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Two-dimensional axisymmetric models of laser induced plasmas relevant to laser induced breakdown spectroscopy ☆

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ABSTRACT

A dynamical model of a laser induced plasma with axial symmetry is developed to systematically study the effects of the plasma equation of state, radiation transfer, various transport phenomena (viscosity, thermal conductivity, diffusion), and the ablation surface on the observable quantities such as spectra emitted by LIBS plasmas containing multiple species. Theoretical and numerical foundations of the model are described in detail. It is shown that the plasma spectra simulated with the equation of state based on the energy balance that includes the kinetic (thermal) energy, ionization energy, and energy of electronic excitations in atoms and ions differ significantly from the spectra obtained for plasmas modeled in the ideal gas approximation (where only the kinetic energy is included into the energy balance). Various transport phenomena, such as viscosity, diffusion, and thermal conductivity, are shown to have a little effect on the spectra. Radiation losses are proved to have noticeable effects. The effects of various interactions (adhesion, heat exchange, mass inflows) of the evolving plasma with the ablation surface are also illustrated by numerical simulations for typical LIBS plasmas. The model provides a numerical tool to assess various settings for LIBS plasma experiments as well as to interpret experimental data.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a popular method for material analysis. Both practical and theoretical aspects of this method are described in the recent excellent reviews by D. Hahn and N. Omenetto [1,2]. A number of laser-induced plasma models have been developed in view of specific applications, e.g., pulsed laser deposition [3], laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) [4], LIBS plasmas (for a review see, e.g., [5,6]), laser micro-machining [7], etc. Although describing the same phenomenon, the models differ in many ways emphasizing processes most relevant to the considered application. The model presented here is pertinent to LIBS plasmas and aimed at improving the understanding and capabilities of this technique. In particular, the model is intended for use in a calibration-free analysis where concentrations of species are inferred from plasma spectra [8]. The calibration-free capability is a "holy grail" of any analytical method, LIBS is not exclusive, as it offers independence of matrix-matched standards.

To fulfill the goal, the plasma model has to be practical, i.e. allowing relatively fast calculations with common computers. From this perspective, the best are analytical models as they avoid whimsical differencing schemes and lengthy calculations. Many have been developed for vacuum [9] and only few for atmospheric plasmas. The reason for this disproportion is that the self-similar and shock-free expansion in vacuum is an analytically solvable problem [9,10] whereas a shocked atmospheric expansion is not and can only be approximated with a certain degree of fidelity. Several analytical approximations have been proposed. Arnold et al. [11] developed a model for the expansion of a spherical plume into an ambient atmosphere that included the almost free initial expansion, strong shock propagation in the intermediate stage, and plume stopping. Wen et al. [12] proposed a similar analytical model for the expansion of a copper plasma accompanied by internal and external shocks. The plasma evolution was divided into four stages depending on the position of the internal shock front. For each stage, integral conservation equations were solved to obtain trajectories of the shock waves and contact surfaces and the distributions of plasma density, pressure, and temperature.

For several years, we have been trying to develop a universal analytical model of LIBS plasmas based on the mass/momentum/energy conservation equations. The model was intended to describe shock dynamics in laser-induced plasmas combined with a semi-analytical approach to evolution of thermodynamic parameters satisfying a simplified equation of state. All our attempts had failed to accurately reproduce vast variety of experimental data; the models showed substantial

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☆ This paper is dedicated to Nicoló Omenetto, on the occasion of his 75th birthday, in recognition of his outstanding contributions to the field of laser spectrochemistry and as an editor of Spectrochimica Acta Part B.

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instability to the choice of initial data. Not to mention, the use of a simplified equation of state (like an ideal gas) is hardly justified from the physical point of view especially at early stages of evolution of laser-induced plasmas. It was our conclusion that a reasonably universal model for LIBS plasmas must be based on a numerical solver of the Navier–Stokes equations. However, the goal was to create an efficient algorithm that could run on a regular PC.

By now, the majority of existing laser-induced plasma models are continuous models based on fluid dynamic equations [5]. Many models include laser–matter interaction with thermal or non-thermal energy transfer depending on the duration of a laser pulse: micro/nano- or pico/femtosecond. Correspondingly, either heat conduction [13] or two-temperature electron-phonon [14] models are employed. In our approach, we avoid modeling the laser–matter interaction because (i) it would require many additional (often-unknown) material parameters and (ii) some data related to the initial ablation can be retrieved from experiment. Besides, the time scales on which the laser–matter interaction and plume expansion proceed are markedly different and therefore the two phenomena can be decoupled. The task in our case, thus, is to guess (or measure) initial plasma parameters and initiate the gas dynamic model. The collisional radiative (CR) and collisional dominated (CD) plasma models are by far the most usable models to describe radiating plasmas. The term “collisional radiative” is related to plasmas in which trapping of radiation affects the population densities of excited levels, thus the deviation from equilibrium conditions may occur [15]. In CR models, atomic processes and radiation transport are always considered together. In contrast to CR plasmas, CD plasmas are driven by mostly collisions; a radiation field is strongly diluted and does not affect thermodynamic properties of the system. CD models exploit the concept of local thermodynamic equilibrium (LTE) which states that (i) collision-induced transitions and reactions are more frequent than radiative ones, and (ii) there exists a micro-reversibility between the processes. In CR models, the LTE concept is relaxed due to a possible shift in reversibility of micro processes. More information on plasma types and equilibriums can be found in Refs. [16,17].

In recent years, there appears a noticeable trend in plasma modeling toward non-equilibrium conditions in laser-induced plasmas. The most rigorous approach for describing non-equilibrium plasmas is to solve a CR model where densities of excited states are treated separately in a so-called state-to-state approach [18]. This helps to model more precisely plasma transport properties that depend upon excitation states of atoms and molecules. However, the state-to-state approach is a formidable problem that requires full information about cross sections of different excited states and their dependence upon internal energy of a relevant system. Examples of CR models, some including chemical kinetics, can be found in [6] and references therein. Noteworthy, the CR plasma models are used not for only low-temperature spectrochemical laser plasmas but also (and mainly) for highly energetic plasmas produced in laser fusion experiments and various technologies. Highly sophisticated codes like, e.g., the SPECT3D [19] and HELIOS-CR [20], were developed capable of performing non-LTE atomic kinetic calculations with up to $\sim 10^3$–10^5 atomic discrete levels. The codes were used, for example, for calculating properties of laser produced plasmas at conditions relevant to extreme ultraviolet lithography [21] or X-ray lasing [22].

It is clear that detailed (numerical) models based on the full Navier–Stokes, kinetic, and radiative transfer formulation require large amount of computational time and knowledge of a large number of thermodynamic and spectroscopic parameters that are not readily available. It is difficult to use such models for fast assessment of laboratory plasmas as needed, for example, in spectrochemical analysis or thin film deposition. Therefore, a number of simpler analytical models have been developed based on the concept of the CD plasma with the emphasis on plasma radiative properties [23–25].

The presented two-dimensional plasma model fills the gap between oversimplified models like [23–25] and overwhelmingly complex plasma models like [19–22]. On the one hand, it includes all essential plasma physics such as the formation of shock waves, partitioning of energy, transport phenomena, and radiative transfer. Yet, it remains relatively simple and can be run on a conventional PC. As mentioned above, the main goal was to create a model which could provide a fast feedback to an experimenter in terms of plasma properties and optimal arrangement of experiments.

1.1. The model and numerical simulations

Here a brief qualitative description of the model is given along with the structure of the paper. As noted before, the ablation process is excluded from consideration so that an initial state of a plasma plume can be chosen at will, e.g., using some physical assumptions about the outcome of a particular ablation process. An evolving plasma plume is assumed to have an axial symmetry. If the line of propagation of an ablating laser pulse is normal to the ablation surface, then this assumption is justified. Yet, the use of two-dimensional Navier–Stokes equations allows one to avoid excessively long simulations. The plasma is assumed to contain an arbitrary number of atomic species, each may be ionized several times (to lose one or more electrons). The dynamics is described by Navier–Stokes equations that include radiation losses, various transport phenomena (diffusion, viscosity, thermal conductivity). One of the main aims of the present study is to investigate the effects of various features of the plasma dynamics, especially the equation of state and transport phenomena, on observable spectra of LIBS plasmas.

Section 2 contains a technical description of the model. A Kurganov–Tadmor high-resolution semi-discrete central scheme is used that is extended to the case of three-dimensional conservation laws with an axial symmetry (Section 2.1). It is one of more accurate generalizations of the celebrated shock-capturing Godunov method. In the scheme, only the spatial computation region is partitioned into cells, while the time remains continuous. The dynamical variables are the cell averages of local thermodynamic parameters of the plasma (mass densities, the velocity vector field, and the energy density). Their evolution is governed by a system of first-order ordinary differential equations that is proved to be equivalent to the original Navier–Stokes equations up to terms of second-order in the dimensions of the spatial cell. The initial value problem for the system is solved by a third-order Runge–Kutta method.

Section 2.2 is devoted to the derivation of the equation of state of plasma that incorporates the processes of ionization and atomic excitations into the local energy balance under the assumption of local thermodynamic equilibrium. The latter allows us to use Saha equations to determine the relative densities of ions, atoms, and electrons. The local energy balance, Saha equations, mass and charge conservation laws are shown to yield a system of three non-linear algebraic equations for each spatial simulation cell that determine the pressure and temperature as functions of the dynamical variables. One of the technical obstacles here is the lack of analytic expressions for partition functions of atoms and ions. A fast algorithm is developed to use tabulated values for the partition functions for solving the above system of non-linear equations.

Section 2.3 contains a brief technical account of various transport phenomena. Viscosity and thermal conductivity is modeled by means of the Chapman–Enskog theory. An effective binary diffusion model is used to describe diffusion processes.

Radiation losses are described in Section 2.4 by a stationary radiation transfer equation in the so called “gray” body approximation in which the absorption coefficient is independent of frequency. It is numerically integrated at each time step of the evolution. The section also contains the algorithm to simulate synthetic spectra of the plasma.

The interaction of a plasma plume with the ablation surface is described in Section 2.5. Adhesive properties of the surface are modeled by Maxwell's boundary conditions on the velocity vector field. The radiant energy exchange between the plasma and the surface is modeled