMaxII-TOP, Coherent Inc.) was employed to measure shot-to-shot laser energy pulses and fluctuations were estimated to be less than 3%. A fiber collimation lens placed at 45° with respect to the laser beam and focused onto an optical fiber was used to collect the optical emissions from the plasma. The fiber was coupled to an Echelle spectrograph (Andor Technology, ME 5000) with an iStar Intensified Charge Coupled Device (ICCD) camera (Andor Technology, DH734-18F O3). The LIBS spectra were collected 300 ns after the Q-switch pulse, with an integration time of 700 μs. These parameters were chosen by finding a balance between optimum reduction of the continuum background and the signal to noise ratio of dominant emission lines. To reduce effects from the surrounding atmosphere, the measurements were performed in a chamber filled and kept at a constant pressure of (760 ± 5) Torr of Helium. The intensity of each emission line generated by a laser shot was determined as such: First, the continuum background was estimated for every laser shot by fitting to a second or higher order polynomial in the wavelength range of interest. Then the fitted background curve was subtracted from the original spectra. Second, the intensity of the emission line was determined by curve fitting of the spectral lines with Gaussian functions.

3. Description of the model

To model the influence of the surface morphology on LIBS emissions, the local packing density of a random close packed system in a confined geometry was computed numerically. Random close packing is generally referred to as a collection of particles randomly packed into the densest possible configuration which corresponds to the lowest free space in the system. To determine if there is a relationship between the fluctuations of the LIBS emission lines and the atomic number density and for the sake of simplicity, we consider a 2-D model where the focused laser beam is assumed to interact with the sample only at its surface. In other words, the penetration depth of the laser beam at the sample surface is assumed to be less than the particle sizes. The fundamental procedure and geometrical algorithms of random close packing are established following the work of Desmond and Weeks [20].

For a binary mixture of hard-disks with size ratio $\sigma = d_l/d_s$, where d_l is the diameter of large disks and d_s diameter of small disks in a box with fixed boundary conditions in all directions, the packing assembly can be constructed using the approach proposed by Desmond and Weeks [20]. This is done by using a minimum energy criteria combined with frictionless particles that interact via a short-range repulsive potential model as a linear spring potential [24,25]. The potential energy between the disks is given by:

$$V\left(r_{ij}\right) = \frac{\varepsilon}{2}\left(1-\frac{r_{ij}}{d_{ij}}\right)^2 \Theta\left(1-\frac{r_{ij}}{d_{ij}}\right) \quad (1)$$

Where r_{ij} is the center-to-center distance between disks i and j, ε is the characteristic energy scale of the interaction ($\varepsilon = 1$ for simulation), $\Theta(x)$ is the Heaviside step function, $d_{ij} = (d_i + d_j)/2 = d_i(1 + \sigma_{ij})/2$, where d_i is the diameter of particle, and σ_{ij} *is the particle size ratio.*

To randomly pack a collection of particles into the densest possible configuration, infinitesimal particles (disks) are placed first randomly in a box of known dimensions and boundary conditions. At the initial state, the particles do not overlap i.e. the total potential energy is zero. Then, the sizes of disks are gradually expanded while keeping the size ratio fixed. Succeeding each expansion, the overlap between disks is checked and if any particles overlapped, the conjugate gradient method was used to decrease the total potential energy by adjusting the position of particles. Finally, after successive expansion and contraction of particles followed by conjugate gradient, the random close packing (rcp) state was achieved in which all the particles collectively jammed and no longer expand. Similarly, rcp state was attained for uniform size particles in confined geometry. In addition, the average packing density as well as the particles' coordinates and sizes were computed from the above-mentioned simulations. First, the computational studies of rcp system are classified with the particular case of $\sigma = 1.4$ and binary mixture of 5000 particles with an equal number of large and small particles, and we found an average packing density of $\varphi_{rcp} \sim (0.843 \pm 0.005)$. The latter result appears to be in good agreement with previous studies [20,25,26].

The local packing density for the single-type rcp system is defined as, the packing density of the area enclosed by the laser focus spot size at different locations of the sample's surface, and given by,

$$\varphi_l = \frac{\sum_i A_i}{\pi\left(\frac{D}{2}\right)^2} \quad (2)$$

Where, $\mathbf{A_i}$ is the covering area between the ith single type particle and laser spot, and **D** is the laser spot diameter.

To establish a relationship between the simulated values of packing density and the atomic number density of an element in the pellet, we assume that the atoms are hard spheres with a fixed radius and are uniformly distributed. Furthermore, we consider that a single type of particle is composed by one type of atoms with similar atomic bonds inside the pellet. With these assumptions, the number of atoms in a particle is proportional to the size of the particle [27]. Therefore, the total number of atoms in a spot area is proportional to the covering area between a single type of particles and the laser focus spot size. The local surface atomic number density for a single type of particles can then be expressed as,

$$N_l = \sigma_{c1}\varphi_l \quad (3)$$

Where, ϕ_l denotes the local packing density of a single type of particles, and $\boldsymbol{\sigma_{c1}}$ is a constant representative of the surface atomic number density for a single type of particles. The surface atomic number densities of carbon and iron particles were determined from the geometry of the pure carbon and pure iron pellets samples with the assumptions of uniform particle distribution in the pellets. Numerical values of the RSD of the local surface atomic number density were obtained using the following procedure. First, two rcp states were generated for each concentration of large and small particles. For each rcp state, the local surface atomic number densities for 50 laser spot locations on the rcp system and the corresponding RSD were obtained using Monte-Carlo simulations. This procedure was repeated 3 times for each rcp state. Finally, the uncertainty in RSD for various concentrations of binary particles is determined. The similar procedure is also used for uniform disks in rcp state.