論文の内容の要旨

論文題目　Generation and diagnostics of gas-temperature-controlled high-pressure plasmas at cryogenic temperatures
(ガス温度を室温以下に制御した高圧プラズマの発生と診断)

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1. Introduction

In this thesis, “cryoplasmas”, whose plasma gas temperature (i.e. the temperature of neutral species in plasmas, T_g) are controlled continuously at lower than room temperature (5 – 300 K), were investigated (Fig. 1). T_g is one of the most important parameters in plasma science and technology, because T_g affects the plasma chemistry and transportation of heavy neutral species including excited species and radicals, and their interaction with condensed-phase materials. However, up to now, the role of T_g in high-pressure plasmas has not been studied sufficiently, and therefore, T_g can be considered as a kind of a “new” parameter in non-equilibrium plasmas. In the new and exotic T_g region of cryogenic temperatures, both phenomena —peculiar to cryogenic temperatures and showing a continuous variation from conventional temperatures higher than room temperature— are expected to appear. To date, our group has reported experimental results specific to cryogenic temperatures, such as the variation of emission species and self-organized pattern formation, and the possibility of the applications of cryoplasmas for materials processing [1,2]. In this thesis, not only the uniqueness of cryogenic temperatures, but also the fundamental role of the parameter of T_g in non-equilibrium plasma chemistry is discussed using cryoplasmas.

On the other hand, plasmas in high-density fluids, such as high-pressure gases, liquids, and supercritical fluids (SCFs), are expected to become established as novel plasma sources possessing a highly non-equilibrium state. In these fluids, the interactions between molecules cannot be ignored and, particularly in SCFs in the vicinity of the critical point (CP), they show an anomalous behavior. In particular, the fluid structure exhibits high local density fluctuations and various phenomena such as transportation display an anomalous behavior near the CP (critical anomaly). Recently, SCF plasmas, in which the density fluctuations are preserved, have attracted much attention, with expectations to provide a unique reaction field [3]. In this thesis, the fundamental mechanisms of the generation of plasmas in high-density fluids with density fluctuations and the motion of charged particles in local density fluctuations, are discussed.

The purposes of the studies in this thesis are (A) to investigate the role of T_g in plasma chemistry, and (B) to clarify the role of the high-density condition and the density fluctuations on electrical breakdown, which precede the generation of plasmas in such conditions. By accomplishing these goals, a

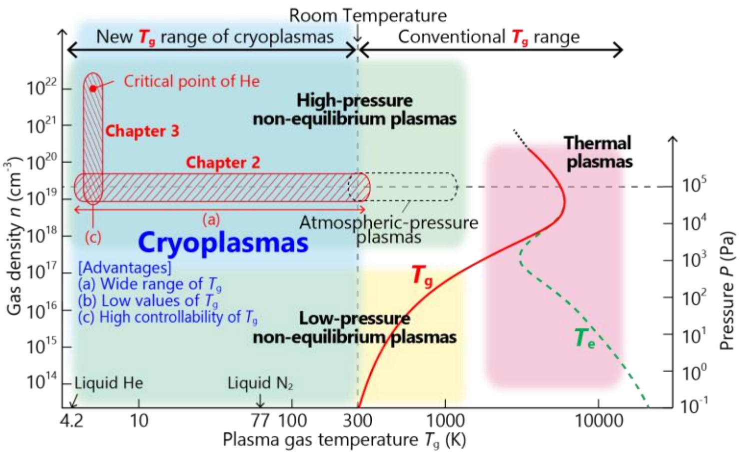

Fig. 1　Plasma gas temperature and gas density domains of cryoplasmas and chapters 2 and 3 with the T_g-n diagram.

better understanding of high-pressure non-equilibrium plasma chemistry and a more precise control of plasmas in high-density fluids is expected to be realized. I think that these points are important for realizing applications based on high-pressure non-equilibrium plasmas for materials processing or other fields, as well as answering fundamental questions related to plasma physics and chemistry.

Ranges of the plasma gas temperature T_g and the gas density n for each chapter are indicated in Fig. 1. For these purposes, the advantageous properties of the cryoplasmas were utilized. The advantage of cryoplasmas of a wide range of T_g [(a) in Fig. 1] was used in Chapter 2 to discuss the variation of the plasma chemistry, and the high controllability of T_g [(c) in Fig. 1] was used in Chapter 3 to generate plasmas in the conditions near the CP in gas, liquid, and supercritical fluids (SCFs). In both chapters 2 and 3, helium (He) gas was used because of its many advantages, such as the lowest boiling point and monatomic gas.

2. Gas-temperature-dependent plasma chemistry

To investigate the role of T_g in plasma chemistry, fundamental diagnostics of He cryoplasmas and their discussion using a reaction model developed in this study were conducted.

At first, T_g, which represented the most important parameter in this study, was evaluated by laser heterodyne interferometry (LI) and thermal simulations, and as a result, the increment of T_g in plasmas in metal electrodes (diameter: 2 mm) with a power consumption of around 30 mW was estimated to be suppressed below around 10 K. By time-resolved optical emission spectroscopy (OES), the differences in the timings showing the maxima of the waveforms of the current, the He emission intensity, and the N_2^+ emission intensity were observed, which were unique to cryogenic temperatures (Fig. 2). In the laser absorption spectroscopy (LAS) measurements, the lifetime (>100 μs) and the density (~10^{12} cm^{-3}) of metastable He atom (He^m) at cryogenic temperatures were a few hundred times longer and several dozen times higher than those at room temperature, respectively.

In order to clarify the mechanisms of these experimental results, a reaction model for He with small amounts of impurities (N_2, O_2, and H_2O) was developed. The most striking feature of the model is that it takes into account the dependencies of the reaction rate constants of elemental reactions and the diffusion constants of the species on T_g. By using the reaction model, the experimental results of OES and LAS were reproduced quasi-quantitatively or qualitatively. In addition, the contributions and the ratio of impurity species were evaluated.

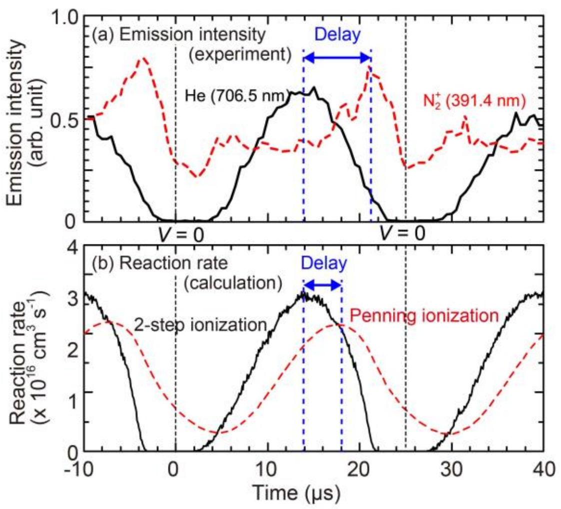

Fig. 2 Time variations of (a) emission intensities of He and N_2^+ (experimental results) and (b) reaction rates of 2-step ionization of He and Penning ionization of N_2 (results of numerical simulation) at T_g = 54 K (ambient temperature: 40 K).

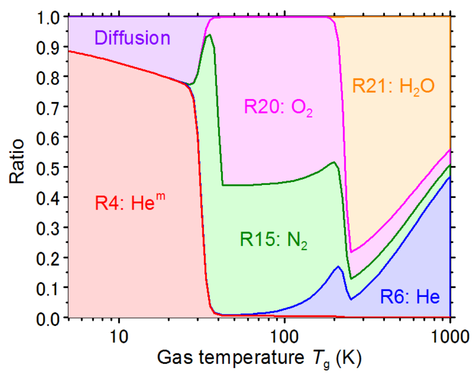

Fig. 3 Cumulative line chart of ratios of the quench frequencies of He^m due to reactions and diffusion as a function of gas temperature T_g.

Finally, the total reactions in He/N_2 and the quench mechanisms of He^m in He/N_2/O_2/H_2O were discussed by using the reaction model for further discussion on plasma chemistry and its dependency on T_g. As a result, both the drastic variation due to phase changes and the gradual variation due to continuous variation in collision parameters (collision frequency, collision cross section, etc.) were confirmed in the plasma chemistry. The dominant species and elemental reactions transforming with decreasing T_g and how the plasma chemistry depend on T_g were clarified (Fig. 3). Even in the T_g range in which the drastic variations of the plasma chemistry do not appear, both absolute values and relative ratios of quench frequencies due to each reaction or diffusion were affected by the variation of T_g. Therefore, it was suggested that the dependency of the plasma reaction should not be ignored not only at cryogenic temperatures, but also above room temperature.

Thus, the role of the “new” parameter T_g for non-equilibrium plasmas was discussed and the importance of T_g was clarified. In He gas, the three-body reaction of He^m with He atoms, which needs a low activation energy comparable to the energy of room temperature, was the most important elemental reaction. In addition, other reactions also showed a variety of T_g dependencies. By the combination of the variations in elemental reactions and the transition of phases, a dynamic variation in the plasma chemistry depending on T_g was caused. For other gas systems, although T_g might be less important compared to T_g for He plasma chemistry, the discussion about T_g should be inevitable to understand plasma chemistry and to control plasma reactions precisely.

3. Electrical breakdown in high-density fluids

In this chapter, we focused on the critical anomaly of the breakdown voltages (U_B) in micrometer gap discharges. The experiments near the critical temperature of He (5.2 K) were enabled by using the temperature controllability of cryoplasmas.

By the improvements of experimental methods, the critical anomaly of U_B was clearly confirmed, and the number and the dispersion of the measured values of U_B were improved sufficiently to be able to discuss the discharge models developed in this study by fitting analyses (Fig. 4).

Three models for reproducing the electrical discharge behavior near the CP were developed. In the first, the power law of a parameter of F_D, which indicates the magnitude of the density fluctuations, was extended to the liquid phase. For this, a bubble model considering electron bubbles generated in liquid He was modified by multiplying the power law of F_D. While further improvement of the electrical discharge model will be necessary for further physical discussions, the existence of the threshold density between gas-like and liquid-like breakdown mechanisms, and the validity of the power law of F_D were confirmed.

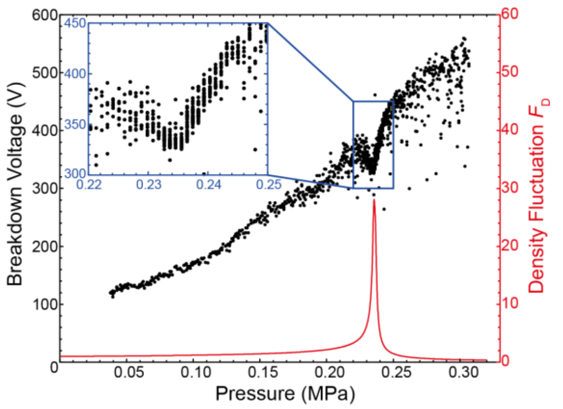

Fig. 4 Measured U_B (black dots) and density fluctuation F_D as a function of helium pressure at T_g = 5.25 K.

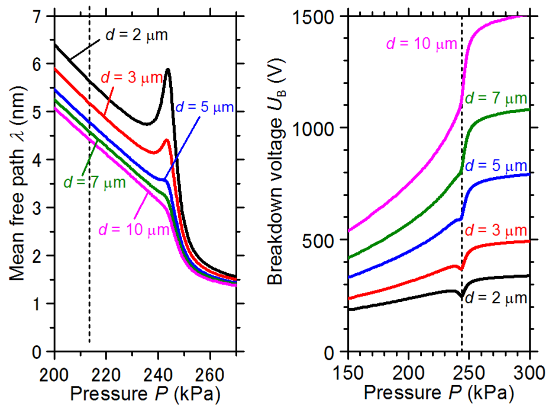

Fig. 5 (a) Calculated breakdown voltages U_B and (b) calculated electron mean free paths λ_{fluc} for different discharge gaps d as a function of the He fluid pressure P at T_g = 5.30 K.

The second model developed was a hard-sphere cluster model. A method to estimate the effective mean free path of electrons in density fluctuating fluids (λ_{fluc}) was proposed. The model is based on assuming that the gas-like local structure of the density-fluctuating fluid consists of artificial "super" atoms whose radius are proportional to the correlation length ξ. The λ_{fluc} estimated by this model and the measured U_B indicated a strong negative correlation. This implied that λ_{fluc} is one of key parameters to describe the electrical breakdown in the density-fluctuating fluids. However, the main drawback of this model was that it could not reproduce U_B quantitatively.

Finally, a local void model was proposed. In this model, instead of focusing on individual clusters, the cylindrical local low-density domains (voids) created by the density fluctuations were assumed to estimate λ_{fluc}. This model was based on the conventional Townsend discharge theory with modifications of the first Townsend coefficient α due to the variation of λ_{fluc}. In addition, the secondary emission coefficient γ was also modified in the model, to include the effect of ion-enhanced field emission (IEFE). The main characteristic of this model was that it included the size effect of the density fluctuations. The simulation results were in good agreement with the measured dependency of U_B on d, and the dependency was suggested to be caused by the behavior of λ_{fluc} (Fig. 5). Moreover, the roles of the density fluctuation and the high-density conditions on α and γ coefficients were discussed. The concepts of this model, such as the size effect of the density fluctuation and the evaluation of the electron motion, may enable a better reaction model in fluctuating fluids.

4. Conclusion

Using the advantageous characteristics of cryoplasmas, the role of T_g in high-pressure non-equilibrium plasmas and the roles of high-density condition and density fluctuations in electrical breakdown were discussed.

The influence of T_g, whose role in plasma chemistry has not been studied sufficiently up to now, was investigated. The dependency of the high-pressure plasma chemistry on T_g were studied using He cyoplasmas over a wide T_g range by a combination of experiments and numerical simulations. In high-pressure plasmas, He^m, which possesses a high potential energy, was the key species. From the discussion, it was suggested that the dependency of He plasma chemistry on T_g was mainly governed by the variation in the reaction rate constants related to the collision between He^m and other neutral species and the phase change of impurity species.

Moreover, the generation mechanisms of high-pressure plasmas in density fluctuating fluids were discussed using the T_g controllability of cryoplasmas. At first, the discharge model for liquid He was introduced and discussed, and the measured U_B was reproduced successfully. Then two models describing the physical fluid structure of the density fluctuations were proposed. From the discussion with the local voids model, it was implied that the critical anomaly of U_B was caused by the variation of λ_{fluc} in locally low-density domains and the size effect of the density fluctuation caused the critical anomaly of U_B.

Thus, the role and importance of the "new" parameter in high-pressure non-equilibrium plasmas, T_g, was clearly demonstrated, and by controlling T_g, the role and importance of the local fluid structure in discharge physics in high-pressure (and close to condensed) conditions were revealed. The results presented in this thesis are expected to allow a more accurate control of the plasma generation and the plasma chemistry in high-pressure non-equilibrium plasmas, such as atmospheric pressure plasmas and SCF plasmas, which may lead to novel applications of plasma-based materials processing.

References

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