50 Years of Non-Equilibrium Kinetics in Laser Physics, Geophysics and Plasma Chemistry:a Tribute to Boris Gordiets

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State-to-state non-equilibrium plasma kinetics is a topic which started in the early sixties with the papers of the Belfast school (1) about the construction of a collisional-radiative (C-R) model, i.e., the solution of a coupled set of differential (kinetic) equations in the so-called quasi-stationary approximation (QSS) describing the population and depopulation mechanisms of each excited state, considered as a different species, taking into account excitation and deexcitation processes by electron impact, ionization and three body recombination, spontaneous emission and radiative recombination. The model was developed for astrophysical applications and was then extended by Russian researchers to plasma physics applications (see Biberman et al (2)). In the same period, Osipov and Stupochenko (3) were developing similar models to understand possible deviations from Boltzmann's law of the vibrational distribution of diatomic molecules in thermal baths, emphasizing the effects on the dissociation rates. In these approaches, use was made of the harmonic oscillator model. However, in the middle sixties, due to the rapid development of laser physics and molecular vibrational lasers, attention was devoted to the analysis of vibrational kinetics at low translational temperature and large available vibrational energy. The harmonic oscillator model was judged inadequate for the description of these situations thus initiating vibrational kinetics analyses using anharmonic oscillators. In 1968, Treanor, Rich and Rehm (4) found the well known Treanor's distribution, i.e., the vibrational distribution resulting from V-V (vibration-vibration) energy exchange processes.

In this general context starts the work of Boris Gordiets who develops and creates a series of applications of paramount importance for science and technology.

One of his first papers published in the European literature (in 1968 (5)) was about a C-R model of atomic hydrogen taking into account the processes of the Belfast school by using both the quasi-stationary approximation QSS and the time-dependent solution in solving the system of differential equations. The approach opened the road to predicting the creation of population inversion between electronically excited states as a result of electron-ion recombination processes (6). The idea was at the basis of laser operation in the visible, the same process being also able to produce X-ray lasers when using hydrogenoid systems.

Soon after these papers, Boris concentrated his activity on the non- equilibrium vibrational kinetics in collaboration with Osipov and Shelepin (7), which led to the formulation of the so-called Treanor-Gordiets non-equilibrium vibrational distribution (8). This very famous equation takes into account both V-V and V-T (vibration-translation) energy exchange processes in the formation of the vibrational distribution function. Roughly speaking, the Treanor-Gordiets distribution describes the non-equilibrium vibrational distribution of a diatomic molecule in the presence of an external pumping of vibrational quanta. This distribution is composed of three portions, the first one describing the low-lying vibrational levels, followed by a slowly declining plateau over an intermediate range of levels and finally ending towards a strongly decreasing Boltzmann distribution at the gas temperature. An

analytical approach instead of a numerical one was used by Boris to solve the system of vibrational master equations. This provided different analytical formulations according to the studied non-equilibrium conditions. Such approach is indeed very useful to control the results obtained from direct integration of the vibrational master equations. Interesting results were obtained by Boris in applying the analytical model to the modeling of the CO laser (9) as well as to the description of vibrational energy exchanges in mixtures of diatomic molecules for isotope separation (10).

Laser physics always interested Boris, who was one of the first researchers to model the CO2 laser (11) as well as lasers pumped by solar energy (12,13).

Soon after these applications, Boris extended these ideas to geophysics (14,15). We remind in this field the study of the effect of solar activity on the Earth's lower atmosphere by considering the mechanism of energy transfer from geomagnetic disturbances to the lower atmosphere via the upper-atmospheric IR flux. An important study was also devoted to the role of the IR emission of CO2 (15 mm) in the cooling process of the lower atmospheres of Venus, Earth and Mars, this analysis being again investigated and extended many years after.

From geophysics applications Boris enters in the domain of plasma chemistry in collaboration with different French, Italian, Portuguese and Spanish groups. The beginning of this strong collaboration started in 1986 with a chapter (16) in the Springer book “Non-equilibrium vibrational kinetics”, the whole book being later translated by Boris in an edition of Mir. In this chapter, Boris presents with Zdhanok a comprehensive analytical theory of non-equilibrium vibrational kinetics with several applications and summarizes his achievements in such topics since approximately 20 years. One of the results outlined in this chapter found future applications in the modeling of high speed atmospheric reentry flows: the so-called Gordiets model for vibration-dissociation coupling, which extended and improved the previous Losev-Shatalov model and allowed a more accurate description of dissociation processes.

The first stay of Boris in Western Europe was at the University of Paris XI- Orsay in collaboration with André Ricard, in the framework of which he developed a self-consistent model of vibrational kinetics coupled with the formation of atomic oxygen and nitrogen under discharge and post-discharge conditions yielding good agreement with the experimental data (17-18). The collaboration with André Ricard opened the road toward Portugal for a long and fruitful collaboration with the Lisbon group. Boris went to Lisbon in the mid 1990’s and worked continuously there for 6 years as a senior invited scientist. Again, a new self-consistent kinetic model was developed to study dc flowing glow discharges in N2/O2 mixtures. This model included the calculation of electron energy distribution functions and electron rate coefficients coupled with detailed vibrational kinetics of N2 molecules, chemical kinetics taking into account a large set of neutral, excited and charged species, interaction of N and O atoms at the discharge tube wall, and the thermal balance of the discharge (19). The results of this model were found to be in good agreement with experimental results opening a new way in the modeling of plasma chemistry reactions in the air system. Similar modeling work was developed for N2/H2 dc and microwave discharges.

Since his stay in Portugal, the collaboration with the Lisbon group lasted, we can say, for all the rest of Boris life (20-22). After his return to Moscow, Boris continued to work together with this group and came back to Lisbon for 1 or 2 months almost every year. In the last years, their joint work was

mainly focused on the study of microwave air-water plasma torches at atmospheric pressure having in view applications in areas such as plasma medicine or plasma pretreatment of biomass. The understanding of the complex kinetics of such sources is a very difficult task and the help of Boris in this endeavor turned out to be crucial for the progress of this investigation (22).

Additionally, this long collaboration led to interesting results in many other fields of plasma chemistry including a new model for heterogeneous recombination of atomic species on reactor walls (23). Very interesting results were also obtained in the study of dusty plasmas (24-25), a topic later continued by Boris in collaboration with E. Beltran in Barcelona, after he left Lisbon (26-27).

In all the reported activities the contribution of Boris was essential. This is well testified by two important books (28-29) on the role of non-equilibrium vibrational kinetics in affecting plasma chemistry and plasma physics, in addition to all the journal papers and conference contributions that Boris authored or co-authored with many collaborators across the world.

We hope that we have been able to provide an idea of the intellectual efforts made by Boris in his life and of his extraordinary scientific achievements. His research, in areas neither trivial nor easy, has always been oriented within the frame of an excellent balance between fundamental aspects and practical applications. Boris multiple activities were strongly interconnected and can be ascribed to the topics of non-equilibrium physical and chemical kinetics, following the long tradition of Russian schools in these topics.

In conclusion, the plasma chemistry and physics community must be grateful to Boris for his numerous scientific advancements where extraordinary creativity, curiosity and physical intuition have been the driving forces (or chemical potential) to reach such important goals.

Boris was also an excellent person and a very good friend of us. We shared with him not only scientific ideas but also many thoughts and feelings of our human lives. We will keep his memory in our hearts and will miss him forever.

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