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Gas-Liquid Transition and Influence of Density Fluctuations in Supercritical Fluid Plasmas

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Supercritical fluids (SCFs) represent a unique state of matter that exists beyond the critical temperature and pressure, where the distinction between gas and liquid phases disappears. These fluids exhibit properties intermediate between gases and liquids, including high density comparable to liquids (~200-1000 kg/m^3), gas-like diffusivity, and continuously tunable properties through pressure and temperature control. The most notable characteristic of SCFs is the presence of extremely strong density fluctuations near the critical point, creating an environment where traditional plasma physics models require fundamental reconsideration.

The exploration of plasma generation in supercritical fluid environments has emerged as a frontier in plasma science, offering insights into the continuity of phase transitions in ionized matter [1]. This research field encompasses two distinct categories: "plasmas in supercritical fluids," where discharges are generated within SCF environments potentially causing local phase changes, and "supercritical fluid plasmas," where the microscopic fluidic structure and density fluctuations of the SCF remain largely unperturbed by the plasma generation process.

Our systematic investigations have revealed notable phenomena occurring near the gas-liquid transition boundary. The breakdown voltage characteristics exhibit significant deviations from Paschen's law, particularly for micrometer-scale electrode gaps. For CO_2 near the critical point, when electrode gap distances are reduced to a few μm, the breakdown voltage shows a pronounced local minimum at pressures around 7 MPa. This behavior has been consistently observed across different molecular systems including CO_2, H_2O, Xe, He, and air suggesting a universal mechanism related to density fluctuations rather than specific molecular properties [1,2].

The fundamental physics underlying these phenomena involves the formation of microscopic density inhomogeneities due to clustering effects near the critical point. These fluctuations create regions of locally reduced density where electrons can gain sufficient kinetic energy for ionization through enhanced mean free paths. Our theoretical modeling incorporating the concept of a modified electron mean free path in density-fluctuating media shows excellent agreement with experimental observations [2].

The influence of density fluctuations extends beyond breakdown characteristics to affect plasma chemistry and reaction pathways. Near the critical point, the large correlation length and enhanced molecular clustering create unique reaction environments where collision-controlled and diffusion-controlled regimes converge. This convergence leads to maximized reaction rate coefficients, explaining the enhanced synthesis yields observed for various nanomaterials near critical conditions.

Supercritical fluid plasmas have demonstrated potential for advanced materials synthesis. The unique combination of high SCF density and plasma reactivity enables the synthesis of novel carbon nanostructures, including higher-order diamondoids - nanometer-sized diamond molecules that are difficult to synthesize through conventional methods. Using dielectric barrier discharge microplasmas in supercritical xenon and CO_2, we have successfully synthesized diamantane (the second diamondoid) from adamantane precursors, with reaction yields maximized near the critical pressure where density fluctuations peak.

Recent developments have explored surface dielectric barrier discharges in supercritical fluids, revealing field-emission-assisted discharge regimes that emerge at high pressures. These discharges exhibit distinct operational modes reflecting the gas-liquid transition: streamer-like behavior below ~1 MPa transitioning to Townsend-like discharges at higher pressures, with field emission dominating above ~2 MPa. Notably, when carbon nanotubes are employed as electrodes, enhanced optical emission intensity and distinct atomic emission line spectra are observed, indicating that field emission effects are significantly amplified in these discharge configurations [3].

This presentation will provide a comprehensive overview of how density fluctuations influence plasma physics across the gas-liquid transition boundary in supercritical fluids. I will discuss the theoretical framework for understanding breakdown phenomena near critical points, the role of clustering in modifying electron transport properties, and the implications for plasma-assisted materials synthesis. The discussion will emphasize how the continuity of phase transitions in SCFs offers unique opportunities to study plasma behavior in intermediate states between traditional gas and liquid environments.

References

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[3] H. Muneoka, R. Ohta, S. Stauss, and K. Terashima, Plasma Sources Sci. Technol. 28 (2019) 075014.