

SUPERCRITICAL DIELECTRIC FLUIDS FOR HIGH POWER DENSITY APPLICATIONS

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To my beloved family

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LIST OF SYMBOLS AND ABBREVIATIONS

SCF	Supercritical Fluid
CB	Circuit Breaker
DC	Direct Current
UHV	Ultra-high Vacuum
EoS	Equation of State
EEDF	Electron Energy Distribution Function
E_{bd}	Breakdown Electric Field
V_{bd}	Breakdown Voltage
P	Pressure
T	Temperature
ρ	Density
σ	Conductivity
ε	Permittivity
ω	Mass Fraction
α	Ionization Coefficient
η	Attachment Coefficient
$\sigma(\varepsilon)$	Electron Scattering Cross Section
ε	Electron Energy
α/N	Density-reduced Ionization Coefficient
η/N	Density-reduced Attachment Coefficient
$(\alpha - \eta)/N$	Density-reduced Effective Ionization Coefficient
$(E/N)_{cr}$	Density-reduced Critical Electric Field

γ	Secondary Electron Emission Coefficient
E_{cr}	Critical Electric Field
F_a	Modulus Rupture
P_c	Critical Pressure
T_c	Critical Temperature
T_e	Experimental Temperature
T_r	Room temperature
P_a	Atmospheric pressure

SUMMARY

The objective of the proposed research is to further the fundamental understanding of dielectric properties of supercritical fluids and their mixtures, especially near the critical point. The electron kinetic process and Boltzmann analyses are conducted on different substances to investigate their dielectric properties. The breakdown characteristics of pure supercritical fluids and their mixtures are investigated and demonstrated experimentally in uniform electrostatic field. Investigations on dielectric properties of promising candidate supercritical fluids and mixtures, such as trifluoroiodomethane (CF_3I), oxygen (O_2), and perfluorinated nitriles, are conducted theoretically and experimentally. A theoretical method that combines the electron kinetics theory and the unique property of supercritical fluids at nanometer scale, also considers the mean free path of electrons, is developed. The method provides a new way to understand electrical breakdown characteristics of supercritical fluids by analyzing the mean free path of electrons and the cluster size. It also gives a quantitative evaluation of the critical anomaly of electric discharge in supercritical fluids. Research tasks discussed in this dissertation are expected to enable the design of numerous applications that require high power density, spanning from particle accelerators over X-ray radiography and radiotherapy to electrical power systems.

CHAPTER 1. PROBLEM STATEMENT

Typically, the choice of dielectric media has been limited to solids, liquids, gases, and vacuum. There is a wide range of applications that suffer from this limited choice of dielectric materials, especially for any application that requires a combination of withstanding strong electric fields, dissipating heat efficiently, and allowing for fast motion. Traditional dielectric media lack at least one of these three requirements. However, it has been recognized that supercritical fluids have the potential to satisfy all these criteria since they combine high dielectric strength, low viscosity, and excellent heat transfer capabilities.

Although pure supercritical fluids have drawn much attention because of their advantageous properties as a dielectric medium, no study has thus far reported any dielectric properties of supercritical fluid mixtures. The blending of supercritical fluids allows adjusting and balancing the material properties, including the critical temperature and pressure. This dissertation focuses on investigating the dielectric strength and the breakdown characteristics of supercritical fluids, especially their mixtures for applications with higher levels of power density and reliability.

CHAPTER 2. STATE OF THE ART

2.1 Overview of supercritical fluids

Supercritical fluid (SCF) describes the state a substance in which the temperature and pressure are above their respective critical points, i.e., where $T \geq T_c$ and $P \geq P_c$, as shown in Figure 1 [1]. At the critical point, the heat of vaporization reaches zero. A stationary inflection point in the isothermal lines on a P - V phase diagram can be observed, which defines the critical point as in equation 1 [2]:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad (1)$$

where V is the volume, P is the pressure, and T_c represents the critical temperature. Above the critical point, phase boundaries between gas and liquid vanish, and the substance assumes a single supercritical phase.

SCFs are widely studied and applied in the field of chemistry, due to favorable properties in diffusivity, solubility, and density. Traditionally, chemical applications of SCFs include extraction of products from natural materials, polymer processing, and drying [3-5]. Beyond chemical applications, SCFs have also drawn much attention because of enabling current and emerging applications as heat transfer fluids in concentrating solar power, solar water heater, and carbon capture and storage [6-8].

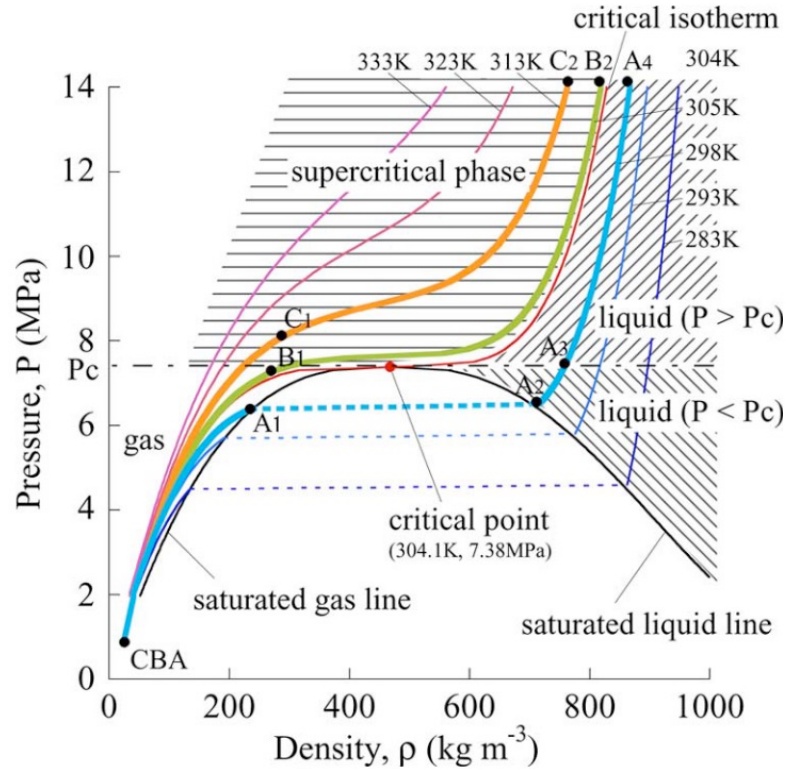


Figure 1 – A phase diagram of CO_2 . It shows the density versus pressure relation for CO_2 as a parameter of temperature [1].

2.1.1 Transport properties of SCFs

In general, SCF represents the intermediate state of matter between liquid and gaseous states. As an example, Figure 2(a) shows a density-pressure ($\rho - P$) diagram of carbon dioxide (CO_2) with isothermal lines. The critical point for CO_2 is represented by the yellow dot at $T_c = 304.1\text{ K}$, $P_c = 7.39\text{ MPa}$ [9]. Small changes in the CO_2 pressure result in large changes in the density near the critical point. During phase change of CO_2 at a constant pressure below the critical pressure ($P < P_c$), CO_2 transits from liquid to vapor for all temperature values. On the other hand, when CO_2 is at a constant pressure above the critical pressure ($P > P_c$), it can condense into the liquid state by cooling, but it cannot achieve the gaseous phase by merely heating the fluid.

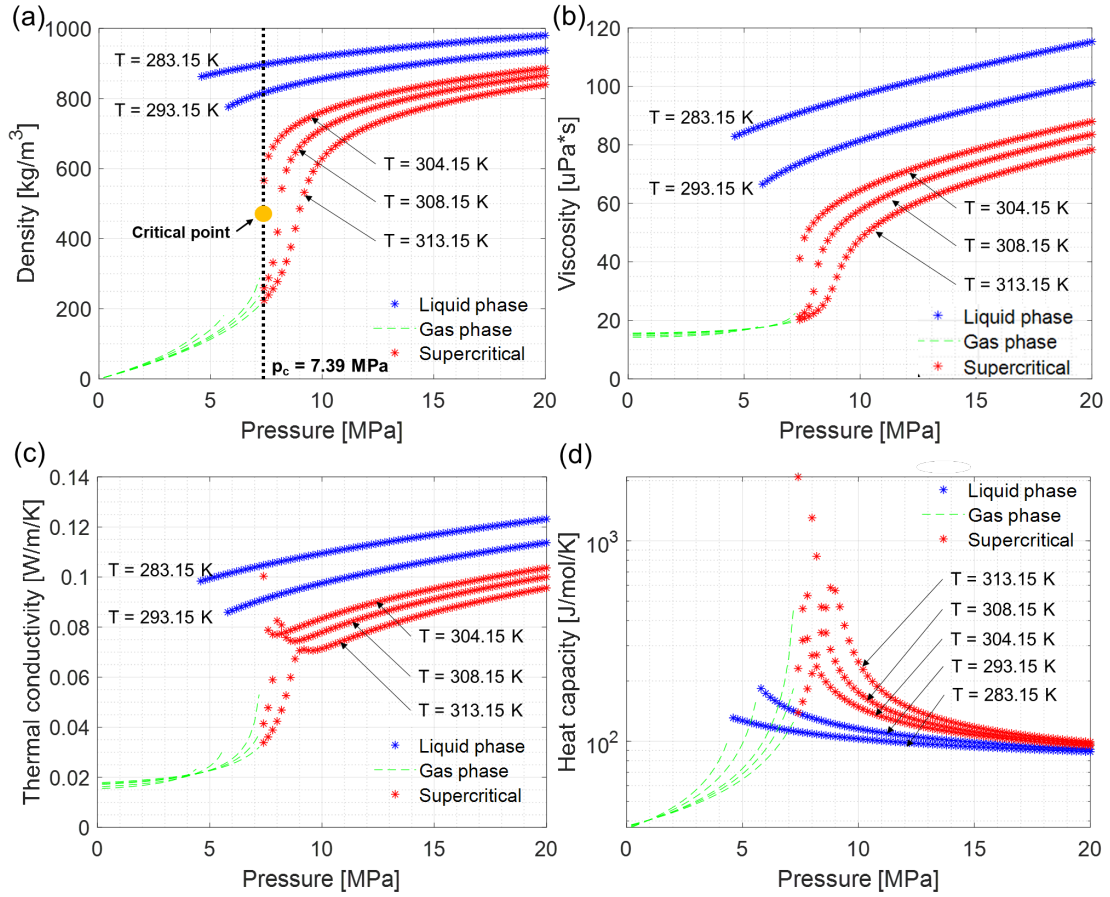


Figure 2 – (a) Density – pressure ($\rho - P$) diagram of carbon dioxide (CO_2) with isothermal lines. The critical point for CO_2 is represented by the yellow dot at $T_c = 304.1 \text{ K}$, $P_c = 7.39 \text{ MPa}$. (b). Comparison of the viscosity of CO_2 in three different states. The viscosity of SCFs lies between that of liquids and gases. (c). Comparison of thermal conductivity of CO_2 , and (d) compares the heat capacity of CO_2 in gaseous, liquid, and SCF. Green dashed lines represent the fluid in the gaseous phase. Blue and red asterisks represent the fluid in the liquid phase and the supercritical state, respectively [10].

Many of the physical properties of SCFs, such as density and viscosity, are between those of liquids and gases, as shown in Figure 2(a) and Figure 2(b). While this is not true for some other properties like thermal conductivity and heat capacity, which exhibit a maximum near the critical point, as shown in Figure 2(c) and Figure 2(d).

2.1.2 Unique structural characteristics of SCFs

One of the intriguing characteristics of SCFs rests in the anomalous behavior of fluids near the critical point. As mentioned in the previous section, some physical properties like thermal conductivity and heat capacity reach maximum values in the vicinity of the critical point. Similar anomalies have also been reported in the electrical discharge area. For example, the decrease of breakdown voltages for micrometer-scale gap electrodes, the local decrease of the plasma temperature, and the local maxima of atomic emission intensities generated by pulsed laser ablation plasmas, are all observed near the critical point. Such critical anomalies can be further explained and investigated from the microscopic point of view by molecular clustering, as well as the macroscopic point of view by density fluctuation.

The formation of clusters greatly influences the transport properties and the structures of SCFs. Comparing with clusters in solids and liquids, clusters in SCFs consist of molecules with relatively weak intermolecular forces such as van der Waals forces. Also, the average cluster lifetime in SCF is much shorter than that in solids and liquids. The cluster size and the number of molecules in an SCF cluster can be calculated from the Ornstein-Zernike correlation length ξ . According to the Ornstein-Zernike theory, the correlation length ξ can be determined experimentally from the characterization of the material using Small Angle X-ray Scattering (SAXS) [11]:

$$I(s) = \frac{I(0)}{1 + \xi^2 s^2} \quad (2)$$

where $I(s)$ is the scattering intensity, and $I(0)$ is the zero-angle scattering intensity at $s = 0$. s is a measure of the scattering angle defined as:

$$s = \frac{4\pi \sin \theta}{\lambda} \quad (3)$$

where θ is the scattering angle, and λ is the X-ray source wavelength.

Data obtained from the SAXS experiment are also related to density fluctuation F_D , which quantifies the extent of the molecular clustering [11]:

$$F_D = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} = \frac{I(0)}{N} \frac{1}{Z^2} = \frac{(n_s V)^2}{n_{ave} V} = \frac{k_T}{k_T^0} \quad (4)$$

where N is the total number of particles in a given volume V , $\langle N \rangle$ is the average of N , Z is the number of electrons in a molecule, n_s is the standard deviation of the local number density, n_{ave} is the average number density, k_T is the isothermal compressibility, and k_T^0 is the value of k_T for an ideal gas. Figure 3(a) schematically illustrates a fluid with negligible molecular clustering and density fluctuation. Figure 3(b) represents a fluid under the condition where the density fluctuation F_D is large.

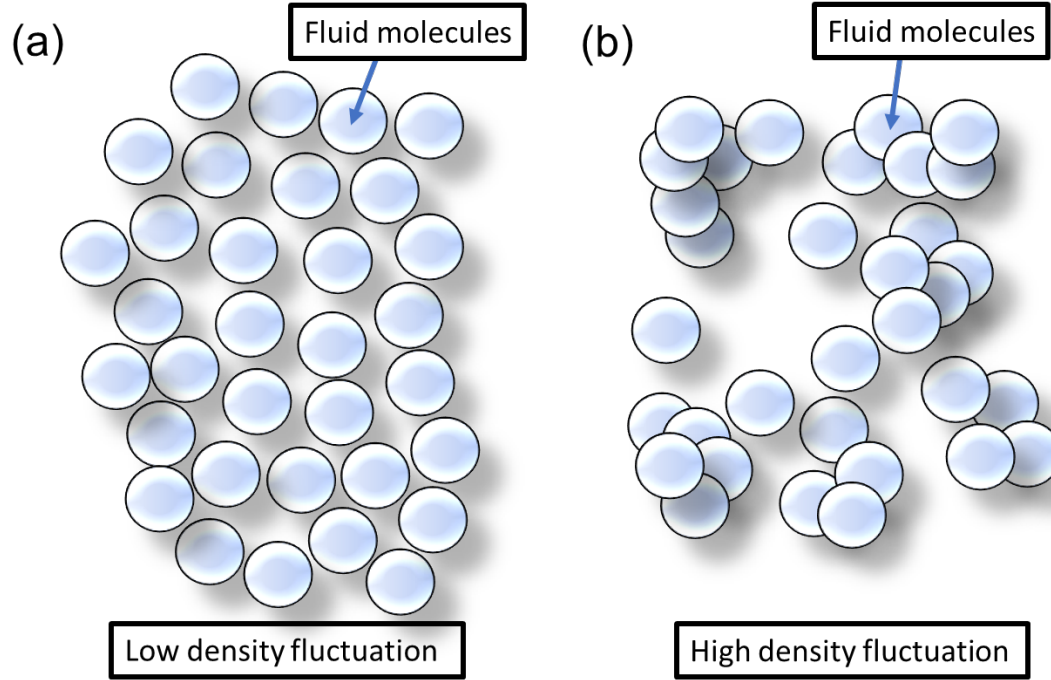


Figure 3 – Schematics of (a) the fluid with molecules with low density fluctuation F_D value, and (b) the fluid with molecules under the condition where the formation of clusters and the density enhancement are substantial, thus the fluid has a high density fluctuation F_D value.

2.1.3 Supercritical fluid mixtures

The mixing laws of the ideal gas mixture are well known as Amagat's law and Dalton's law. Amagat's law states that the volume of an ideal gas mixture is equal to the sum of the component volumes of each individual component in the gas mixture at the same temperature and total pressure of the mixture [12]. The mathematical expression of Amagat's law is:

$$V_{mixture} = V_1 + V_2 + V_3 + \dots + V_N = \sum_i V_i \quad (5)$$

where $V_{mixture}$ is the total volume, and $V_1, V_2, V_3 \dots V_N$ are considered to be the partial volumes of components in the gaseous mixture.

Dalton's law states that in a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressure of the individual gases [13]. Mathematically, Dalton's law can be defined as:

$$P_{mixture} = P_1 + P_2 + P_3 + \dots + P_N = \sum_i P_i \quad (6)$$

where $P_1, P_2, P_3 \dots P_N$ represent the partial pressure of each component, and $P_{mixture}$ is the pressure of a mixture.

It should be noted that both Amagat's law and Dalton's law predict the properties of ideal gases. For real gases, the results are different. Dalton's law of partial pressures takes the assumption that the components in the mixture do not interact with each other, and each component applies its own pressure independently. As a result, the sum of the pressure of each component is the total pressure. Similarly, Amagat's law assumes that the volumes of each component are additive at the same temperature and pressure. The interactions of different components equal the average interactions of the components [14].

As for the liquid, the mixing law is mainly illustrated by Raoult's law. Raoult's law states that the partial pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture [15]. Raoult's law only applies to the ideal mixture of liquids. Mathematically, Raoult's law equation is written as:

$$p_i = p_i^* x_i \quad (7)$$

where p_i is the partial pressure of the component i in the mixture, p_i^* is the equilibrium vapor pressure of the pure component i , and x_i is the mole fraction of the component i in the mixture [16].

For a mixture of liquids A and B, the above equation reads:

$$\begin{aligned} p_A &= p_A^* x_A \\ p_B &= p_B^* x_B \end{aligned} \quad (8)$$

In this equation, p_A and p_B represent the partial vapor pressure of the components A and B. When the components in the liquid mixture have reached equilibrium, the total vapor pressure of the solution can be determined by Raoult's law to give:

$$p = p_A + p_B = p_A^* x_A + p_B^* x_B \quad (9)$$

where p is the total vapor pressure of this liquid mixture.

While the mixing laws of both gas and liquid have been widely accepted and studied, the mixing law of SCF remains not extensively investigated. Traditionally, SCF binary mixtures have been implemented in applications such as carbon capture or SCF injection, where mixtures of multiple SCF species are required. SCF binary mixtures, for example, have been used to modify the solvation character of the fluid. Other major applications of SCF binary mixtures are optimizing the processes of extraction, separation,

or chemical reaction by taking advantage of the tuning solubility property of SCF mixtures [17]. There are relatively few studies devoted to exploring the possibility of utilizing SCF mixtures for dielectric purposes.

SCF mixtures are able to achieve a more optimal trade-off between dielectric strength, viscosity, and thermal characteristics. Just as important, mixtures can exhibit a lower critical temperature than each of its constituents, if they form an azeotropic blend [18]. This property is important because it allows for a wider range of applications. Some reports in the literature suggest that such a mixture could provide improved properties and more potential applications than the pure substance. Kravanja et al. evaluated the heat transfer performance of the $\text{CO}_2\text{--C}_2\text{H}_6$ azeotropic mixture under supercritical conditions. Their results revealed that the heat transfer coefficient of the $\text{CO}_2\text{--C}_2\text{H}_6$ azeotropic mixture fell between the values for pure CO_2 and C_2H_6 , which proves that such a mixture has the capability to be used as an alternative fluid in heat power cycles [19]. Considering its thermal properties, the investigation of the dielectric properties of such mixtures would be an imperative task in order to show the feasibility of a SCF as a promising dielectric medium.

2.2 Supercritical fluids as a dielectric medium

From the literature review, it can be shown that SCFs combine the advantages of both gases and liquids. Their potential for outstanding dielectric strength, efficient heat transfer, and low viscosity could enable the design and operation of numerous applications that require high power density, spanning from particle accelerators over X-ray radiography and radiotherapy to electrical power systems.

Supercritical fluids can be considered as matter in an intermediate state between gas and liquid and have been recently considered for being used as insulating media owing to properties that show exceptional dielectric strength, high heat transfer capability, and low viscosity. SCFs have been widely implemented and studied in chemistry because of their advantageous properties in chemical and material processing [5, 20, 21]. Newer applications include the use of SCFs in combination with electrical discharge. The investigation of electric discharge in SCFs has been a continuing effort for decades, yet most studies are related to the generation of electric plasmas in SCFs for chemical synthesis and nanomaterials fabrication [22, 23]. There are few reports on utilizing SCFs as dielectric media for power applications. As a relatively new field of research, the feasibility of SCFs to replace conventional insulating media has come into public notice. However, data specifically about the dielectric and insulating characteristics of SCFs are still scarce. Therefore, the main objective of this section is to compare and summarize available literature related to dielectric properties of SCFs, and present recent progress on the effective characterization methods for evaluating dielectric properties of SCFs.

2.2.1 Breakdown characteristics of SCFs

Experimental investigations on the dielectric property of SCFs always require the testing apparatus to have the capabilities to endure high temperature and high pressure while maintaining sufficient sealing capabilities. Stainless steel has been commonly chosen as the material of the main body. If measurements involving the optical method is required, such as SAXS or laser schlieren, optically transparent materials including sapphire [24], diamond [25], quartz [26], and zinc selenide (ZnSe)[27] have been used as the observing window on the testing apparatus.

The electrical breakdown characteristics of SCFs have been investigated under different conditions and methods, as summarized in Table I. The discharge phenomenon in SCFs has usually been compared with the established theory of gas discharge known by the work of Townsend and Paschen [28, 29]. Dielectric breakdown is not only important for insulation purposes but also crucial for semiconductor device/circuit/system reliability. For example, Zhang *et al.* focuses on simulators which calculate how dielectric breakdown impacts the lifetime of circuit under various scenarios [30-34]. The gas discharge theory illustrates that under a uniform electric field, the breakdown voltage V_{bd} can be expressed as [29]:

$$V_{bd} = \frac{BPd}{\ln \left[\frac{APd}{\ln \left(\frac{1}{\gamma} \right)} \right]} \quad (10)$$

where A and B are constants about a specific gas type determined by experiments, γ is the third Townsend ionization coefficient which represents the average of secondary electron emissions per positive ion hitting the cathode, P is the pressure, and d is the electrode gap.

Given that the type of gas and the material of the cathode are determined, and A , B , and γ are known, V_{bd} is only the function of the product of pressure P and gap distance d . However, the theory only applies well at the situation of the discharge test at a low pressure, with a small Pd value. Under the circumstance where the discharge happens in a highly dense medium like SCF, especially when the electrode gap distance is below 10 μm , V_{bd} starts to deviate from values estimated from Paschen's law. Particularly, in the vicinity of the critical point, this breakdown anomaly is more notable by showing a local decrease in breakdown voltage. Such breakdown anomaly near the critical point has been found and

reported by Ito *et al.* under the DC discharge in supercritical CO₂, with gap distances d of 1 μm and 10 μm [35, 36]. Similarly, Sawada *et al.* conducted experiments on supercritical H₂O and Xe and found the anomalous breakdown behavior near the critical point with a coplanar film electrode setup in a 1 μm gap [37]. Supercritical He has also been reported to exhibit such breakdown anomaly by Muneoka *et al.* with tungsten electrodes separated by a 3 μm gap [38]. The formation of molecular clusters can explain this breakdown anomaly, given the increased electron mean free paths near the critical point. In a supercritical state, the microscopic structure of the fluid is characterized by inhomogeneity in the molecular distribution due to the distinct clusters of molecules. Especially, under the conditions close to the critical point, the density fluctuation F_D increases substantially due to constant aggregation and dispersion of clusters, which affects the breakdown strength significantly.

Electrical conductivity σ quantifies how strongly the material conducts electric current. It is defined as the ratio of the density of the current to the electric field [39]:

$$\sigma = \frac{J}{E} \quad (11)$$

where J is the current density, and E is the electric field. In the case that the SCF is considered as the dielectric medium, positive and negative ions are the main current carriers. The current density is determined by the formula [40]:

$$J = qnv_a \quad (12)$$

where q is the charge of carriers, n is the density of charge carriers, and v_a is the average speed of the charge carrier's movement.

There are few reports on the electrical conductivity of SCFs available in the literature. In general, the values of the electrical conductivity σ of SCFs are very low. Hefner *et al.* conducted the electrical conductivity measurement of supercritical mercury (Hg), and σ values are below 10^{-1} S/m [41]. Like the anomalous behavior observed in the electrical breakdown, the electrical conductivity also exhibits such critical anomaly near the critical point. Hoshino *et al.* found the electrical conductivity of selenium (Se) drops sharply toward more insulating behavior in supercritical state [42].

Another important parameter that helps to understand the dielectric properties of SCFs is the complex permittivity ε , which represents the material's ability to respond to the electric field by its polarization. The complex permittivity ε has the real component ε' and the imaginary component ε'' such that:

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad (13)$$

where the real part ε' quantifies the charge storage capacity, and the imaginary part ε'' attributes to bound charge and dipole relaxation phenomena.

Studies on the permittivity of SCFs are also very scarce. Testemale *et al.* observed that the permittivity of water shows a decrease as getting closer to the critical point [43]. Skaf *et al.* performed a theoretical analysis of the permittivity of supercritical water. Their result shows the highest relative permittivity of 16.3 at 650 K [44].

Zhang *et al.* investigated the breakdown strength, dielectric recovery, and arc interruption capability of the supercritical N₂ [45, 46]. To analyze the breakdown voltage of supercritical N₂, Zhang *et al.* used three pulsed voltage sources with relatively slow, moderate, fast voltage rising edges. Their breakdown result indicates that for a low pd value, the measured E_{BD} matches the prediction by Paschen's law. When the pd value gets higher, the streamer inception criterion gives a better prediction in supercritical N₂. In general, the breakdown voltage of supercritical N₂ increases with pressure and saturates at higher pressure. The measured E_{BD} in supercritical N₂ reached as high as 180 kV/mm. In addition to the breakdown strength, the dielectric recovery capability of supercritical N₂ is analyzed by Zhang *et al.* with a thermodynamic model and experimental methods. As a result, the model estimates that the recovery time of the supercritical N₂ based switch is five times shorter than that of an air plasma switch. According to experimental results, the recovery breakdown voltage increases with N₂ pressure and gap width, and decreases at a higher repetition rate at a gap width of 0.25 mm.

Experimental investigations are conducted to investigate the current interruption capability of high-frequency (above 7 kHz) and low (below 500 A) current of the supercritical N₂ switch. Their result indicates the supercritical N₂ switch with fixed electrodes and a millimeter range gap distance can interrupt the current at approximately 2 ms after arc initiation, within a 2.2 mm gap. The value of the current rise slope first increases with pressure. However, it decreases with pressure when P is above 2 MPa. The voltage slope increases with pressure, which is consistent with the result in conventional gas media. The current is interrupted earlier with higher pressure and under forced flushing

situation. The result also shows that forced flushing can achieve faster recovery of the previous arc channel.

For studies involving supercritical N₂ based switches, although the breakdown voltage investigation of supercritical N₂ has been studied in detail, a more precise numerical model needs to be developed to predict the recovery rates. In addition, to further the study of the arc interruption of SCFs, a new SCF test setup with the capability to move electrode contacts and enable flushing medium should be considered.

2.2.2 Boltzmann analysis

The electrical breakdown characteristics of gaseous media can be analyzed by the electron kinetic process and estimated by the ionization (α) and attachment (η) coefficients. Boltzmann analysis has been widely used to obtain these coefficients theoretically [47]. In particular, the electron energy distribution function (EEDF) determines coefficients concerning electrons. The electron transport coefficients have been measured and tabulated as functions of the reduced electric field (E/N) for common gases [48].

The Boltzmann equation for an ensemble of electrons in an ionized gas is:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f - \frac{e}{m} \mathbf{E} \cdot \nabla_v f = C[f] \quad (14)$$

where f is the electron distribution in six-dimensional phase space, $\mathbf{v}$ are the velocity coordinates, e is the elementary charge, m is the electron mass, $\mathbf{E}$ is the electric field, ∇_v is the velocity-gradient operator, and C represents the rate of change in f due to collisions.

A common method to solve the Boltzmann equation is the two-term approximation. It expands f in terms of Legendre polynomials of $\cos(\theta)$ (spherical harmonics expansion) and then constructs from Equation 9 a set of equations for the expansion coefficients. This method has been widely investigated and used in different Boltzmann equation solvers, such as BOLSIG and ELENDIF [49, 50]. The calculation error of the transport coefficients and rate coefficients is acceptable for fluid discharge modeling in common discharge conditions, even though the method fails for high values of E/N when most collisions are inelastic, and f becomes strongly anisotropic [51].

The EEDF is calculated from the cross section data by solving the electron Boltzmann equation using the two-term approximation method. Generally, inelastic collisions require higher electron energy for their occurrence compared to elastic collisions. Thus, when comparing the dielectric strength, the gas that is supposed to have a higher dielectric strength should have the EEDF inclined to the left of the EEDF-electron energy figure compared to the gas that is expected to have a lower dielectric strength [52].

Dielectric properties of a gas can be explained by swarm parameters, including the density reduced ionization coefficient (α/N), the density reduced attachment coefficient (η/N), and the density reduced effective ionization coefficient ($(\alpha - \eta)/N$), which describe the kinetic process of electrons. Specifically, α indicates the number of ionization collisions per unit length, and η indicates the number of attachment collisions per unit length in the direction of the E/N .

The density reduced effective ionization coefficient ($(\alpha - \eta)/N$) indicates the net ionization collisions occurring in a gas. At low E/N range, $(\alpha - \eta)/N$ is negative because

the rate of electrons being attached to the neutral particles is generally greater than that of ionizing the neutrals. In contrast, at a higher E/N range, $(\alpha - \eta)/N$ is a positive value since the ionization is dominant.

The density reduced critical electric field $(E/N)_{cr}$ is defined as the E/N value when the rate of ionization and attachment collisions of free electrons are equal to each other. However, since the actual breakdown of gaseous media involves the secondary electron emission coefficient γ , $(E/N)_{cr}$ is not able to always provide the most accurate estimation of the actual breakdown voltage because the Boltzmann analysis does not take γ into consideration.

2.2.3 SCF breakdown modeling by the electron scattering cross section data

Haque *et al.* developed a correlation between the breakdown characteristic of SCFs and the clustering effect by analyzing the electron scattering cross section data of SCFs modified from those of gas. Boltzmann analysis is then used to estimate the dielectric strength based on the electron scattering cross section data of supercritical CO₂ clusters of various sizes. The density normalized ionization coefficients and density normalized attachment coefficients are determined by solving the Boltzmann equation with the two-term approximation [53-55].

The cross section data of clusters from those of gas are obtained from the following equation:

$$\sigma(N, W_{e0}) = \left[2\pi \int_0^{R_c} h \left\{ 1 - \exp \left[-n_0 \int_0^{2\sqrt{(R_c^2 - h^2)}} \sigma_0(1, W_e(x)) F(x) dx \right] \right\} \right] / N, \quad (15)$$

where W_{e0} is the initial electron energy upon impact, $\sigma(N, W_{e0})$ is the electron scattering cross section data of cluster, R_c is the radius of the cluster, n_0 is the molecular density of the cluster, $\sigma_0(1, W_e(x))$ is the electron scattering cross section data of gas, and $F(x)$ is the probability of secondary electrons produced by ionization processes escaping out of clusters [56]. Electron energy $W_e(x)$ at position x accounts for electron energy loss occurring inside clusters as the electron traverses along the electron trajectory. Electron energy loss in clusters is defined as:

$$W_e = W_{e0} - \int_0^x \left(\frac{dW_e}{ds} \right) ds, \quad (16)$$

where W_{e0} is the electron energy at the moment of impact with a cluster and $\frac{dW_e}{ds}$ is the energy loss rate of electron traversing in a cluster. Based on Bethe's formula, the electron energy loss rate is estimated from the following equation:

$$\frac{dW_e}{ds} \cong -\frac{\alpha_1 z}{W_e} \ln \left(\frac{\alpha_2 W_e}{z} \right) eV \text{ m}^{-1}, \quad (17)$$

where $\alpha_1 = \frac{K_1 q^2 n}{8\pi \epsilon_0^2}$, W_e is the electron energy, n is the atomic density of the cluster, K_1 is the empirical factor of correction, z is the atomic number, and q is the elementary charge.

Haque *et al.* numerically solved the Boltzmann equation. They obtained the density normalized ionization coefficient, the density normalized attachment coefficient, and the density normalized effective ionization coefficient from the modeled electron scattering cross section data of various cluster sizes near the critical point [53]. The cross section data of cluster size 25 are compared with those of gaseous CO₂. The result shows that the cross section data of clusters decrease from those of gases. Specifically, their result indicates that the $(E/N)_{cr}$ of supercritical CO₂ with cluster size of 25 falls to 55.6 Td from the 77.8 Td of gaseous CO₂.

Table 1 Representative research on the experimental demonstration of the electrical breakdown characteristics of SCFs

Investigator	Year	Test medium	Experimental demonstration			
			Experimental condition (P , T , ρ)	Experimental method	Electrode and gap distance (d)	Measured breakdown voltage / field (V_{bd} / E_{bd})
Furusato <i>et al.</i> [57]	2018	CO ₂	$\rho = 27.9 - 613.7 \text{ kg/m}^3$ $T = 306 \text{ K}$	Pulsed voltage rising rate = 0.7 kV/ns	Point-to-plane $d = 1 \text{ mm}$	$V_{bd} = 30 - 60 \text{ kV}$
Abid <i>et al.</i> [58]	2018	N ₂	$P = 0.1 - 9.8 \text{ MPa}$	DC	Sphere-to-sphere 10 mm diameter, $d = 20 \text{ mm}$	$V_{bd} = 60 - 450 \text{ V}$
Seeger <i>et al.</i> [59]	2017	Synthetic air, CO ₂ , CO ₂ /O ₂ mixture, and CF ₄	$P = 0.5 - 10 \text{ MPa}$	Impulse	$d = 5 \text{ mm}$	$E_{air_saturate} = 26 - 30 \text{ kV/mm}$ $E_{CO2_saturate} = 22 - 30 \text{ kV/mm}$ $E_{CO2/O2_saturate} = 40 \text{ kV/mm}$ $E_{CF4_saturate} = 20 - 30 \text{ kV/mm}$
Zhang <i>et al.</i> [46]	2015	N ₂	$P = 1 - 4 \text{ MPa}$	Impulse with 2 kV/ns, 2.5 kV/ μ s, and 1.66 kV/ms	$d = 0 - 1.2 \text{ mm}$	$E_{bd_max} = 180 \text{ kV/mm}$
Zhang <i>et al.</i> [45]	2014	N ₂	$P = 1 - 8 \text{ MPa}$ $T = 300 \text{ K}$	Impulse No flow and slight flow	$d = 0.18 - 0.5 \text{ mm}$	$V_{BD} = 70 \text{ kV}$
Yang <i>et al.</i> [60]	2014	CO ₂	$T = 305, 298, 293 \text{ K}$ $P = 7.5, 6 \text{ MPa}$	Pulsed voltage rising rate = 0.75 kV/ns	Sphere-to-sphere 10 mm radius, $d = 50 \mu\text{m}$	$V_{max} = 16 \text{ kV}$
Pai <i>et al.</i> [61]	2014	CO ₂	$P = 0.1 - 7.9 \text{ MPa}$ $T = 304.3 \text{ K}$	10 kHz AC	Surface dielectric barrier discharges setup, borosilicate glass thickness = 50 μm	$V_{saturate} = 2.5 \text{ kV}$
Ihara <i>et al.</i> [62]	2012	CO ₂	$P = 0.1 - 12 \text{ MPa}$ $T = 298, 305 \text{ K}$	Impulse	Needle-to-plane, tip radius = 5 μm $d = 5 \text{ mm}$	$V_{bd_max} = 30 \text{ kV}$
Ihara <i>et al.</i> [63]	2011	CO ₂	$P = 7.8 \text{ MPa}$ $T = 305 \text{ K}$	Impulse	Needle-to-plane, tip radius = 5 μm $d = 7 \text{ mm}$	$V_{bd} = 65 \text{ kV} / E_{bd} = 9 \text{ kV/mm}$
Kiyan <i>et al.</i> [64]	2011	CO ₂	$T = 313 \text{ K}$ $\rho = 50 - 600 \text{ kg/m}^3$	DC	Spherical with diameter of 5 mm and 20 mm; cone-to-cone 1 mm diameter tip $d = 140 \mu\text{m}$	$V_{bd_max} = 55 \text{ kV}$
Kiyan <i>et al.</i> [1]	2007	CO ₂	$P = 0.1 - 14 \text{ MPa}$ $T = 298, 305, 313 \text{ K}$	DC	Point-to-plane, tip radius = 35 μm $d = 200 \mu\text{m}$	$V_{bd_max} = 35 \text{ kV}$
Sawada <i>et al.</i> [37]	2006	H ₂ O and Xe	$P_{H2O} = 0.1 - 28 \text{ MPa}$ $T_{H2O} = 650.65 \text{ K}$ $P_{Xe} = 0.1 - 8 \text{ MPa}$ $T_{Xe} = 292.15 \text{ K}$	DC	Plane-to-plane (coplanar film electrodes) $d = 1 \mu\text{m}$	$V_{H2O_max} = 2.5 \text{ kV}$ $V_{Xe_max} = 0.8 \text{ kV}$
Lock <i>et al.</i> [26]	2005	CO ₂	$P = 8 \text{ MPa}$ $T = 310 \text{ K}$	DC	Point-to-plane and wire-to-plane $d = 110 \mu\text{m}$	$V_{bd} = 18 \text{ kV}$
Ito <i>et al.</i> [35]	2002	CO ₂	$P = 0.1 - 10 \text{ MPa}$ $T = 305.65, 308.15, 313.15 \text{ K}$	DC	Plane-to-plane (coplanar film electrodes) $d = 1, 10 \mu\text{m}$	$V_{bd} = 500 \text{ V}$

CHAPTER 3. RESEARCH OBJECTIVES

In many aspects, supercritical fluids show a dielectric behavior that is different from that of ideal gases. While the chemical and thermal properties of some supercritical fluids have been investigated and documented in the literature, only very few dielectric studies exist. In particular, there is no theory or data known that documents the breakdown characteristics of supercritical fluid mixtures. Thus, the objective of this dissertation is to further the fundamental understanding of the dielectric properties of supercritical fluids and their mixtures, especially near the critical point.

The primary objectives of this dissertation are:

- To identify and rank possible candidates of supercritical fluid insulation media considering the range of critical point value, the environmental impact, and the dielectric strength.
- To design and conduct experiments to investigate the breakdown characteristics and dielectric strength of supercritical fluids and their mixtures.
- To develop a model that provides an accurate estimation of the breakdown characteristics and gives a quantitative evaluation of the critical anomaly of electric discharge in supercritical fluids.

The outline of the succeeding chapters is listed below:

- Chapter 4 discovers the possible candidate of supercritical insulation media.

- Chapter 5 explores the dielectric strength of supercritical carbon dioxide and different supercritical fluid mixtures, including the azeotropic mixture and supercritical mixtures with strong electronegative substances.
- Chapter 6 presents an improved analytical model that provides the estimation of the breakdown characteristics and gives a quantitative evaluation of the critical anomaly of electric discharge in supercritical fluids.
- Chapter 7 draws the conclusion of this dissertation.
- Chapter 8 discusses the future work that needs to be studied to further the fundamental understanding of the dielectric properties of supercritical fluids.

CHAPTER 4. THE SELECTION OF POTENTIAL SCF CANDIDATES

4.1 Identify suitable candidates of SCF insulation media

Looking for promising candidates for SCF insulation media will be a continuous effort in order to advance the understanding of the dielectric strength of SCFs. When a substance is chosen as a dielectric medium, there are several factors to consider:

1. First, the substance should be easy to obtain and maintain, which means the critical temperature and the critical pressure should be within a certain range for technical applications.
2. Second, the substance should show satisfactory performance in breakdown strength when it is in the supercritical phase.
3. Third, the substance should exhibit low global warming potential and low ozone depletion potential.

Besides the above-mentioned factors, for electrical power applications, the SCF candidate should also be compliant with the following specifications:

- High heat dissipation;
- Low boiling point;
- Low toxicity;
- Fast arc-quenching capability;
- Compatible with electrical power applications (non-corrosive);

- Chemically inert;
- High stability;
- Market availability; and
- Easy to handle during maintenance work.

Some of these properties have been expanded to explain why it is necessary to include these in the requirements for a possible SCF candidate:

By definition, a critical point is a point on a phase diagram at which both the liquid and gas phases of a substance have the same density and are therefore indistinguishable [11]. At higher temperatures, the gas cannot be liquified by increasing the pressure alone. At the critical point, defined by a critical temperature T_c and a critical pressure P_c , phase boundaries vanish. Each substance has its own critical values. It is important to choose a supercritical dielectric fluid substance whose critical temperature and pressure are easily achievable. Figure 4 shows critical points of different substances in a pressure-temperature diagram [10]. The room temperature (between 20 and 26 °C) is indicated as a solid yellow line.

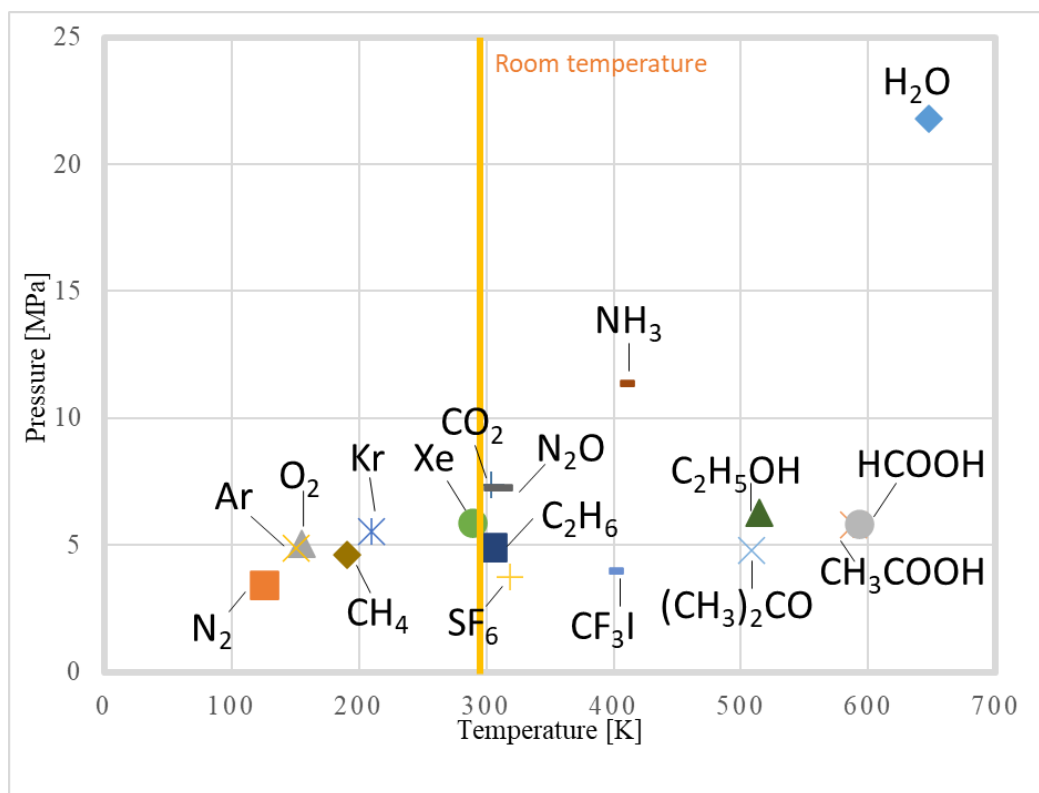


Figure 4 – Critical points of different substances. The yellow vertical line indicates the room temperature (298 K).

Another necessary property of the potential SCF candidate is that it should exhibit high dielectric strength. Electronegative gases are highly preferred in this context. It has been recognized that one process that offers high dielectric strength to a gas is the electron attachment in which free electrons get attached to neutral atoms or molecules to form negative ions. Negative ions like positive ions are too massive to produce ionization due to collisions, so the attachment gives an effective way of removing electrons which otherwise would have led to current growth and breakdown at low voltage [65, 66]. The gases in which attachment plays an important role are called electronegative gases. Those gases have the tendency of an atom to attract shared electrons to itself [67].

Table 2 – Comparison of critical points, GWP, and atmospheric lifetime of suitable substances.

	Molecular formula	T_c (K)	P_c (MPa)	GWP	Estimated atmospheric lifetime (Years)
Carbon dioxide	CO ₂	304.25	7.38	1	200
Ethane	C ₂ H ₆	305.3	4.90	5.5	12
Oxygen	O ₂	154.6	4.98	-	-
Hydrogen	H ₂	33	1.3	5.8	100
Trifluoroiodomethane	CF ₃ I	395.15	4.04	0.4	0.082
Fluoronitrile	C ₄ F ₇ N	395	2.5	2,100	22
Perfluoropentanone	C ₅ F ₁₀ O	419	2.14	1	0.044
Perfluorohexanone	C ₆ F ₁₂ O	441.8	1.87	1	0.014
Tetrafluoromethane	CF ₄	227	3.7	6,630	50,000
Hexafluoroethane	C ₂ F ₆	293	3.1	12,200	10,000
Perfluoropropane	C ₃ F ₈	345	2.6	8,830	2,600
Octafluorocyclobutane	C ₄ F ₈	388.2	2.78	10,300	3,200
Sulfur Hexafluoride	SF ₆	318.72	3.76	22,800	3,200

Perfluorocarbons, such as hexafluoroethane (C₂F₆), tetrafluoromethane (CF₄), perfluoropropane (C₃F₈), and octafluorocyclobutane (C₄F₈) as shown in Table 2, have attracted much attention as potential SF₆ alternatives due to their strong electronegative

property. However, the atmospheric lifetime of CF_4 and C_2F_6 reach as high as 50,000 and 10,000 years. Therefore, CH_4 and C_2F_6 are not suitable for SCF candidates. C_3F_8 , on the other hand, is harmless to O_3 in the atmosphere. It also has low toxicity, good thermal stability, and comparable dielectric strength to SF_6 [68, 69]. Similarly, C_4F_8 also exhibits high dielectric strength, non-toxicity, no O_3 destruction, and high thermal stability. It should be used with other buffer gas such as N_2 and CO_2 as the SF_6 alternative because of its high boiling point [70-72]. The disadvantage of C_3F_8 and C_4F_8 is that their global warming potential values are too high. Furthermore, a tiny amount of O_2 can promote the decomposition of C_4F_8 and generate COF_2 , which is a very toxic and corrosive substance [73]. Thus, C_3F_8 and C_4F_8 are not the ideal SCF candidate.

Table 3 – Major advantages and disadvantages of substances presented in Table 2.

	Molecular formula	Major advantages and disadvantages
Oxygen	O_2	It helps avoid carbon deposits; increase stability of medium after repeated dissociation.
Hydrogen	H_2	It helps increase thermal conductivity; increase arc stability.
Ethane	C_2H_6	It forms an azeotropic mixture with CO_2 ; decrease the critical temperature of the mixture.
Sulfur Hexafluoride	SF_6	Decomposition products are toxic.

The dielectric strength of trifluoroiodomethane (CF_3I) is comparable to SF_6 due to its excellent electronegative property. Besides, the global warming potential of CF_3I is only 0.4, which is far less than that of SF_6 . The C-I bond of CF_3I can be easily broken under UV irradiation [74]. Thus, its atmospheric lifetime is only thirty days. CF_3I also exhibits many benign properties: it is non-toxic and non-flammable. However, pure CF_3I suffers from a low vapor pressure, which can cause a severe problem for practical applications [75-77]. Therefore, buffer gases such as N_2 and CO_2 have been used to decrease the partial pressure of CF_3I . Even though the critical temperature of CF_3I is high, the critical temperature of the CF_3I - CO_2 mixture has been experimentally demonstrated to be lower than 100 °C [78]. Due to the excellent dielectric property and low environmental impact of CF_3I , it has been investigated as one of the SCF mixtures in this dissertation [79, 80]. The result is presented in Chapter 5.

Perfluorinated ketones ($\text{C}_n\text{F}_{2n}\text{O}$: $\text{C}_5\text{F}_{10}\text{O}$ and $\text{C}_6\text{F}_{12}\text{O}$), initially used as fire extinguishing substances due to their incombustibility, are recently found to be able to act as new eco-friendly and promising dielectric gases [81]. They both show very high dielectric strength, which is above the dielectric strength of SF_6 . $\text{C}_5\text{F}_{10}\text{O}$ and $\text{C}_6\text{F}_{12}\text{O}$ are unstable under UV radiation. Therefore, their atmospheric lifetime is extremely short. In addition, $\text{C}_5\text{F}_{10}\text{O}$ and $\text{C}_6\text{F}_{12}\text{O}$ do not cause any damage to O_3 . They also exhibit low greenhouse effects and other atmospheric environmental impacts. One major disadvantage of $\text{C}_5\text{F}_{10}\text{O}$ and $\text{C}_6\text{F}_{12}\text{O}$ is that their boiling points reach as high as the room temperature (about 27 °C). As a result, pure $\text{C}_5\text{F}_{10}\text{O}$ and $\text{C}_6\text{F}_{12}\text{O}$ cannot be used as SF_6 alternatives without adding other buffer gases with low boiling points. Extensive research has been conducted on the decomposition mechanism of $\text{C}_5\text{F}_{10}\text{O}$ and $\text{C}_6\text{F}_{12}\text{O}$ with N_2 , CO_2 , and air

[82]. The most common decomposition products include CF_4 , C_2F_6 , C_3F_6 , C_3F_8 , C_4F_{10} , C_5F_{12} , and C_6F_{14} . Although the global warming potentials of these decomposition products are much higher than those of $\text{C}_5\text{F}_{10}\text{N}$ and $\text{C}_6\text{F}_{12}\text{O}$, studies show that the concentration of decomposed products is very low under normal working conditions [83]. So, $\text{C}_5\text{F}_{10}\text{N}$ and $\text{C}_6\text{F}_{12}\text{O}$ are safe as insulating gases. Due to the benign dielectric properties and a lower critical temperature than $\text{C}_6\text{F}_{12}\text{O}$, $\text{C}_5\text{F}_{10}\text{N}$ has been chosen as one of the SCF mixture candidates in this dissertation.

Heptafluoroisobutyronitrile, $\text{C}_4\text{F}_7\text{N}$ (known as 3M NOVEC 4710 dielectric fluid), is one of the potential alternatives to SF_6 with a global warming potential value of 2100. $\text{C}_4\text{F}_7\text{N}$ exhibits an atmospheric lifetime of 22 years, and it has a zero ozone depletion potential. The dielectric strength of $\text{C}_4\text{F}_7\text{N}$ is two times higher than that of SF_6 under normal operating condition [84]. Similar to perfluorinated ketones, one of the disadvantages of $\text{C}_4\text{F}_7\text{N}$ is that it has a high boiling point at -4.7°C . Therefore, many studies have been conducted on $\text{C}_4\text{F}_7\text{N}$ mixing with CO_2 , N_2 , and dry air in power applications [85, 86]. Despite its high boiling point, $\text{C}_4\text{F}_7\text{N}$ has been proved to be a promising alternative to SF_6 in electrical insulation systems [87]. The latest research found that the dielectric strength of $\text{C}_4\text{F}_7\text{N}$ gas mixture containing 20% $\text{C}_4\text{F}_7\text{N}$ can reach that of pure SF_6 [88].

4.2 Substance ranking process

A systematic substance ranking process is required to identify the most suitable SCF substances for different applications. In this section, an analytical method called the Ashby method has been chosen and modified to rank the suitable SCF substances listed in Table 2. The Ashby method includes four steps [89]:

1. Translation: express design requirements as constraints and objectives;
2. Screening: eliminate substances that do not satisfy requirements;
3. Ranking: sort the substances based on objectives;
4. Supporting information: conduct detailed study of the top-ranked substances.

In order to rank the most suitable SCF substances, the objectives and the constraints in this study are listed in Table 4:

Table 4 – Objectives and constraints for identifying and ranking suitable SCF substances for power applications

Suitable SCF substances for power applications	
Objectives	• Minimize the difference between critical temperature and room temperature • Minimize the difference between critical pressure and atmospheric pressure • Minimize the environmental impact (GWP and atmospheric lifetime)
Constraints	• Good material compatibility (non-corrosive) • High dielectric strength • No Montreal protocol controlled substances (no ozone-depleting substances, such as CFCs and HCFCs) • Low toxicity • Chemically inert • Market availability • Easy to handle during maintenance work

The first objective is to minimize the difference between the critical temperature and room temperature. The critical temperature of a substance is defined as the maximum

temperature at which a gas can be liquified by pressure [2]. The van der Waals equation is given by:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = N_A k_B T \quad (18)$$

where V_m is the molar volume, b is the volume that is occupied by one mole of the molecules, N_A is the Avogadro number, k_B is the Boltzmann constant, T is temperature, P is pressure, and V is volume, and a is a constant whose value depends on the molecular interaction. This equation accounts for the intermolecular attraction from molecules. At the critical point, the heat of vaporization reaches zero. A stationary inflection point in the isothermal lines on a P-V phase diagram can be observed, which defines the critical point as in [2]:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad (19)$$

Solving the above two equations, we get:

$$T_c = \frac{8a}{27N_A k_B b} \quad (20)$$

Since N_A and k_B are constants, the critical temperature is directly related to a and b , as known as van der Waals constants. a provides a correlation for the intermolecular forces. b represents the volume occupied by the gas particles. It is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules [90]. Table 5 lists van der Waal's constants of some common gases [91]. Since the first objective

in this study is to minimize the difference between critical temperature and room temperature, the following parameter is chosen as the ranking index instead of a and b :

$$M_1 = |T_c - T_r| \quad (21)$$

where T_c represents the critical temperature of the substance, and T_r represents the room temperature (the room temperature is assumed to be 298 K in this study).

Table 5 – The van der Waal's constants for some gases listed in Table 2 [91].

	Molecular formula	a ($L^2 \cdot kPa/mol^2$)	b (L/mol)
Carbon dioxide	CO ₂	365	0.0428
Ethane	C ₂ H ₆	557	0.0649
Hydrogen	H ₂	245	0.0265
Oxygen	O ₂	138	0.0318
Tetrafluoromethane	CF ₄	404	0.0632
Perfluoropropane	C ₃ F ₈	129	0.1338
Sulfur hexafluoride	SF ₆	785	0.0878

The second objective is to minimize the difference between critical pressure and atmospheric pressure. The critical pressure of a substance can also be represented by van der Waal's constants a and b by solving Equation 18 and Equation 19:

$$P_c = \frac{a}{27b^2} \quad (22)$$

Similar to the first ranking index, the second ranking index about the critical pressure is defined as:

$$M_2 = |P_c - P_a| \quad (23)$$

where P_c represents the critical pressure of the substance, and P_a represents the atmospheric pressure (the atmospheric pressure is assumed to be 0.1 MPa in this study).

The third objective is to minimize the environmental impact, quantitatively represented by the global warming potential (GWP) and atmospheric lifetime. GWP is the heat absorbed by any greenhouse gas, as a multiple of the heat that would be absorbed by the same mass of CO₂ [92]. The GWP of a substance is dependent on the following factors [93]:

1. The absorption of infrared radiation by a given substance
2. The spectral location of its absorbing wavelengths
3. The atmospheric lifetime of the substance

In general, a high infrared radiation capability and a long atmospheric lifetime can cause a high GWP value [94]. Atmospheric lifetime indicates the duration of time a

substance remains in the atmosphere before decomposition. The atmospheric lifetime is dependent primarily on the reaction rate of the substance itself with hydroxyl radical [95]. For example, trifluoriodomethane (CF_3I) exhibits a relatively short atmospheric lifetime due to the weak chemical bond of C-I. On the other hand, almost all of the perfluorocarbons, such as hexafluoroethane (C_2F_6), tetrafluoromethane (CF_4), perfluoropropane (C_3F_8), and octafluorocyclobutane (C_4F_8), have very long atmospheric lifetimes because of the stable C-F bond.

Considering that the atmospheric time is included in GWP, further analysis in this study is proceeded based on GWP only for the third ranking index:

$$M_3 = \text{GWP} \quad (24)$$

The ranking of the SCF substances can be further conducted by weighing the relative performance of their ranking index as below:

$$W_i = w_i \frac{(M_i)_{\min}}{M_i} \quad (25)$$

where w_i is a weight factors sum up to 1, M_i is the substance ranking index value, and $(M_i)_{\min}$ is the minimum substance ranking index value in the candidate set. In this study, the summation of three weighted values is the overall performance P of each SCF candidate:

$$P = \sum W_i \quad (26)$$

The weight factors w_1 , w_2 , and w_3 correspond to W_1 , W_2 , and W_3 , respectively. These three weight factors can be selected based on specific design requirements for different applications. Table 6 shows the substances ranked from high to low based on these three ranking indices.

Table 6 – Substance ranking based on each objective

Ranking index	Expression	Substance ranking (high to low)
M_1	$ T_c - T_r $	C ₂ F ₆ , CO ₂ , C ₂ H ₆ , SF ₆ , C ₃ F ₈ , CF ₄ , C ₄ F ₈ , C ₄ F ₇ N, CF ₃ I, C ₅ F ₁₀ O, C ₆ F ₁₂ O
M_2	$ P_c - P_a $	C ₆ F ₁₂ O, C ₅ F ₁₀ O, C ₄ F ₇ N, C ₃ F ₈ , C ₄ F ₈ , C ₂ F ₆ , CF ₄ , SF ₆ , CF ₃ I, C ₂ H ₆ , CO ₂
M_3	GWP	CF ₃ I, CO ₂ , C ₅ F ₁₀ O, C ₆ F ₁₂ O, C ₂ H ₆ , C ₄ F ₇ N, CF ₄ , C ₃ F ₈ , C ₄ F ₈ , C ₂ F ₆ , SF ₆

As shown in Table 6, if the particular application has a main objective of minimizing the temperature difference, substances such as hexafluoroethane, carbon dioxide, ethane, and sulfur hexafluoride are the most suitable substances. If minimizing pressure difference is the primary objective, perfluorinated ketones and heptafluoroisobutyronitrile are more suitable options. If the application requires a low GWP substance, trifluoroiodomethane, carbon dioxide, and perfluorinated ketones are the most suitable choices.

In this chapter, the substance ranking is shown for three cases. In the first case, minimizing the temperature difference and GWP are given equal importance at 0.4, and minimizing pressure difference is given at 0.2. This case is suitable for applications that avoid high temperature and require low GWP substances. In the second case, minimizing the temperature and pressure differences are given equal importance at 0.4, and minimizing GWP is given at 0.2. For the third case, minimizing the pressure difference and GWP are given equal importance at 0.4, and minimizing the temperature difference is at 0.2.

Case 1: $w_1 = 0.4, w_2 = 0.2, w_3 = 0.4$

Table 7 – Weighted substance ranking for case 1

Substance	Performance index value (P)
CO ₂	0.513
CF ₃ I	0.4815
C ₂ F ₆	0.48
C ₂ H ₆	0.3531
C ₆ F ₁₂ O	0.3095
C ₅ F ₁₀ O	0.2942
SF ₆	0.1621
C ₃ F ₈	0.1386
C ₄ F ₇ N	0.1207
C ₄ F ₈	0.1117
CF ₄	0.0949

Case 2: $w_1 = 0.4, w_2 = 0.4, w_3 = 0.2$

Table 8 – Weighted substance ranking for case 2

Substance	Performance index value (P)
C ₂ F ₆	0.56
CO ₂	0.4659
C ₂ H ₆	0.3885
C ₆ F ₁₂ O	0.3651
CF ₃ I	0.3424
C ₅ F ₁₀ O	0.3318
C ₃ F ₈	0.2346
SF ₆	0.2277
C ₄ F ₇ N	0.2207
C ₄ F ₈	0.2013
CF ₄	0.1615

Case 3: $w_1 = 0.2, w_2 = 0.4, w_3 = 0.4$

Table 9 – Weighted substance ranking for case 3

Substance	Performance index value (P)
CF ₃ I	0.5321
C ₆ F ₁₂ O	0.4381
C ₅ F ₁₀ O	0.4036
CO ₂	0.3859
C ₂ F ₆	0.36
C ₂ H ₆	0.2661
C ₃ F ₈	0.2133
C ₄ F ₇ N	0.2104
C ₄ F ₈	0.1902
SF ₆	0.1794
CF ₄	0.1474

4.3 Summary

This chapter discussed how the potential SCF candidates are selected. Several important factors, such as global warming potential and electronegativity, have been expanded to explain why it is necessary to include these in the selection requirements for SCF candidates. The Ashby method is modified and implemented to systematically rank and identify the most suitable SCF substances by translating the requirements of SCF candidates into objectives and constraints. Three ranking indices are derived to describe the objectives. The potential SCF candidates are ranked based on their performance for each objective. The selection of the SCF substance depends on the relative weight assigned to each of these objectives. The result shows that substances such as hexafluoroethane, carbon dioxide, ethane, and sulfur hexafluoride are the most suitable substances if the particular application has the main objective of minimizing the temperature difference. If minimizing pressure difference is the primary objective, perfluorinated ketones and heptafluoroisobutyronitrile are more suitable options. If the application requires a low GWP substance, trifluoroiodomethane, carbon dioxide, and perfluorinated ketones are the most suitable choices.

However, experimental data on every single substance in the SCF state are not available in the literature. The substances must be investigated for availability, pricing, and dielectric strength to identify the most suitable materials. Experimental investigations on the top-ranked substances are required to be conducted further to find the most suitable SCF candidate.

In conclusion, the global warming potential values of perfluorocarbons (C_2F_6 , CF_4 , C_3F_8 , and C_4F_8) are too high to be listed as promising SCF candidates. The global warming potential values of $\text{C}_4\text{F}_7\text{N}$, and CF_3I are low, and they manifest low toxicity and high dielectric strength. In addition, they also have the achievable critical temperature and critical pressure. Therefore, these strong electronegative substances have been chosen to be investigated in this dissertation. CO_2 has also been listed as the SCF candidate due to its benign characteristics: non-toxic, low global warming potential value, easily available, and low cost. It is also the most used buffer gas for mixtures. C_2H_6 is selected in this dissertation for similar reasons. It is also non-toxic, has low GWP, and is easily available and low in cost. It also has a similar critical point to CO_2 , which results in a critical point that is technically easier to achieve compared to pairs of substances with very different critical points. A more significant reason why C_2H_6 is chosen in this study lies in the fact that C_2H_6 forms an azeotropic mixture with CO_2 , which has a critical temperature that is lower than either of the constituents [19, 96]. This property is important because it allows for more selectivity and accessibility for various purposes. O_2 is also investigated in this dissertation as the addition of O_2 to CO_2 is beneficial for electrical insulation. For example, it has been proved that adding O_2 to CO_2 helps carbon control [97]. In addition, the by-products after arcing are less severe than they are for SF_6 gas. Most importantly, the thermal interruption capability of the CO_2/O_2 mixture is better than using CO_2 alone [98].

CHAPTER 5. DIELECTRIC STRENGTH INVESTIGATIONS ON SUPERCRITICAL CARBON DIOXIDE AND SUPERCRITICAL FLUID MIXTURES

5.1 Dielectric strength investigation on the supercritical carbon dioxide

The experiments are conducted under DC voltage (Spellman SL60PN1200, rated 60 kV and 20 mA). The voltage is ramped up at 0.5 kV/s, and the gap between the two electrodes is set to be 0.1 mm. Five breakdowns are performed initially to season the electrodes before collecting the data. The breakdown voltage is then measured and recorded fifteen times at each condition. The time interval between two successive breakdown events is about two minutes to reduce the effect of the density fluctuation caused by the arc discharge. The complete experimental setup is described in Appendix B.

CO₂ is one of the most frequently studied dielectric media due to its benign characteristics: high dielectric strength, non-toxic, low global warming potential (GWP), easily accessible, and low in cost. Furthermore, supercritical conditions are achievable with little effort ($T_c = 304.1$ K, $P_c = 7.38$ MPa) [9].

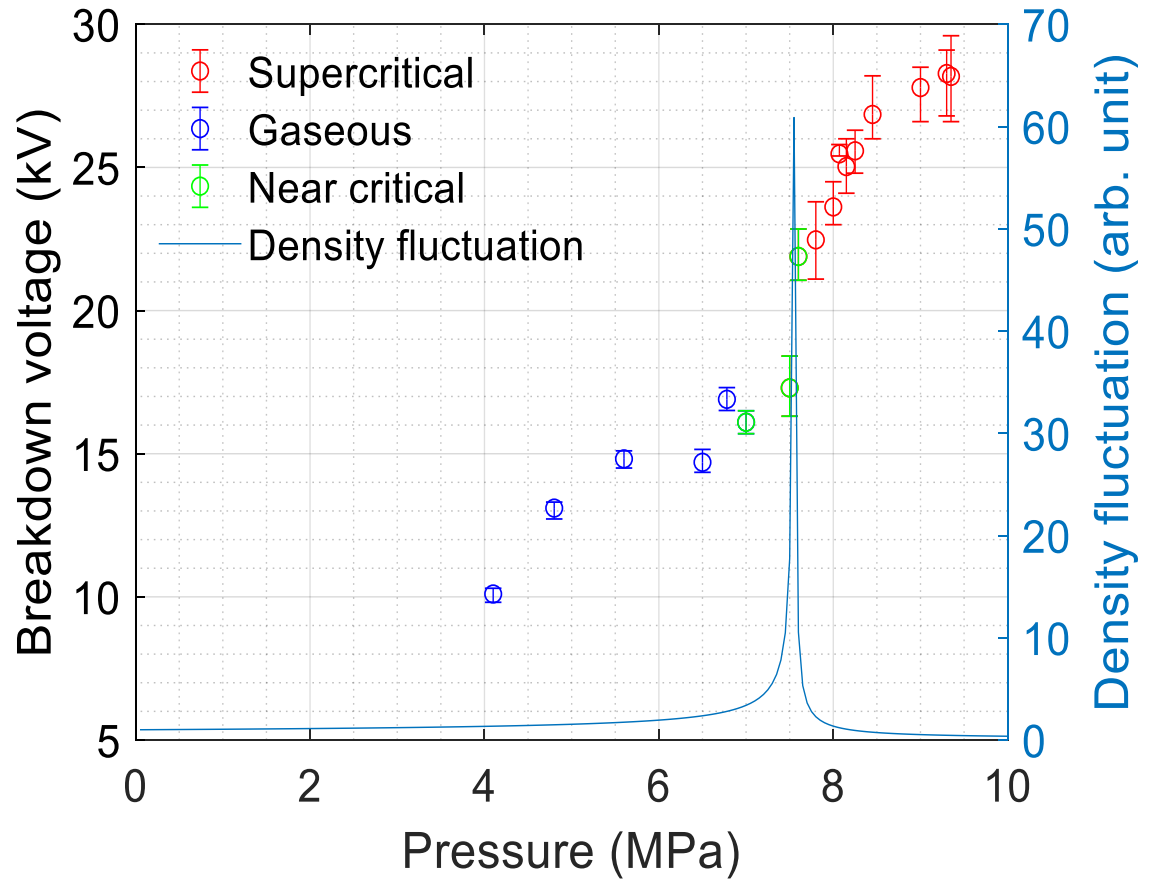


Figure 5 – Experimental results for the dielectric strength of supercritical carbon dioxide up to 10 MPa. The breakdown voltage as a function of the pressure of CO₂ in a uniform electric field at a 0.1 mm gap. Experiment is conducted at the isothermal condition of 308 K.

The breakdown voltage measurements of pure CO₂ are conducted at the temperature of 308 K from the gaseous phase to supercritical condition. Figure 5 shows the measured breakdown voltages as a function of pressure, and Figure 6 shows the measured breakdown voltages as a function of the density. The average breakdown voltage of fifteen measurements and their scattering data at one experimental condition are represented by an open circle and a vertical error bar. The density values are calculated by using the equation of state (EoS) [99] from pressure and temperature during the experiment and confirmed by weighing the mass of substance inside the high pressure chamber. In

Figure 7, Red circles represent the average breakdown voltage for carbon dioxide under the supercritical condition. Blue circles represent the average breakdown voltage at the gaseous phase. Green circles represent the average breakdown voltage measured near critical point of carbon dioxide. Vertical error bars represent the corresponding experimental scattering data.

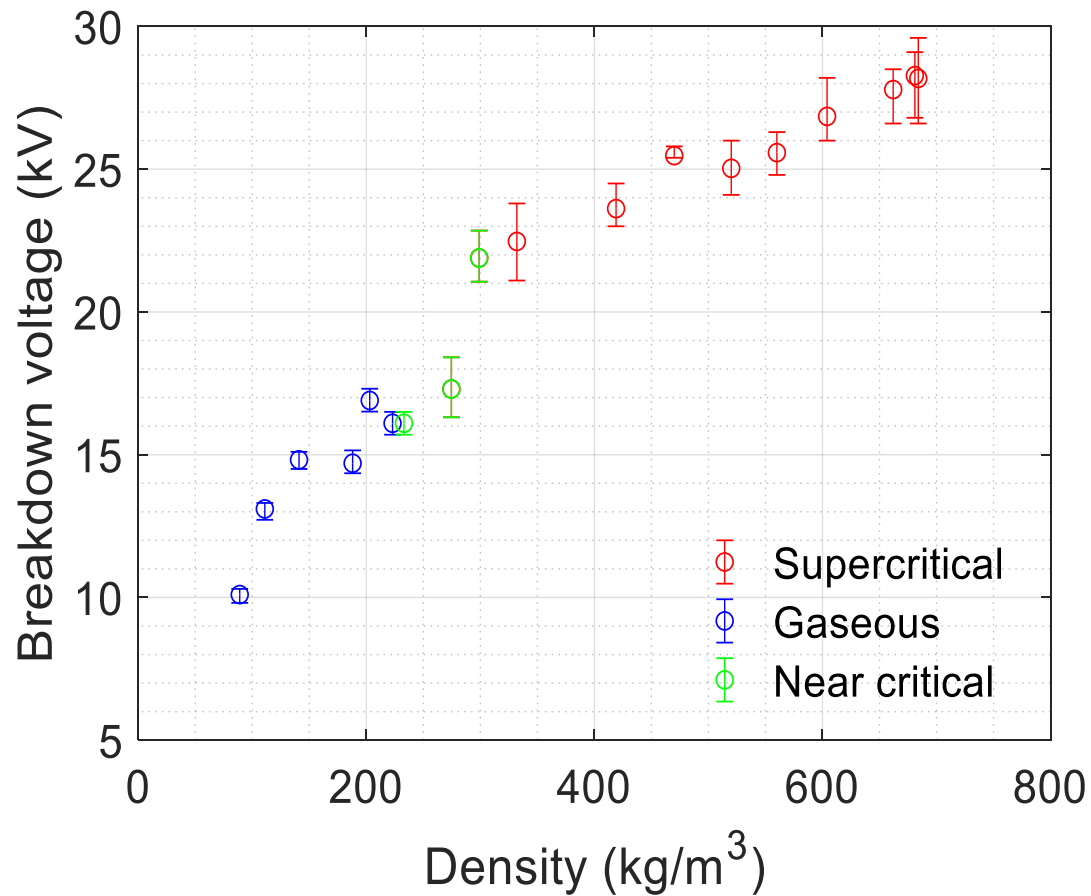


Figure 6 – Experimental results of the breakdown voltage of CO₂ as a function of density in a uniform electric field at a 0.1 mm gap. Experiment is conducted at the isothermal condition of 308 K. It is the same experimental data set as shown in Figure 5.

As shown in Figure 5, the right y-axis indicates the density fluctuation F_D , which quantifies the molecular clustering. F_D values are calculated as demonstrated in Appendix E.

Clearly, the measured breakdown voltage increases with the density of CO₂, and scatters more in the supercritical region. An obvious discontinuity of slope can be observed near the critical point where the substance experiences phase change. In supercritical conditions, the composition of the fluid is characterized by inhomogeneity in the molecular distribution due to the distinct clusters of molecules. Especially under the conditions close to the critical point, the density fluctuation F_D increases substantially due to repeated aggregation and dispersion of clusters, which influences the breakdown strength significantly. A larger F_D means larger density fluctuations, and F_D reaches local maxima at the critical point.

The density inhomogeneity is caused by the clustering effect, which forms a large mean free path where electrons could gain enough energy and ionize particles. Although the phenomenon of the discontinuity in breakdown versus density near the critical point in the experiment is pronounced, the decrease in breakdown voltage near the critical point reported by Ito *et al.* is not observed [35, 36]. This is expected because the gap length in this study is relatively large, even the discharges happen under the condition of being close to the critical point, clustering and density fluctuation F_D decrease due to the local increase of the temperature caused by discharges. If the gap length is smaller than 1 μm , the cluster structure can be preserved because more effective heat dissipation is enabled by the large specific surface area. Thus, a reduction of breakdown voltage can be observed.

The reason for the deviation between the breakdown voltage in SCFs and the gaseous state is that the gaseous discharge theory cannot explain the situation when the mean free path of electrons in SCFs starts to decrease. In this circumstance, SCFs deviate considerably from the ideal gas behavior, and a small change in the pressure causes a large change in the density. Paschen's law cannot precisely predict the breakdown voltage in high pressure gases and SCFs. Specifically, Paschen's law fails to estimate the breakdown characteristics in the compressed medium when the electric field is of the order 10 – 20 kV/mm. The deviation from Paschen's law depends on the material, separation and area of the electrodes, and particles of dust near the electrodes. Similarly, the failure of the Townsend mechanism for SCFs is that the Townsend theory does not take the field emission of electrons from the cathode in a high density medium into consideration [100].

5.2 Dielectric strength investigation on the supercritical azeotropic mixture

5.2.1 Electron kinetic process and Boltzmann analysis on CO₂ and C₂H₆

The electrical breakdown characteristics of gaseous media can be analyzed by the electron kinetic process and estimated by the ionization (α) and attachment (η) coefficients. Boltzmann analysis has been widely used to obtain these coefficients theoretically. In this section, the dielectric properties of gaseous CO₂ and C₂H₆ are investigated by the two-term approximation of the Boltzmann equation [47].

The electron scattering cross section $\sigma(\epsilon)$ affects the electron energy distribution function (EEDF) and the electron kinetic process. Every gas species has its own sets of electron scattering cross sections as a function of electron energy (ϵ). The Boltzmann analysis requires the electron scattering cross sections of CO₂ and C₂H₆, presented in

Figure 7. The cross section data are collected from numerous datasets available in the LXCat project [101]. Specifically, cross section data of CO_2 are extracted from the SIGLO database [102], and cross section data of C_2H_6 are extracted from the Hayashi database [103].

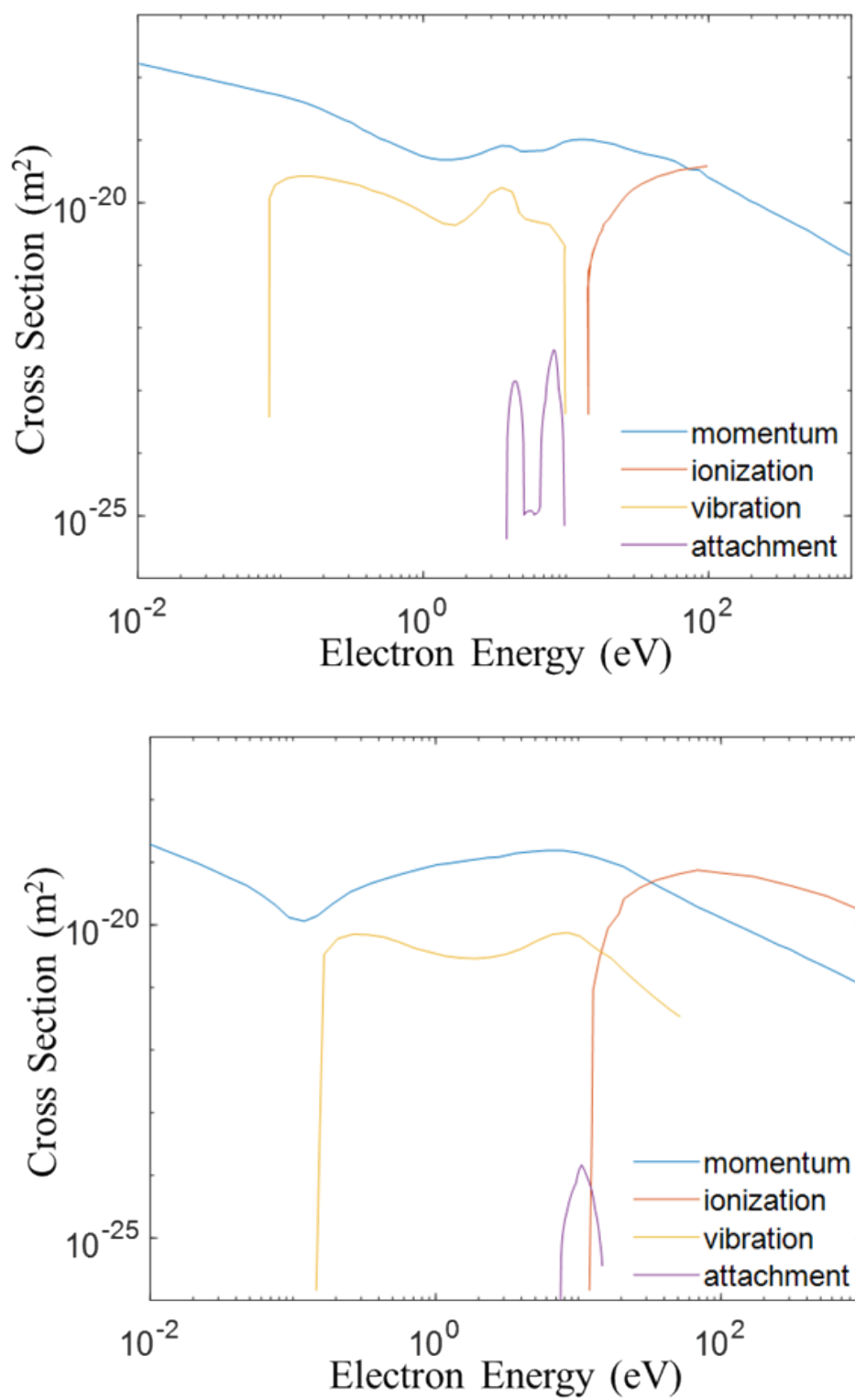


Figure 7 – Electron scattering cross sections of CO_2 (above) and C_2H_6 (below).

The pattern of cross sections of both gas species is very similar: they both have a high momentum-transfer electron scattering cross sections over the entire energy range. Ionization electron cross sections are more substantial at higher electron energy. However, the attachment cross section of CO₂ is higher than that of C₂H₆. This indicates that CO₂ has a relatively stronger electron attachment ability than C₂H₆, which leads to higher dielectric strength.

The Boltzmann equation describes the transport coefficients and rate coefficients for the given discharge condition [47]:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f - \frac{e}{m} \mathbf{E} \cdot \nabla_v f = C[f] \quad (27)$$

where f is the electron distribution function, $\mathbf{v}$ is the velocity vector, e is the elementary charge, m is the electron mass, $\mathbf{E}$ is the electric field, ∇_v is the gradient in the velocity space, and $C[f]$ represents the rate of change in f due to collisions.

In this part, the EEDF is calculated from the cross section data by solving the electron Boltzmann equation using a two-term approximation method. EEDFs of CO₂ and C₂H₆ with the E/N of 7 Td obtained from the Boltzmann analysis are presented in Figure 8.

The similarity in EEDFs of both gaseous species is pronounced. Only a small variation is observed in the values of EEDF at the lower energy region, where values of CO₂ are higher than that of C₂H₆.

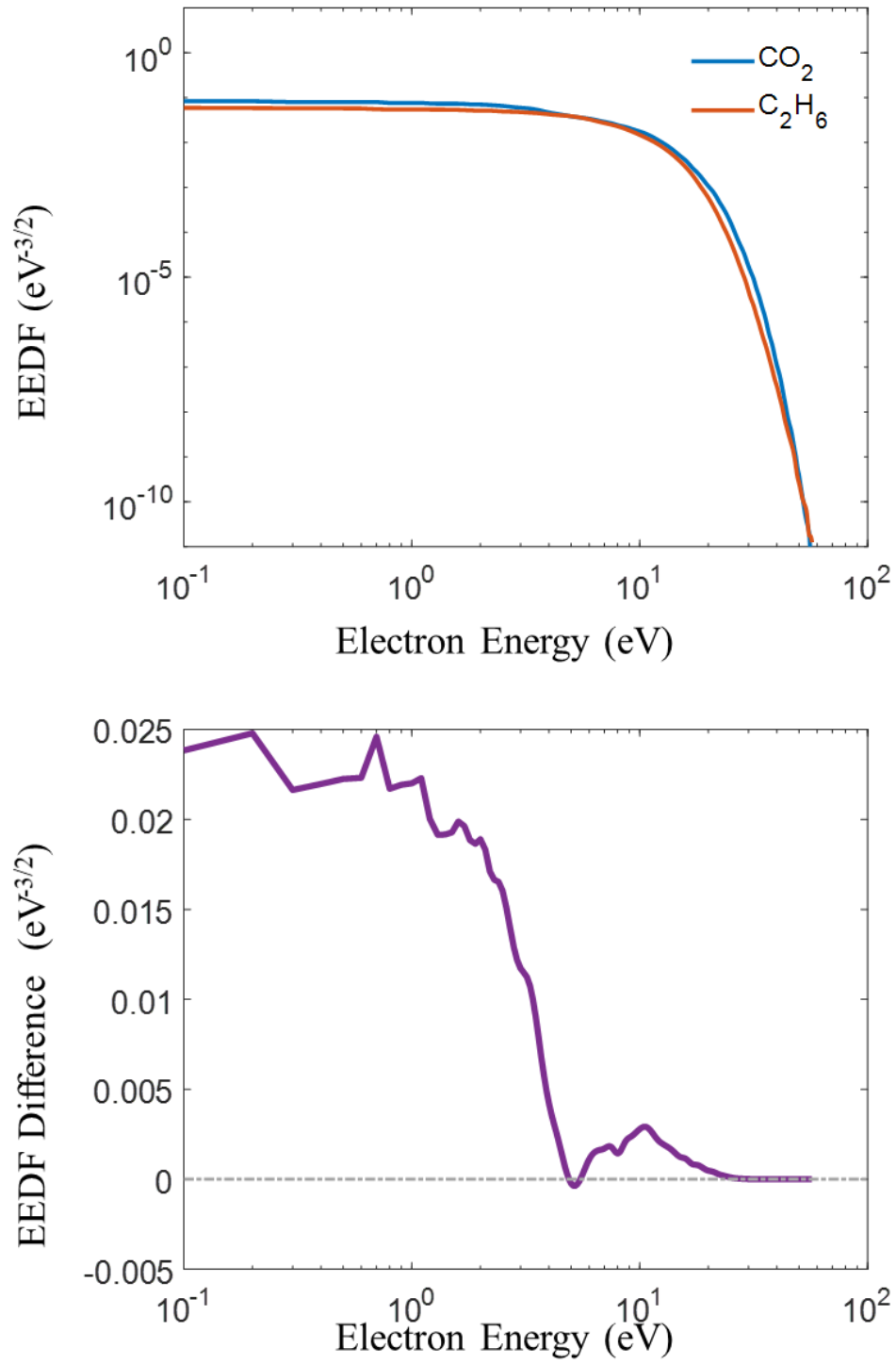


Figure 8 – EEDFs of CO_2 and C_2H_6 with the E/N of 7 Td (above). The difference of EEDFs of CO_2 and C_2H_6 with the E/N of 7 Td (below).

The dielectric strength of CO₂ and C₂H₆ can be estimated based on the electron kinetic processes represented by the density-reduced ionization coefficient (α/N) and the density-reduced attachment coefficient (η/N). Figure 9 presents α/N and η/N values calculated based on EEDFs of CO₂ and C₂H₆, as a function of E/N . The results show a small variation in α/N values of both species. However, η/N values of CO₂ are apparently higher than η/N values of C₂H₆.

The density-reduced critical electric field ($(E/N)_{cr}$) is defined as the density-reduced electric field (E/N), in which the rates of ionization and attachment processes are equal, that is, E/N corresponding to $(\alpha - \eta)/N = 0$. For gaseous CO₂, this value is about 80 Td, while for gaseous C₂H₆, the value is about 50 Td.

Theoretically, an increasing dielectric strength can be indicated from larger values of EEDF at low electron energy region, smaller α/N , and larger η/N . From the results of the above Boltzmann analysis, in general, relatively small variations are shown in the results of EEDFs and α/N values between CO₂ and C₂H₆. However, CO₂ exhibits higher values of η/N as well as in the attachment cross section [52, 104].

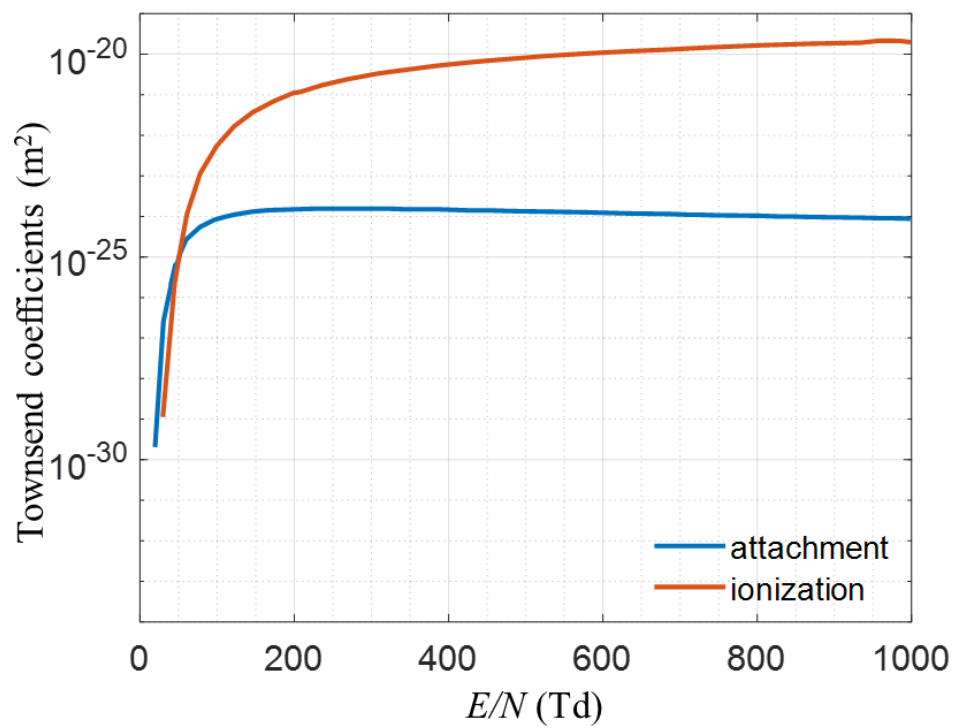
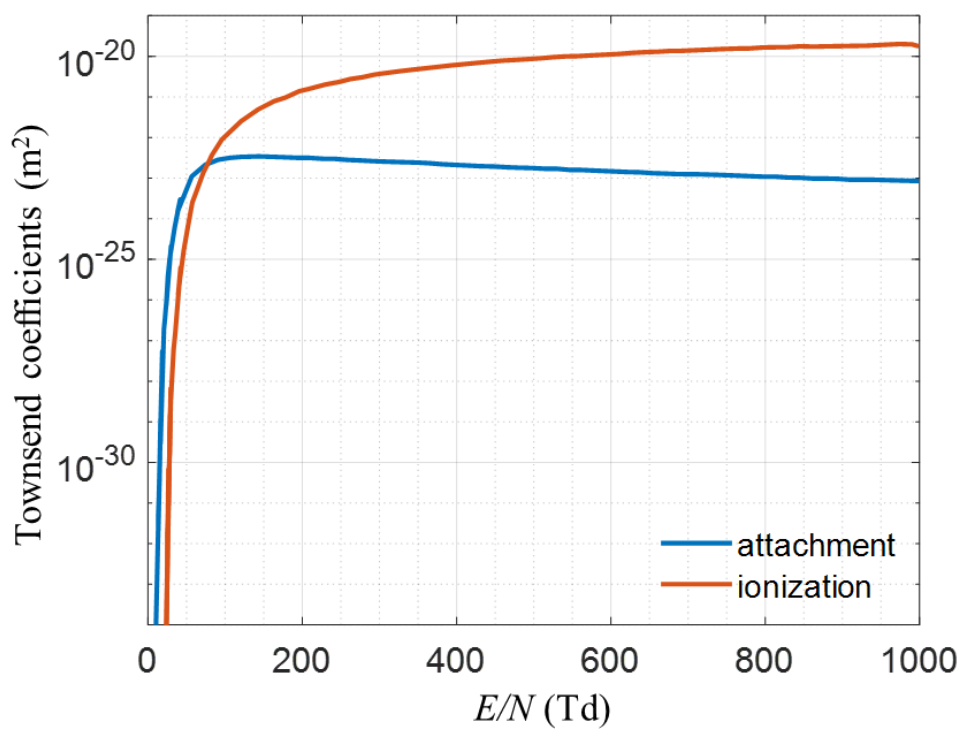


Figure 9 – Density-reduced ionization coefficient (α/N) and density-reduced attachment coefficient (η/N) of CO₂ (left) and C₂H₆ (right).

5.2.2 Electrical breakdown experiments on supercritical CO₂-C₂H₆ mixtures

C₂H₆ is selected in this study for similar reasons: It is also non-toxic, low GWP, easily available, and low in cost. It also has a similar critical point as CO₂ ($T_c = 305.3$ K, $P_c = 4.87$ MPa) [105], which results in a critical point that is technically easier to achieve than for pairs of substances with very different critical points. A more significant reason why C₂H₆ is chosen in this study lies in the fact that C₂H₆ forms an azeotropic mixture with CO₂, which has a critical temperature that is lower than either of the constituents. This property is important because it allows for more selectivity and accessibility for various purposes. Some reports in the literature suggest that such a mixture could provide improved properties and more potential applications than the pure substance. Kravanja *et al.* evaluated the heat transfer performance of CO₂-C₂H₆ azeotropic mixture under supercritical conditions. Their results revealed that the heat transfer coefficient of CO₂-C₂H₆ azeotropic mixture fell between the values for pure CO₂ and C₂H₆, which proves that such a mixture has the capability to be used as an alternative fluid in heat power cycles [19]. Considering its thermal properties, the investigation on the dielectric properties of such mixtures would be an imperative task in order to show the feasibility of SCF as a promising dielectric medium. Figure 10 shows the density versus pressure diagram of both CO₂ and C₂H₆ by two isothermal lines [10]. The red line represents the carbon dioxide under the supercritical condition. The dotted green line represents the carbon dioxide at the gaseous phase. The solid blue line represents the ethane under the supercritical condition. The pink dotted line represents the ethane at the gaseous phase. Experiments are conducted at a constant temperature of 308 K, and breakdown voltages are measured from gaseous to supercritical conditions.

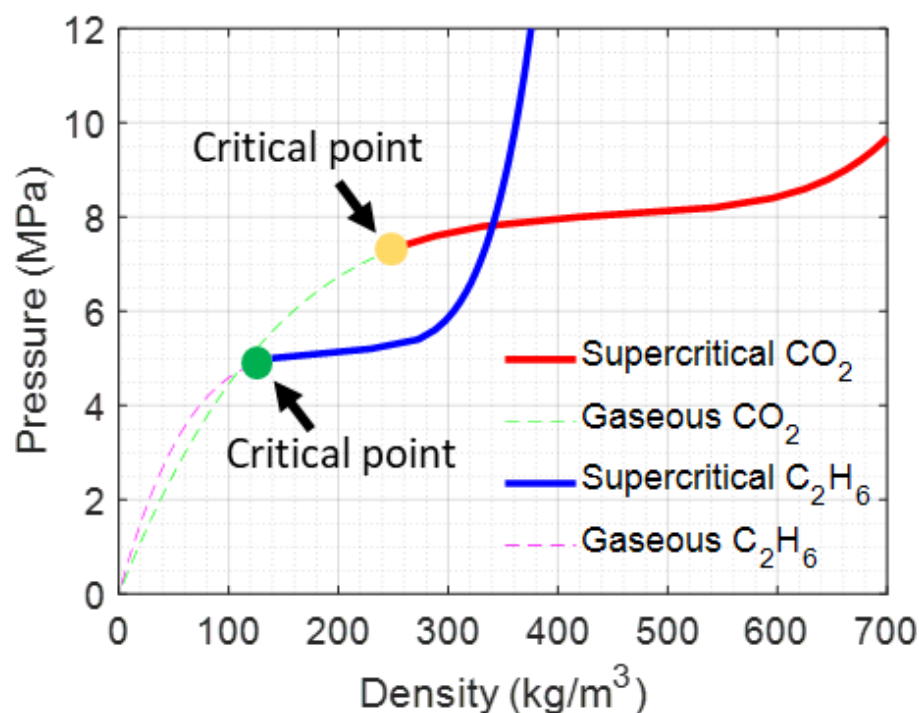


Figure 10 – Phase diagram of carbon dioxide and ethane. Experimental conditions represented by isothermal lines of CO₂ and C₂H₆ density-pressure diagram, at 308 K ($T_r = T/T_c = 1.012$) [10].

Besides the pure substances, it is also necessary to know the critical points of mixtures with different mixing ratios so that the thermodynamic phase inside the high pressure chamber can be confirmed. A high pressure optical vessel is used to observe the phase transition of mixtures visually. The design of the optical vessel is described as shown in Appendix B. Specifically, the critical opalescence is observed to determine the critical state of such a binary mixture. Critical points of the mixtures from the optical diagnostics are in good agreement with the critical points calculated from the PSRK (predictive Soave–Redlich–Kwong) model. The PSRK model is able to reliably predict the thermodynamic properties of carbon dioxide and alkanes by using one pair of temperature-dependent group interaction parameters. Such a model has been widely used in process simulators because

it combines the advantages of EoS, the local composition concept, and the group contribution approach [106].

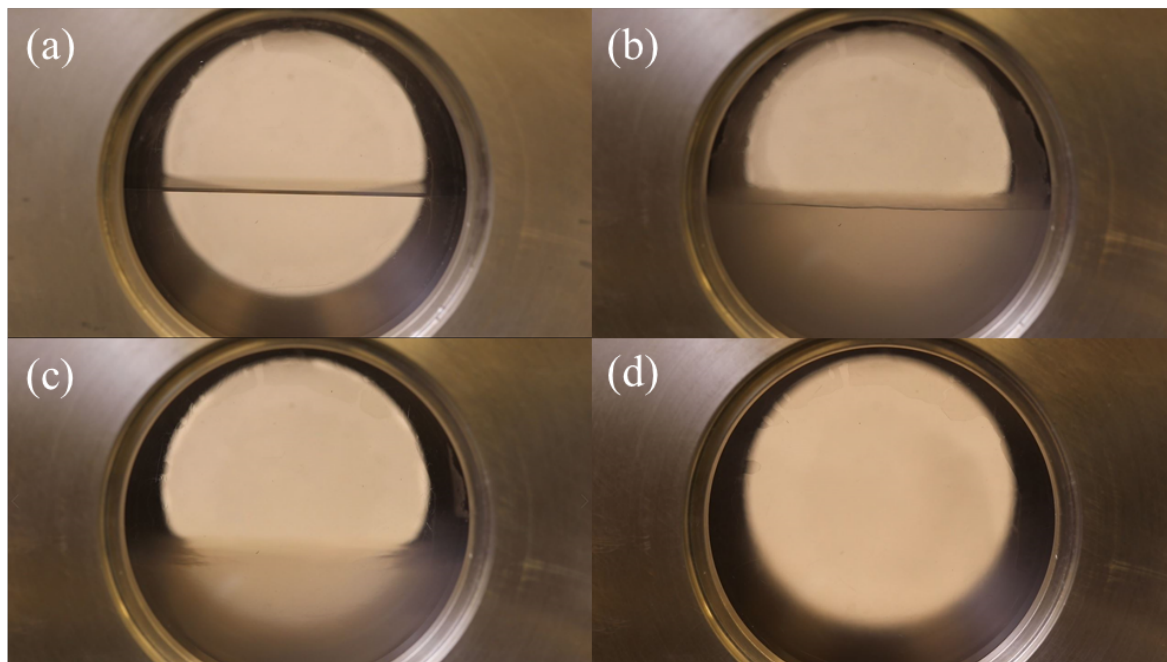


Figure 11 – Determination of the critical point of a sample of $\text{CO}_2\text{-C}_2\text{H}_6$ by observing the critical opalescence.

Figure 11 shows a sample of $\text{CO}_2\text{-C}_2\text{H}_6$ near the critical point observed in transition on Earth (with gravity directed downwards). Figure 11(a) shows the sample below its critical point: both the liquid and vapor phases are compressed under their own weight. The boundary between gas and liquid is obvious. Figure 11(b) and Figure 11(c) show the sample very close to the critical point: the gas-liquid phase boundary starts to vanish. Figure 11(d) shows the sample significantly above its critical point: the phase boundary between the gas and liquid phases of the $\text{CO}_2\text{-C}_2\text{H}_6$ mixture disappears.

Table 10 compares the critical points observed from the optical cell and calculated from the PSRK model with respect to the mass fraction of C_2H_6 (ω). The error between

two methods as shown in Table 10 is expected to be caused in part due to the presence of impurities.

Table 10 – Comparison of the critical temperature T_c and critical pressure P_c for $\omega\text{C}_2\text{H}_6 + (1-\omega)\text{CO}_2$

	Optical Diagnostics		PSRK Model	
ω	$T_c [K]$	$P_c [MPa]$	$T_c [K]$	$P_c [MPa]$
0.1	300	6.75	298	6.73
0.25	295	6.50	292	6.35
0.3	294	6.05	291	5.94
0.4	294	5.82	292	5.70
0.5	293	5.55	292	5.52

To ensure consistency in the experimental results with the pure CO_2 data, the gap between the copper electrodes is also set to 0.1 mm. C_2H_6 mass percentages of 10%, 25% (azeotropic), 30%, 40%, and 50% are tested in the breakdown experiment. An oily substance between two electrodes is observed after the first breakdown when the C_2H_6 mass percentage (ω) is greater than 60%. Rosocha *et al.* conducted experiments to determine the decomposition of C_2H_6 under dielectric-barrier discharges at 77.3 kPa and a temperature range of 293 to 323 K. The primary decomposition products they found are molecular hydrogen (H_2), methane (CH_4), acetylene (C_2H_2), and ethylene (C_2H_4) [107]. Oro *et al.* also observed a similar phenomenon that organic compounds are formed under the influence of electric discharges with C_2H_6 at a pressure range of 10 to 30 kPa at 303 K.

Their results indicate that the product caused by the electric discharge could be a highly cross-linked polyethylene-type polymer [108].

A similar anomalous breakdown behaviour near the critical point of pure CO₂ as shown in Figure 5 is also observed in the CO₂-C₂H₆ mixture at the azeotropic mixing ratio, as shown in Figure 12. Figure 13 shows the measured breakdown voltage at different mixing ratios as a function of the density.

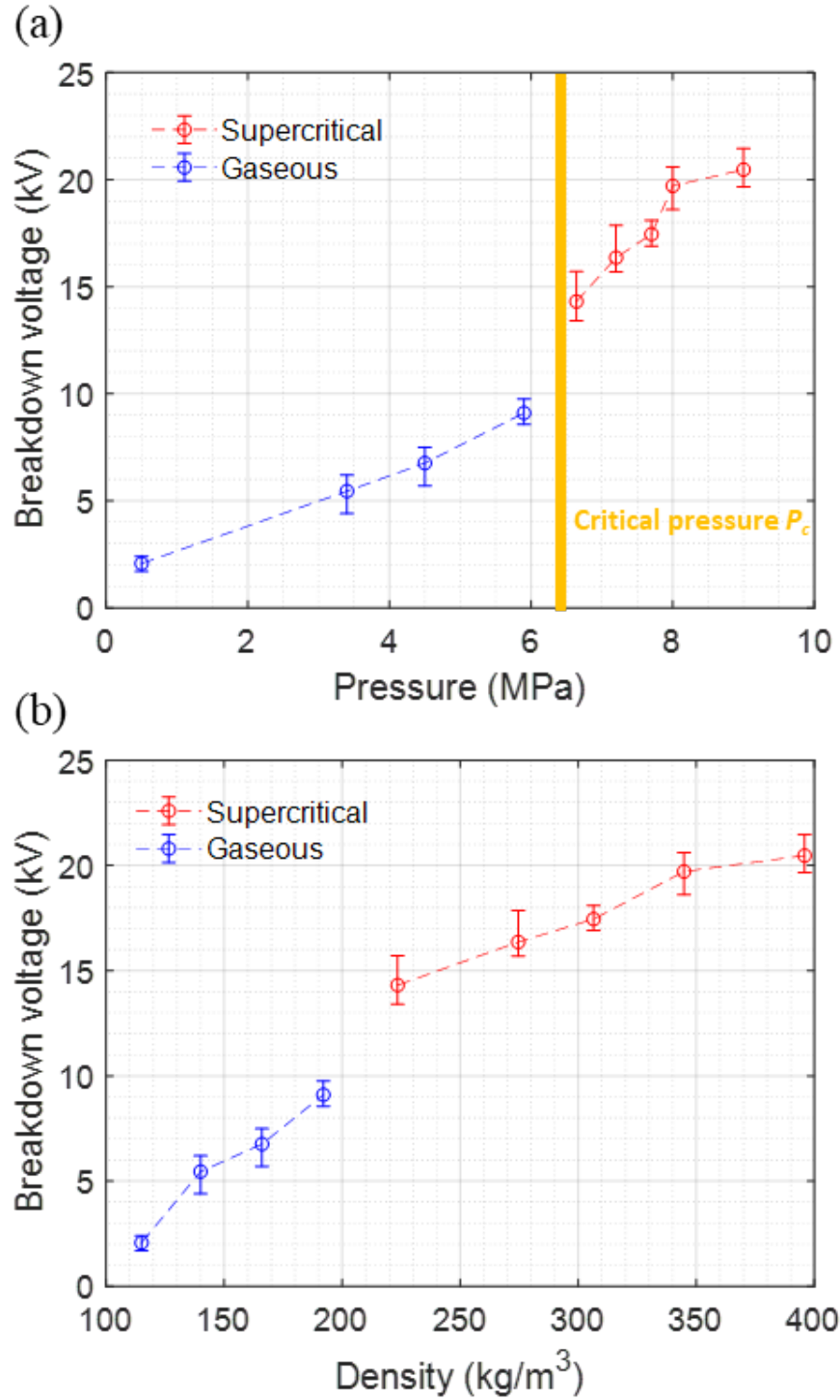


Figure 12 – a, Breakdown voltage as a function of the pressure of the CO₂-C₂H₆ mixture at the azeotropic mixing ratio in a uniform electric field at a 0.1 mm gap. b, Breakdown voltage as a function of density of the CO₂-C₂H₆ mixture at the azeotropic mixing ratio.

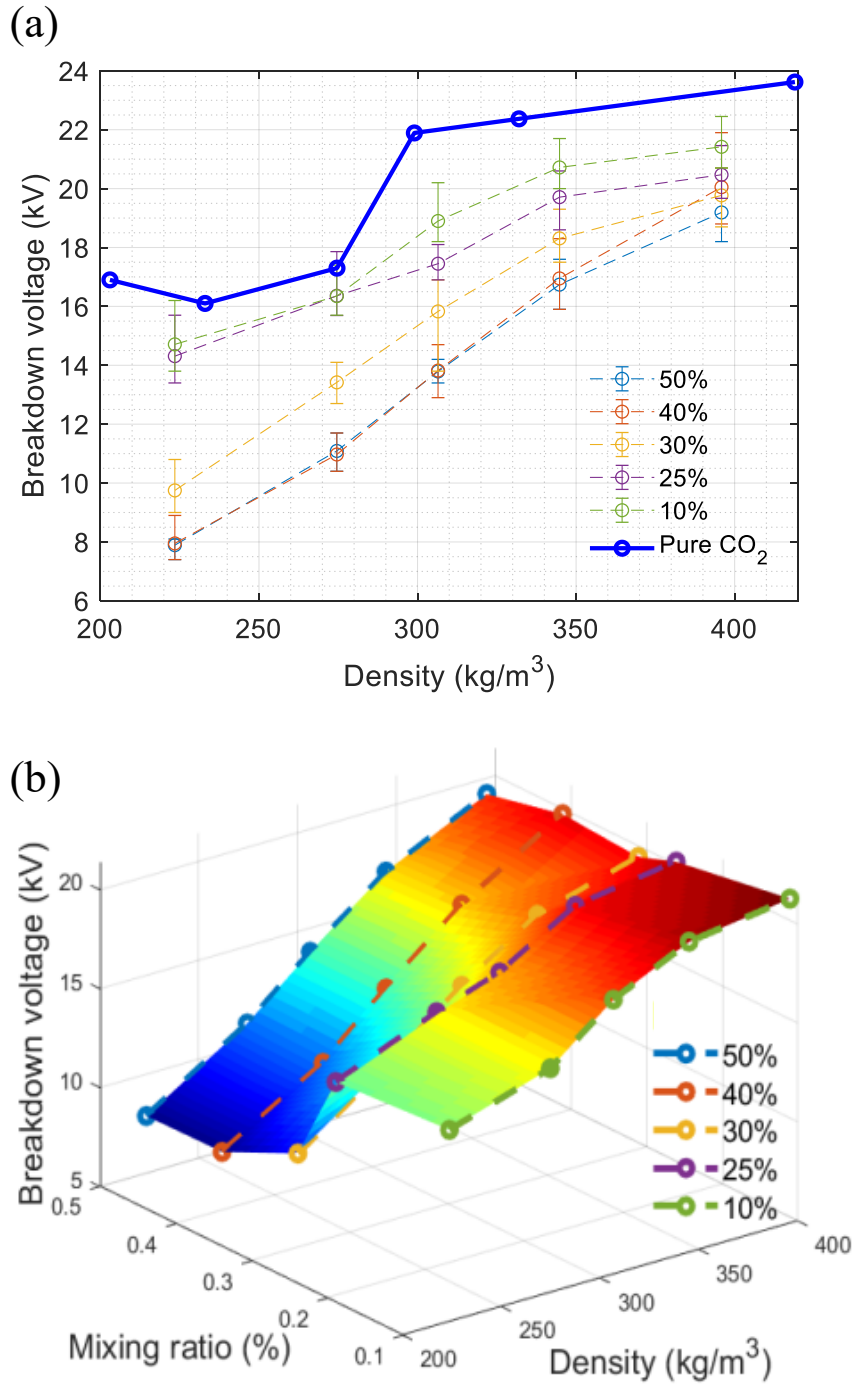


Figure 13 – a, A 2-D plot of the breakdown voltage at different mixing ratios as a function of density. The solid blue line indicates the average of measurement data of pure CO_2 . b, Breakdown voltage at different mixing ratios as a function of density at the temperature of 308 K. ω : the mass percentage of C_2H_6 . The C_2H_6 mixing ratio varies from 10% to 50% by mass into CO_2 .

All the breakdown values presented in Figure 13 are measured under the supercritical condition. The average breakdown voltages have a trend to decrease as the C_2H_6 concentration increases. Also, the measured breakdown voltage of mixtures scatters more widely compared to the values of pure CO_2 . Similar phenomena have been observed in gases [52, 104]. At the lower density region between 220 kg/m^3 to 300 kg/m^3 , the difference in the breakdown voltage of mixtures tends to be more obvious than in the higher density region. The data also indicate that breakdown voltages of different mixing ratios saturate at higher density. The breakdown voltage of mixtures at the lower density region also shows a more pronounced reduction compared to pure CO_2 . For the azeotropic mixture of CO_2 and C_2H_6 (25% mass fraction of C_2H_6 and 75% mass fraction of CO_2), the breakdown voltage shows an average of 20.5% reduction compared to the dielectric strength of pure CO_2 in the vicinity the critical point of CO_2 . At the higher density region far away from the critical point, the reduction of dielectric strength of the mixture drops to about 13.5% compared to pure CO_2 .

In this section, we found that the anomalous breakdown characteristics discovered in the pure SCF is also observable in binary mixtures of supercritical fluids at azeotropic mixture ratio. The similar behavior suggests that the unstable molecular clustering could significantly affect the discharge phenomenon observed in both pure SCFs and supercritical mixtures. Unique properties of SCF mixtures with respect to dielectric strength, viscosity, specific heat capacity, and tunable critical point are expected to attract interest for a wide range of applications. Besides the applications in power and energy, where they could be used for switchgear and electrostatic machines [109-111]. SCF

mixtures could also enable affordable van-de-Graaff generators for particle accelerators, used in high energy physics and medical applications such as radiation therapy [112, 113].

5.3 Dielectric strength investigation on the supercritical fluid mixture with trifluoroiodomethane

Traditionally, SCF binary mixtures have been implemented in applications such as carbon capture or SCF injection, where mixtures of multiple SCF species are required. SCF binary mixtures, for example, have been used to modify the solvation character of the fluid. Other major applications of SCF binary mixtures are optimizing the processes of extraction, separation, or chemical reaction by taking advantage of the tuning solubility property of SCF mixtures [17]. There are relatively few studies devoted to exploring the possibility of utilizing SCF mixtures for dielectric purposes. In this context, our previous study presented the breakdown characteristics of supercritical carbon dioxide-ethane ($\text{CO}_2\text{-C}_2\text{H}_6$) mixtures. The study found that mixtures of SCFs can yield tunable combinations of properties such as the dielectric strength and the critical point, thus allowing for a broader range of applications [96].

Trifluoroiodomethane (CF_3I) is a gas known for its high dielectric strength and is thus considered as one of the candidates to replace sulfur hexafluoride (SF_6) in electrical power applications. It has several beneficial physical properties. It is nonflammable, colorless, and chemically stable. In addition, CF_3I has a low global warming potential (GWP) of 0.4 compared to that of SF_6 which is approximately 22,800. Also, the overall atmospheric lifetime of CF_3I is very short due to the weak chemical bond of C-I. However, pure CF_3I suffers from a low vapor pressure, which can cause a severe problem for practical

applications in gaseous form. This is why buffer gases such as N₂ and CO₂ have been added to decrease the partial pressure of CF₃I. Comparisons of key physical properties are given in Table 11 [114-117].

Table 11 – Comparison of critical points, GWP, and atmospheric lifetime of CO₂, CF₃I, and SF₆.

Molecular formula	T_c (K)	P_c (MPa)	GWP	Atmospheric lifetime (Years)
CO ₂	304	7.39	1	200
CF ₃ I	395	4.04	0.4	30 (days)
SF ₆	319	3.76	22,800	3,200

Extensive research has been carried out on the electric discharge generated in supercritical CO₂ and N₂, yet there is no consideration of many other highly promising supercritical substances or their mixtures. This is especially true for power applications, where there has not been any investigation of SF₆ alternatives in the supercritical phase. Similarly, although numerous research efforts have focused on the insulation performance of CF₃I and its mixtures with CO₂ and N₂ over the past few years [75, 76, 118], these studies are all conducted in the gaseous phase, which lacks the heat transfer and dielectric strength provided by SCFs.

This section demonstrates the first experimental measurement on the breakdown characteristics of supercritical CO₂-CF₃I fluid mixtures. The present research also explores,

for the first time, the effects of clustering in SCF binary mixtures on the electrical breakdown characteristics caused by the density fluctuation near the critical point.

5.3.1 *Thermodynamic properties of supercritical CO₂, CF₃I, and mixtures*

SCF represents an intermediate state between gas and liquid states [23]. As an example, Figure 2 and Figure 14 compare the thermodynamic properties including density, thermal conductivity, viscosity, and heat capacity of CO₂ and CF₃I with isothermal lines [10, 119, 120]. The critical points for both substances are represented by the yellow dots at $T_c = 304.1$ K, $P_c = 7.39$ MPa for CO₂, and $T_c = 395.2$ K, $P_c = 4.04$ MPa for CF₃I, respectively. Small changes in the pressure result in large changes in the density near the critical point. During phase change at a constant pressure below the critical pressure ($P < P_c$), the substance transits from liquid to vapor for all temperature values. On the other hand, when the substance is at a constant pressure above the critical pressure ($P > P_c$), it can condense into the liquid state by cooling, but it cannot achieve the gaseous phase by heating the fluid.

Many physical properties of SCFs, such as density and viscosity, are between those of liquids and gases, as shown in Figure 2 and Figure 14. While this is not true for some other properties like heat capacity, which are maximized near the critical point, as shown in Figure 2 and Figure 14. It is worth noting that the heat capacity shows a dramatic change near the critical point. Specifically, it reaches the peak value, which is several times higher than the nearby values. The reason is that the specific heat capacity is a derivative of the enthalpy. The system expands when the temperature increases at a constant pressure P . As the molecules move apart, work must be done against the intermolecular forces. In

addition, work also must be done against the atmosphere as the system expands. The coefficient of thermal expansion at constant pressure near the critical point can be more than ten times higher, so the effect on the specific heat capacity is also substantial [17, 121].

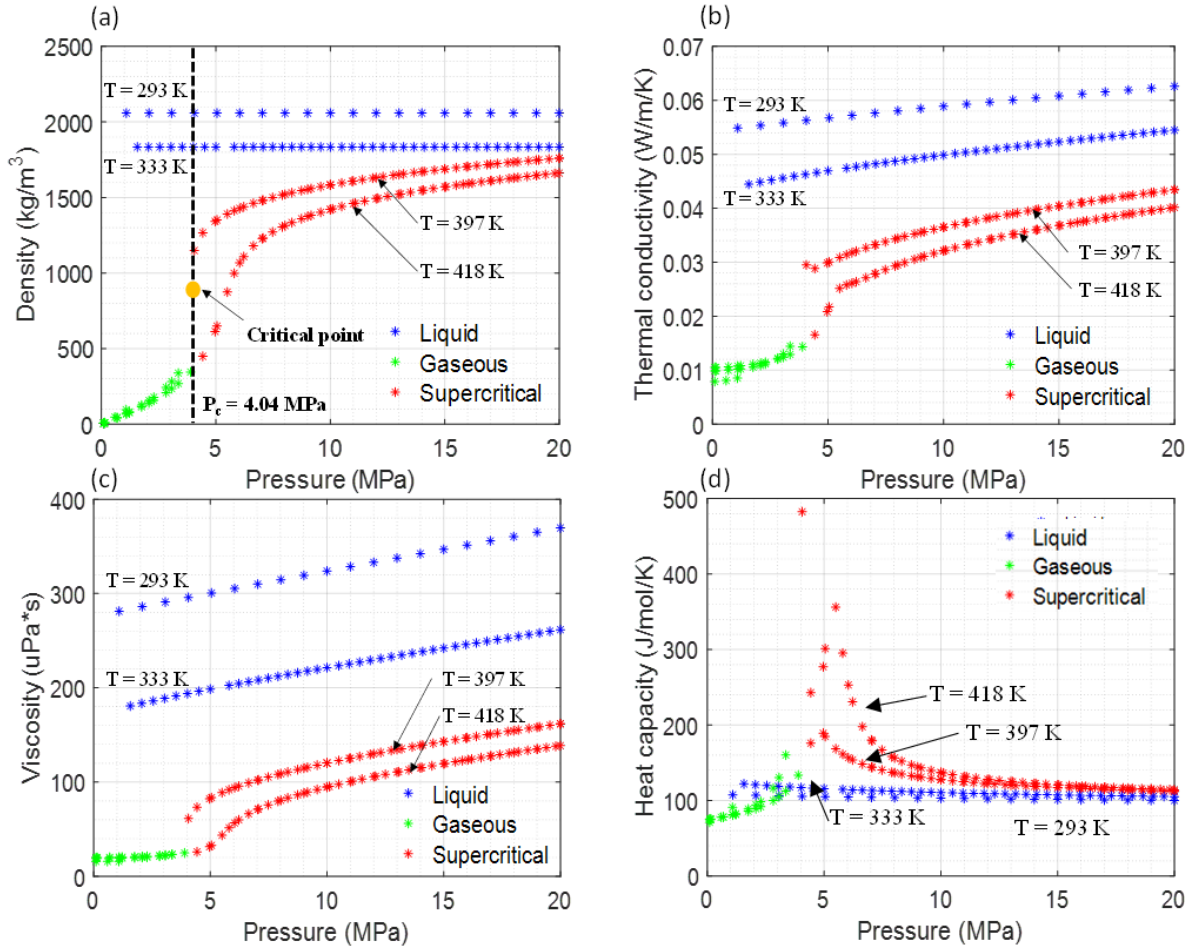


Figure 14 – Thermodynamic properties of CF_3I in gaseous, liquid, and supercritical fluid phase with isothermal lines. (a) density, (b) thermal conductivity, (c) heat capacity, and (d) heat capacity. The critical point is indicated by a yellow dot at $T_c = 395.2 \text{ K}$, $P_c = 4.04 \text{ MPa}$.

The anomalous behavior of fluids near the critical point has become the most distinctive characteristics of SCFs. As mentioned above, some physical properties like heat capacity achieve the maximum value near the critical point. Such critical anomalies have

also been observed and reported in the electrical discharge area. For example, the decrease of breakdown voltages for micrometer-scale gap electrodes [35, 36, 38], the local decrease of the plasma temperature [57], and the local maxima of atomic emission intensities generated by pulsed laser ablation plasmas [122] are all observed near the critical point. These phenomena can be further investigated from the microscopic point of view by the molecular clustering, and the macroscopic point of view by the density fluctuation.

The formation of clusters greatly influences the transport properties and the structures of SCFs. The cluster size and the number of molecules in an SCF cluster can be calculated from the Ornstein-Zernike correlation length ξ , which is obtained from the characterization of the material based on small angle X-ray scattering (SAXS):

$$I(s) = \frac{I(0)}{1 + \xi^2 s^2} \quad (28)$$

where $I(s)$ is the scattering intensity, $I(0)$ is the zero-angle scattering intensity at $s = 0$, and s is defined as:

$$s = \frac{4\pi \sin \theta}{\lambda} \quad (29)$$

where θ is the scattering angle, and λ is the wavelength of the X-ray source.

Data obtained from the SAXS experiment are also related to density fluctuation F_D , which quantifies the extent of the molecular clustering [123]:

$$F_D = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} = \frac{I(0)}{N} \frac{1}{Z^2} = \frac{(n_s v)^2}{n_{ave} v} = \frac{k_T}{k_T^0} \quad (30)$$

where N is the total number of particles in a given volume v , Z is the number of electrons in a molecule, $\langle N \rangle$ is the average of N , n_s is the standard deviation of the local number density, n_{ave} is the average number density, k_T is the isothermal compressibility, and k_T^0 is the value of k_T for an ideal gas.

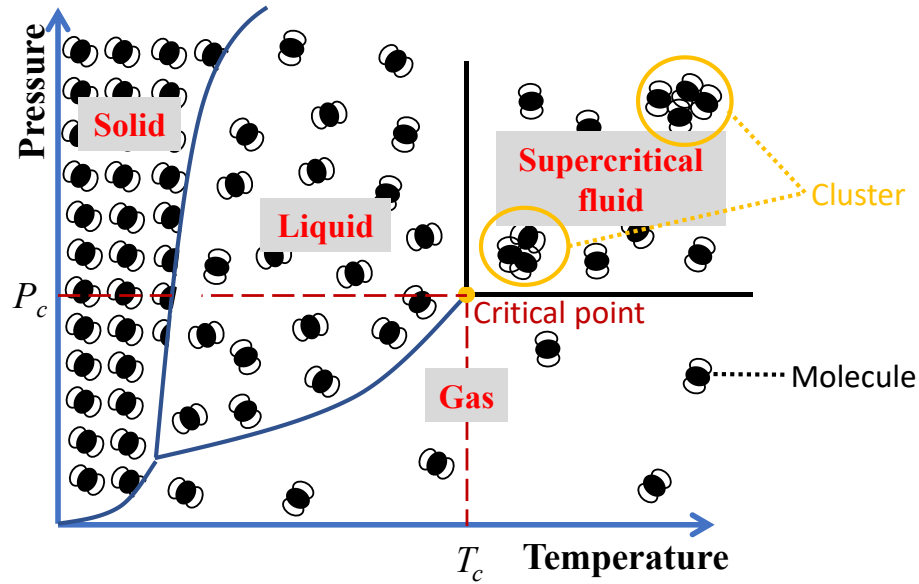


Figure 15 – A phase diagram showing four thermodynamic phases, with schematics of molecular distributions. In the supercritical fluid region, molecular clusters can cause regions with high and low densities where the FD value is substantial.

Figure 15 schematically shows a phase diagram with different molecular structures of the four different phases. Molecular clustering that occurs around critical point results in density fluctuation, which can be quantified by the density fluctuation F_D . SCFs appear to be homogeneous macroscopically, the structure of SCFs is very heterogeneous since the molecular distribution in SCFs is inhomogeneous. Especially near the critical point, the

aggregation and redispersion of clusters happens frequently [23]. The molecular clustering in SCFs causes the density to fluctuate strongly. It is known that the density fluctuates most strongly near the critical point, but density fluctuation also occurs far from the critical point.

This fluctuation theory is based on the concept of a grand canonical ensemble, where a single substance is divided into many small systems of equal volume v . Since the substance is assumed to be at equilibrium, the temperature and the chemical potential in those small systems will be the same. In Eq. (13), $N - \langle N \rangle$ represents the difference between the number of particles in a small system and the mean number. The mean squared fluctuation $\langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$ is a finite value. Thus, the mean squared fluctuations of the number of molecules as a fraction of the mean number of molecules in the system is proportional to the isothermal compressibility k_T .

The fluctuation theory can also be applied to supercritical binary mixtures. A grand canonical ensemble is again considered: molecules can travel between a large number of small systems of equal volume v . Let the system contain N_1 and N_2 molecules of two substances. Thus, $\langle N_1 N_2 \rangle - \langle N_1 \rangle \langle N_2 \rangle$ represents the tendency of interaction between two substances. If the quantity is positive, it means the two components tend to associate together [17]. Near the critical point, density fluctuations in the binary mixture are significant because the isothermal compressibility k_T is large. For CO₂, the isothermal compressibility near the critical pressure can be fifty times higher than that far from the critical pressure [96, 124]. The fluctuation can be even enhanced because the effect of the partial molar volume of the second substance in the mixture is also substantial. For example, Kim *et al.* showed that by using spectroscopic measurements the partial molar

volume of naphthalene in supercritical fluid CO₂ is 7,800 cm³/mol at 308.5 K and 7.98 MPa, which corresponds to eighty CO₂ molecules cluster around one molecule of naphthalene under this condition [125].

In the present study of supercritical CO₂-CF₃I binary mixtures, molecular interactions can occur among CO₂ molecules, among CO₂ and CF₃I molecules, and among CF₃I molecules. Since the mole fractions of CF₃I are relatively low, the CF₃I-CF₃I molecule encounters will be infrequent. As a result, the impact of CF₃I-CF₃I molecule interactions will not be very significant.

5.3.2 Boltzmann analysis on the dielectric properties of CO₂-CF₃I mixtures

The electrical breakdown characteristics of gaseous media can be analyzed by the electron kinetic process and estimated by the ionization (α) and attachment (η) coefficients. Boltzmann analysis has been widely used to obtain these coefficients theoretically. In this section, the dielectric properties of gaseous CO₂ and CF₃I are investigated by the two-term approximation of the Boltzmann equation.

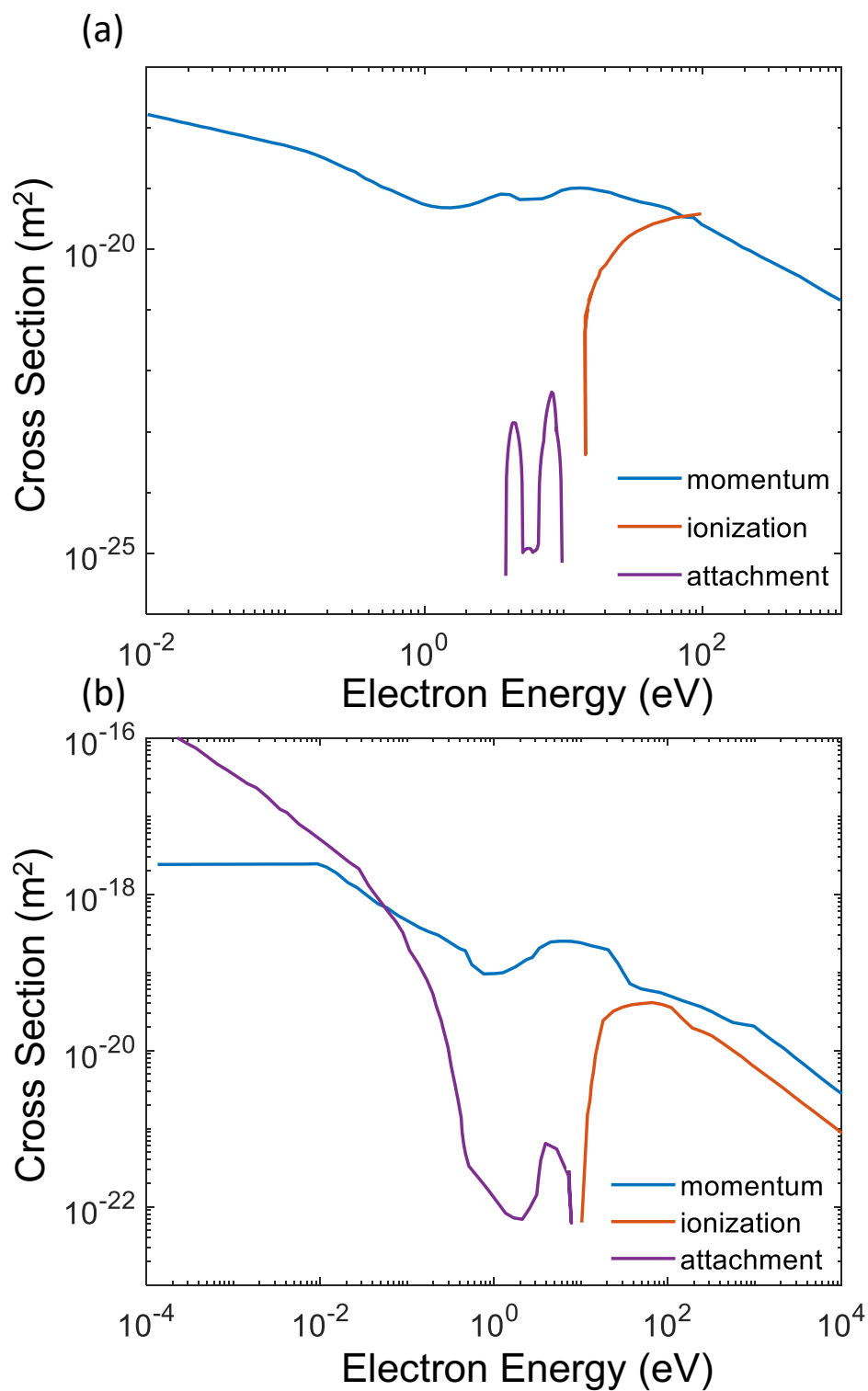
The electron-scattering cross section $\sigma(\epsilon)$ affects the electron energy distribution function (EEDF) and the electron kinetic process. Every gas species has its own sets of electron-scattering cross sections as a function of electron energy (ϵ). The Boltzmann analysis requires the electron-scattering cross sections of CO₂ and CF₃I, presented in Figure 16. The cross section data are collected from numerous datasets available in the LXCat project [101]. Specifically, cross section data of CO₂ are extracted from the SIGLO database [102], and cross section data of CF₃I are extracted from the Christophorou database [126]. It is obvious that the attachment cross section of CF₃I is higher than that of

CO₂. This indicates that CF₃I has a stronger electron attachment ability than CO₂, which leads to higher dielectric strength.

The Boltzmann equation describes the transport coefficients and rate coefficients for the given discharge condition [47]:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f - \frac{e}{m} \mathbf{E} \cdot \nabla_{\mathbf{v}} f = C[f] \quad (31)$$

where f is the electron distribution function, $\mathbf{v}$ is the velocity vector, e is the elementary charge, m is the electron mass, $\mathbf{E}$ is the electric field, $\nabla_{\mathbf{v}}$ is the gradient in the velocity space, and $C[f]$ represents the rate of change in f due to collisions.



In this part, the EEDF is calculated from the cross section data by solving the electron Boltzmann equation using a two-term approximation method. The dielectric strength of CO₂ and CF₃I can be estimated based on the electron kinetic processes represented by the density-reduced ionization coefficient (α/N) and the density-reduced attachment coefficient (η/N). Figure 17 presents α/N and η/N values calculated based on EEDFs of CO₂, CF₃I, and their mixtures at 50% CF₃I mass fraction, as a function of E/N . The results show a small variation in α/N values of these species. However, η/N values of CF₃I are apparently higher than η/N values of CO₂.

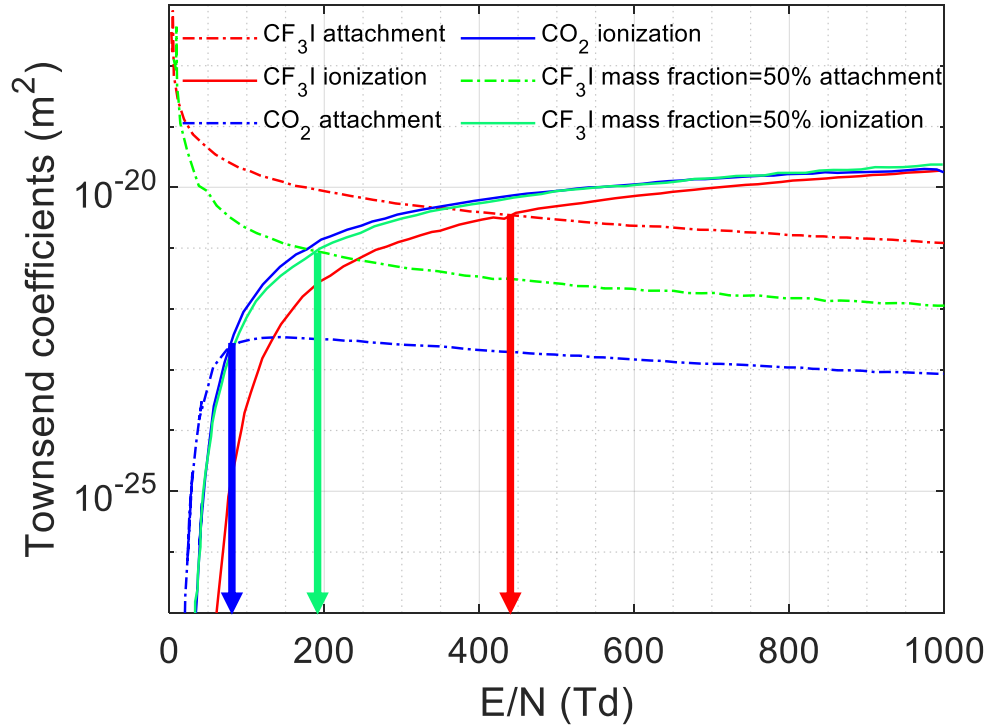


Figure 17 – The density-reduced ionization coefficient (α/N) and the density reduced attachment coefficient (η/N) of CO₂ (blue), CF₃I (red), and the mixture at 50% CF₃I mass fraction (green). Solid lines show values of α/N , and dashed lines show values of η/N . The density-reduced critical electric field ($(E/N)_{cr}$) of CF₃I reaches as high as 440 Td, the mixture at 50% reaches 190 Td, and pure CO₂ reaches 80 Td.

The density-reduced critical electric field ($(E/N)_{cr}$) is defined as the density-reduced electric field (E/N), in which the rates of ionization and attachment processes are equal, that is, E/N corresponding to $(\alpha - \eta)/N = 0$. For CO_2 , this value is about 80 Td, while for gaseous CF_3I , the value is about 440 Td. As for their mixture with a CF_3I mass fraction of 50%, this value is about 190 Td.

Theoretically, an increasing dielectric strength can be indicated from larger values of EEDF at low electron energy region, smaller α/N , and larger η/N [104, 127]. From the results of the above Boltzmann analysis, in general, relatively small variations are shown in the results of EEDFs and α/N values between CO_2 , CF_3I , and their mixtures. However, CF_3I exhibits much higher values of η/N as well as in the attachment cross section than those of CO_2 . Similarly, the density-reduced critical electric field of CF_3I is also 5.5 times higher than that of CO_2 , and 2.3 times higher than that of CF_3I - CO_2 mixture at 50% CF_3I mass fraction.

5.3.3 *Experimental investigation of the dielectric strength*

Breakdown voltage measurements of CO_2 - CF_3I mixtures are conducted in a uniform electric field formed between a 0.1 mm gap from gaseous phase to supercritical phase. CF_3I mass fractions of 10%, 20%, 30%, 40%, and 50% are chosen to be tested during the experiments. To know the thermodynamic phase inside the high-pressure chamber, we confirmed the critical points of the mixtures of the studied mix ratios separately in an optical chamber. Since the binary mixture scatters visible light in the region around the critical point, the optical pressure vessel is built to observe the phase transition and to measure the critical points of the mixtures. The phenomenon, known as critical

opalescence, indicates that there are significant density fluctuations over distances equal to the wavelength of visible light. In the situation that the density fluctuations reach to the size of the wavelength of light, the light is effectively scattered [17]. Table II compares the critical points obtained from the optical diagnostics and calculated from literature of EoS with respect to the mass fraction [119, 120]. Results from the two methods are in good agreement.

As shown previously in Figure 2 and Figure 14, the density-pressure ($\rho - P$) diagram shows that ρ changes rapidly at around the critical pressure P_c . The change is less dramatic and moves to higher pressures as the temperature T is increased. Thus, it is difficult to precisely control the density near the critical temperature T_c . Another consideration lies in the fact that the scale and magnitude of the density fluctuation F_D achieve maxima on the Widom line [27, 128], where the correlation length and the thermodynamic response functions have maximum values. It sets the boundaries of the liquid-like and the gas-like regions, even though no physically observable difference between liquid and gas exists in the SCF phase [128, 129]. So, in this study, to avoid the drastic change of fluid properties near the critical point, experiment temperatures T_e slightly (1-3 K) above the observed critical temperature T_c of different mixtures are selected. The experiment temperatures T_e are also listed in Table 12.

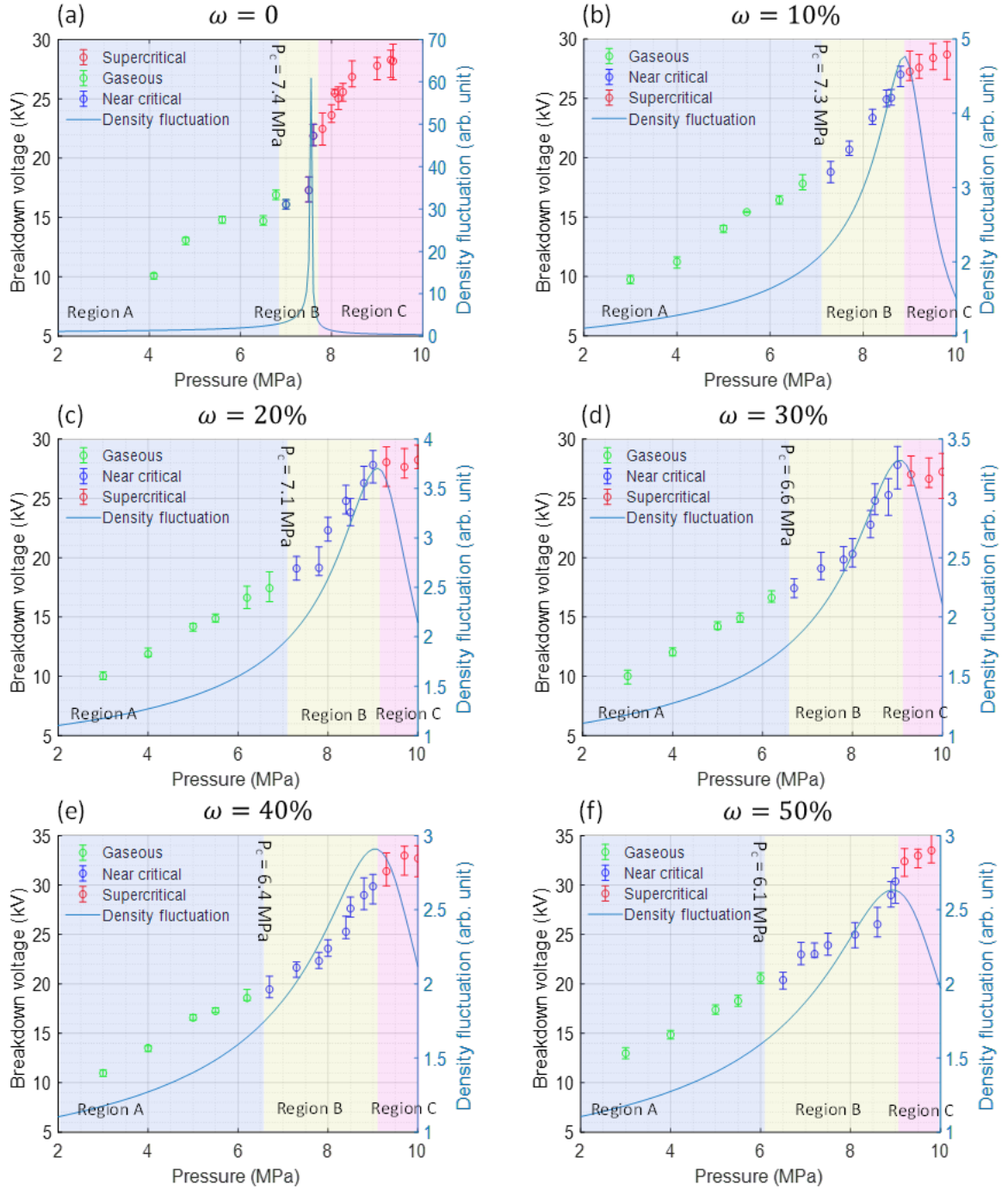


Figure 18 – Experimental results for the breakdown voltage of $\text{CO}_2\text{-CF}_3\text{I}$ mixtures at different CF_3I mass fraction values (ω). The dielectric strength measurement of pure CO_2 is also given as shown in (a). (b) – (f) represent the experimental result at different CF_3I mass fraction from 10% to 50%, respectively. Experiments are conducted in a high pressure chamber in a uniform electric field with an electrode gap distance of 0.1 mm. The medium undergoes a phase change from gaseous phase to supercritical state. The right y-axis indicates values of density fluctuation F_D , which

quantifies the molecular clustering. F_D is calculated based on the isothermal compressibility $k_T = k_s C_P / C_V$, where k_s is the isentropic compressibility, C_P is the heat capacity for the isobaric process, and C_V is the heat capacity for the isochoric process. Each figure is divided into three regions: region A indicates the breakdown of the medium in gaseous phase; region B indicates breakdown occurs when the medium changes its phase near its critical point before F_D reaches the maximum value, where breakdown voltages show the discontinuity; region C shows the breakdown occurs when the medium is significantly above its critical point after F_D reaches the maximum value. Green, blue, and red circles represent the average breakdown voltage for fifteen measurements in gaseous, near critical point, and in supercritical fluid phase, respectively. Please note that the diagrams have different scales.

Figure 18 shows the experimental results for the dielectric strength of CO₂-CF₃I mixtures up to 10 MPa. The mass fraction of CF₃I is adjusted from 0 to 50%, which corresponds to Figure 18, respectively. Every time when CF₃I mass fraction is changed, the medium undergoes a phase change from the gaseous phase to supercritical. The average breakdown voltage of fifteen measurements is represented by an open circle, and their scattering data are represented by a vertical error bar. For each mixture with a certain CF₃I mass fraction, the breakdown voltage figure can be divided into three regions: region A indicates the breakdown strength is measured with the medium being gaseous; region B emphasizes an apparent discontinuity of breakdown strength as a function of the medium pressure. In region B, F_D gradually increases to the maximum value; In region C, F_D starts to decrease, and it shows the dielectric strength of the medium significantly above the critical pressure P_c , where the breakdown voltage values tend to saturate.

As shown in Figure 18, breakdown voltage values for all mixtures from Region A show a linear pattern. This is because for electrical discharge in gaseous media, the breakdown phenomenon follows established theories known by Townsend discharge mechanism [28] and Paschen's law. The gas discharge theory illustrates that under a uniform electric field, the breakdown voltage V_{bd} can be expressed as [29]:

$$V_{bd} = \frac{BPd}{\ln \left[\frac{APd}{\ln(\frac{1}{\gamma})} \right]} \quad (32)$$

where A and B are constants based on the gas type determined from experiments, γ is the third Townsend ionization coefficient which describes the average of secondary electron emissions per positive ion bombarding the cathode, P is the pressure, and d is the electrode gap distance.

Table 12 – Comparison of the critical temperature and critical pressure for $\omega\text{CF}_3\text{I} + (1 - \omega)\text{CO}_2$. The last column indicates the experiment temperature. (ω : mass fraction of CF_3I)

ω	Optical diagnostics		EoS model		Experimental condition
	T_c (K)	P_c (MPa)	T_c (K)	P_c (MPa)	T_e (K)
10%	317	7.32	315	7.20	323
20%	324	7.13	322	6.90	325
30%	331	6.61	329	6.60	332
40%	340	6.38	337	6.30	342
50%	347	6.08	345	6.00	349

In cases where the type of gas and the cathode material are known, V_{bd} is only the function of the product of pressure P and gap distance d since A , B , and γ are determined. Region B and Region C show the breakdown voltage values in the situation near the critical point and above the critical point. The discontinuity of breakdown strength is observable

in these two regions, especially in Region B. In Region B and Region C, gas discharge theory fails to explain the phenomena where ideal gas law is no longer applicable. Paschen's law is not able to predict the breakdown voltage in these circumstances when a small change in the pressure could cause a large change in the density. According to Cookson *et al.*, Paschen's law shows the breakdown characteristics deviation in the compressed medium where the electric fields are on the orders of 10-20 kV/mm [100], which is much lower than those of SCFs (up to 350 kV/mm). Townsend discharge mechanism, on the other hand, also does not consider the field emission of electrons from the cathode in a high density medium environment.

This section discussed the theoretical and experimental research on the breakdown characteristics of supercritical CO₂-CF₃I binary mixtures at various mixing ratios. We show that supercritical CO₂-CF₃I binary mixtures have a dielectric behavior analogous to that of a pure fluid near the critical point. The present study fills a gap in the SCF research by providing the experimental validation of breakdown strength variations due to the density fluctuation in an SCF binary mixture. The average dielectric strength of the CO₂-CF₃I mixture at 50% CF₃I mass fraction shows a 20% improvement to that of the pure CO₂ at the supercritical phase. Since 50% of CF₃I mass fraction in this binary mixture fluid is only equivalent to 18.3% of mole fraction, the improvement of dielectric strength is not significant. The mole fraction gives direct information about the impact onto the dielectric strength from an electronic point of view since it correlates with the probability of electron-molecule collisions with one over the other constituents. In the present study, an 18.3% mole fraction of CF₃I indicates that electrons collide less frequently with the strongly electronegative CF₃I molecules, so the overall effect onto the dielectric strength is limited.

Nevertheless, our results show that such an SCF binary mixture exhibits a dielectric strength of up to 300-350 kV/mm, which is much higher than what could ever be achieved by a dielectric gas. Thus, this study indicates the suitability of using SCF mixtures as dielectric and insulating media for applications that require strong electric fields. Meanwhile, the low viscosity and high heat transfer capability of SCFs also make it possible to utilize SCFs in applications that need the effective heat dissipation and high-speed motion. For example, ultra-fast switchgear can benefit from such a dielectric medium by reducing the required contact separation, thereby allowing faster switching operation [109]. Graber *et al.* proposed a new generation direct-current circuit breaker, with SCFs as a new switching medium in the fast mechanical switch. Such a circuit breaker could play an enabling role for the materialization of wide-spread use of more reliable and resilient DC power applications in microgrids, shipboard power systems, wind collector systems, and railway applications [130]. Similarly, electrostatic rotating machines need to spin at high speed to develop power. However, gaseous dielectric media enable limited torque due to the low dielectric strength. Liquid dielectrics, on the other hand, introduce drag, which limits the speed of the machine. SCFs, which provide both high dielectric strength as well as low viscosity, are expected to be suitable for this application [110]. Moreover, linear particle accelerators equipped with van de Graaff generators that generate high-voltage DC for supplying ions can benefit from SCF insulation as it enables the reduction of size, cost, and ultimately allow more widespread use.

5.4 Dielectric strength investigation on the supercritical fluid mixture with perfluoronitrile

5.4.1 Physical and dielectric properties of perfluoronitrile

Sulfur hexafluoride (SF₆) has been the most commonly used insulation gas in power applications for decades since it combines excellent dielectric properties and material compatibility. However, SF₆ has been recognized as one of the most potent greenhouse gases with a long atmospheric lifetime [115]. The high global warming potential (GWP) of 22,800 of SF₆ is one of the reasons why numerous studies have been conducted to reduce SF₆ leakages [131, 132] as well as identify new candidates to replace SF₆ [133, 134]. Recently, a perfluoro-nitrile gas compound NOVEC 4710 (C₄F₇N) developed by 3M has drawn much attention due to its high breakdown strength and a significant reduction in GWP [84].

Compared with SF₆, C₄F₇N is known for its substantial reduction in environmental impacts. A comparison of the GWP values for a 100-year time horizon and some important physical properties of C₄F₇N and SF₆ is given in Table 13 [10, 84].

Table 13 – Physical properties of CO₂, SF₆, and C₄F₇N

	Molecular formula	Condensation temperature (°C)	Atmospheric lifetime (Years)	GWP
Carbon dioxide	CO ₂	-78.4	200	1
Sulfur hexafluoride	SF ₆	-68.3	3,200	22,800
Perfluoronitrile	C ₄ F ₇ N	-4.8	30	2,100

As shown in Table 13, the condensation temperature at the standard pressure of C₄F₇N is -4.8 °C. Thus, C₄F₇N has often been diluted into other gases to keep the partial

pressure low and thus prevent liquefaction in a low-temperature environment. Another reason why C_4F_7N is mixed with other gases is to reduce the GWP further. Dry air, CO_2 , and N_2 are often chosen as buffer gases. The mixture of C_4F_7N - CO_2 has been extensively researched recently due to its better arc quenching capability for disconnectors and circuit breakers [135, 136].

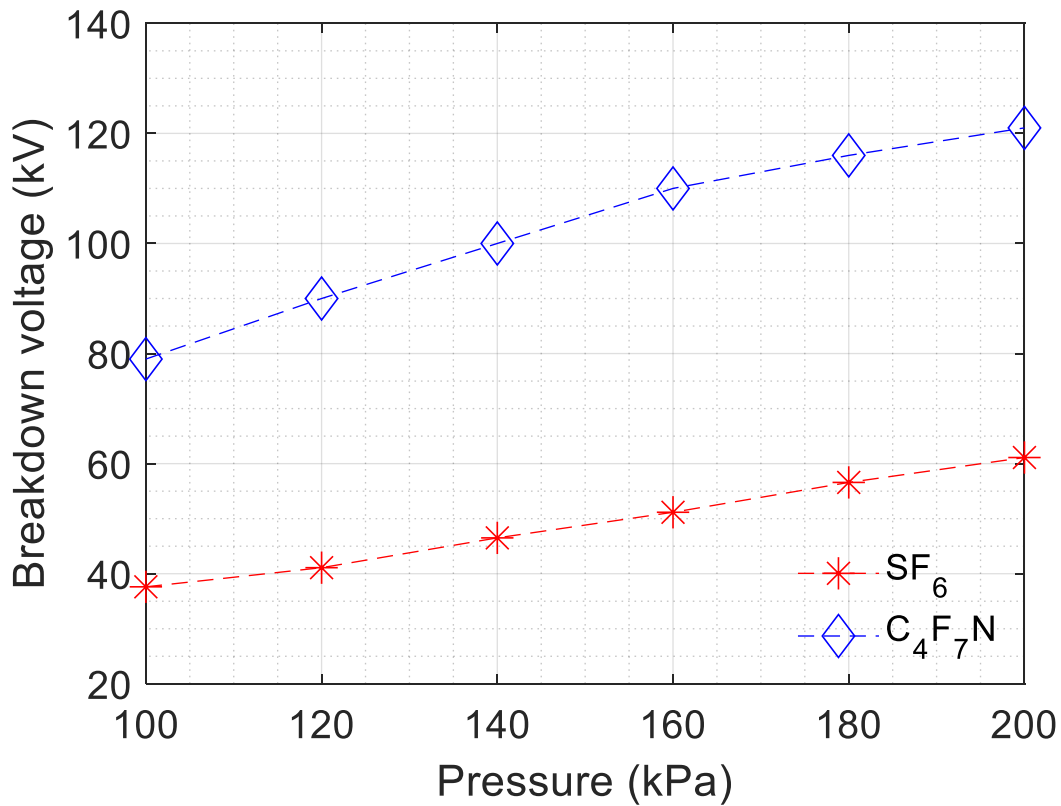


Figure 19 – Breakdown voltages of pure C_4F_7N and SF_6 under uniform field with a 10 mm gap, from 100 kPa to 200 kPa [136]. The recorded values are the peak value of the 60 Hz AC voltage. The gap length is 10 mm.

So far, the dielectric strength of SF_6 and C_4F_7N has been widely studied under different types of electrode configurations. The experimental demonstration shows that C_4F_7N has better dielectric performance than SF_6 in a uniform field. Specifically, Zhang *et al.* conducted breakdown experiments and directly compared the breakdown voltage of SF_6

and C_4F_7N using a 60 Hz AC voltage with a ramping rate of 2 kV/s [136]. Figure 19 shows the breakdown voltage of these two gases with a plane-plane electrode configuration and a gap of 10 mm. In the uniform field, C_4F_7N exhibits a dielectric strength of about two times higher than SF_6 from 100 kPa to 200 kPa.

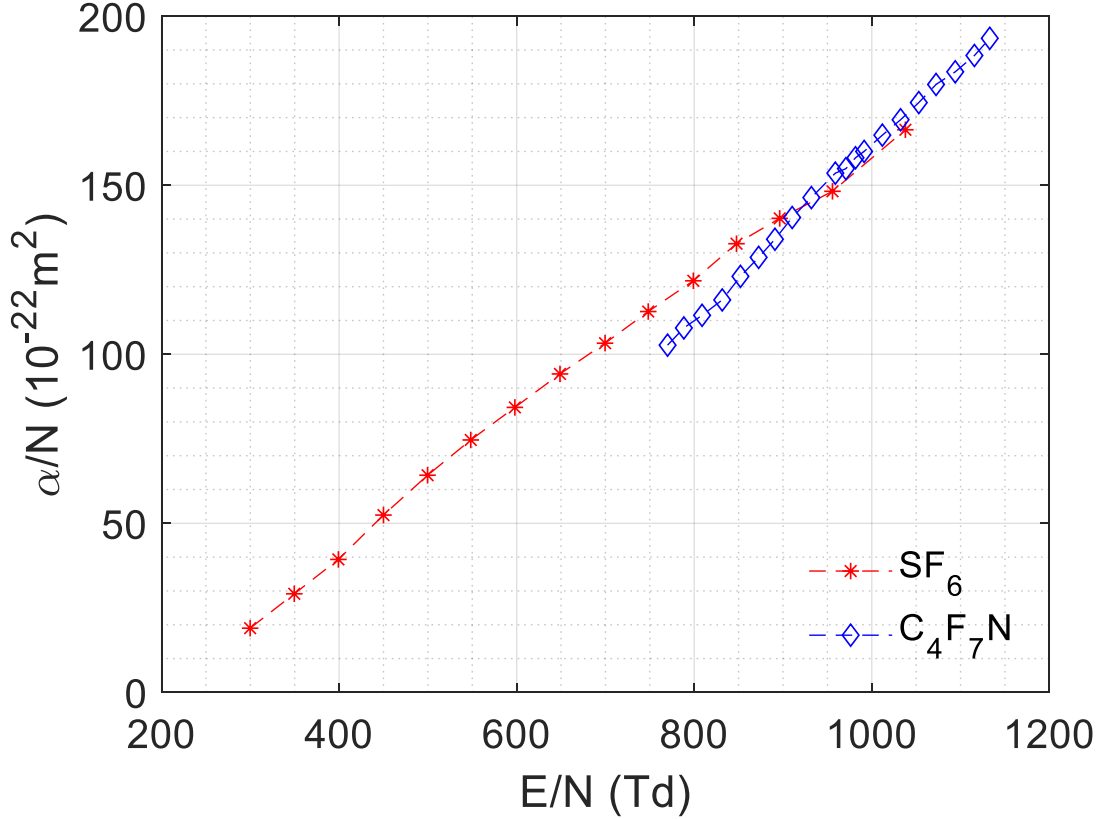


Figure 20 – The density-normalized ionization coefficient α/N of pure C_4F_7N and SF_6 [137, 138].

Figure 20 and Figure 21 give the direct comparison of the density-normalized ionization coefficient α/N and total attachment cross-sections between SF_6 and C_4F_7N , respectively. As shown in the figure, C_4F_7N shows smaller values of α/N than that of SF_6 when $E/N < 900$ Td. C_4F_7N 's α/N values are higher than that of SF_6 when $E/N > 900$ Td.

In general, SF_6 and $\text{C}_4\text{F}_7\text{N}$ have similar values of ionization coefficients. However, according to the total attachment cross-sections, $\text{C}_4\text{F}_7\text{N}$ shows larger values than that of SF_6 at energy above 0.1 eV. This indicates that $\text{C}_4\text{F}_7\text{N}$ has a stronger electron attachment ability than SF_6 . Therefore, $\text{C}_4\text{F}_7\text{N}$ has a better insulation performance because the attachment coefficient is much higher than that of SF_6 .

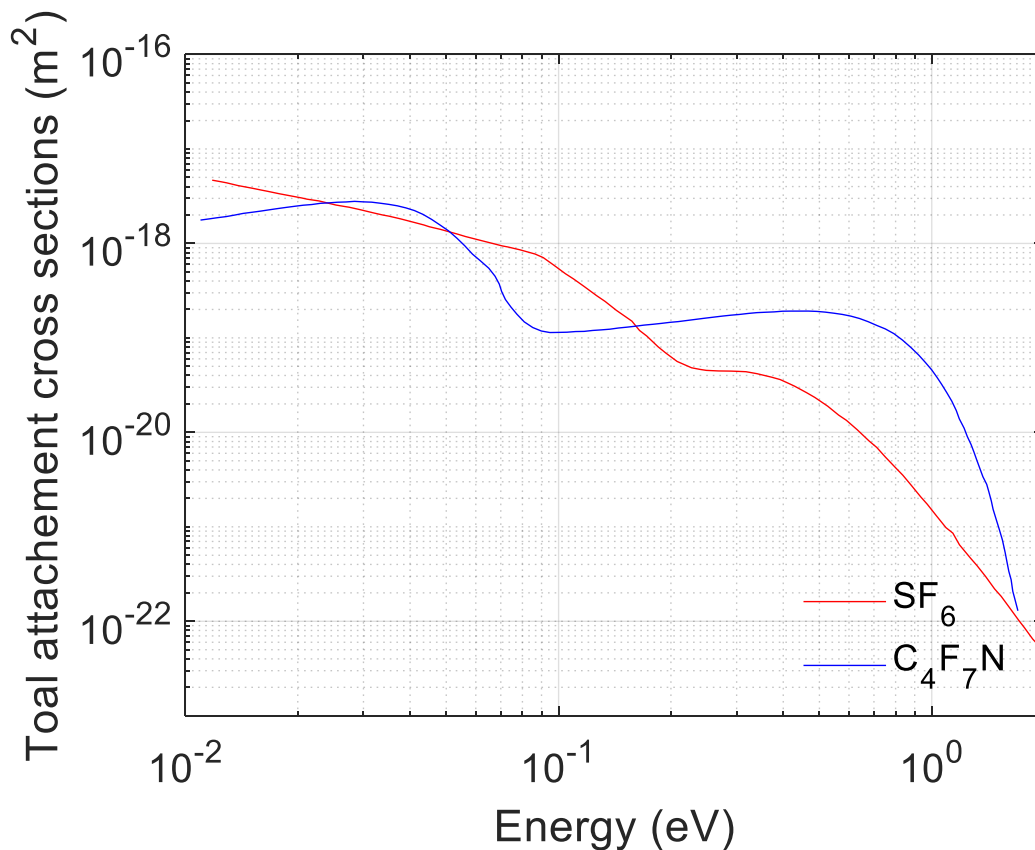


Figure 21 – Total attachment cross-sections of $\text{C}_4\text{F}_7\text{N}$ and SF_6 [86, 139].

Studies have been conducted on the electric discharge generated in supercritical CO_2 and N_2 , but there is no consideration of many other highly promising supercritical substances or their mixtures. This is especially true for power applications, where there has not been any investigation of SF_6 alternatives in the supercritical phase. Similarly, although

extensive research has focused on the dielectric property of C_4F_7N and its mixtures with CO_2 and N_2 over the past few years, these studies are all conducted below 1 MPa, which lacks the heat transfer and dielectric strength provided by SCFs.

The following section demonstrates the first experimental investigation on the breakdown characteristics of the supercritical CO_2 - C_4F_7N fluid mixture.

5.4.2 Breakdown characteristics of supercritical CO_2 - C_4F_7N fluid mixture

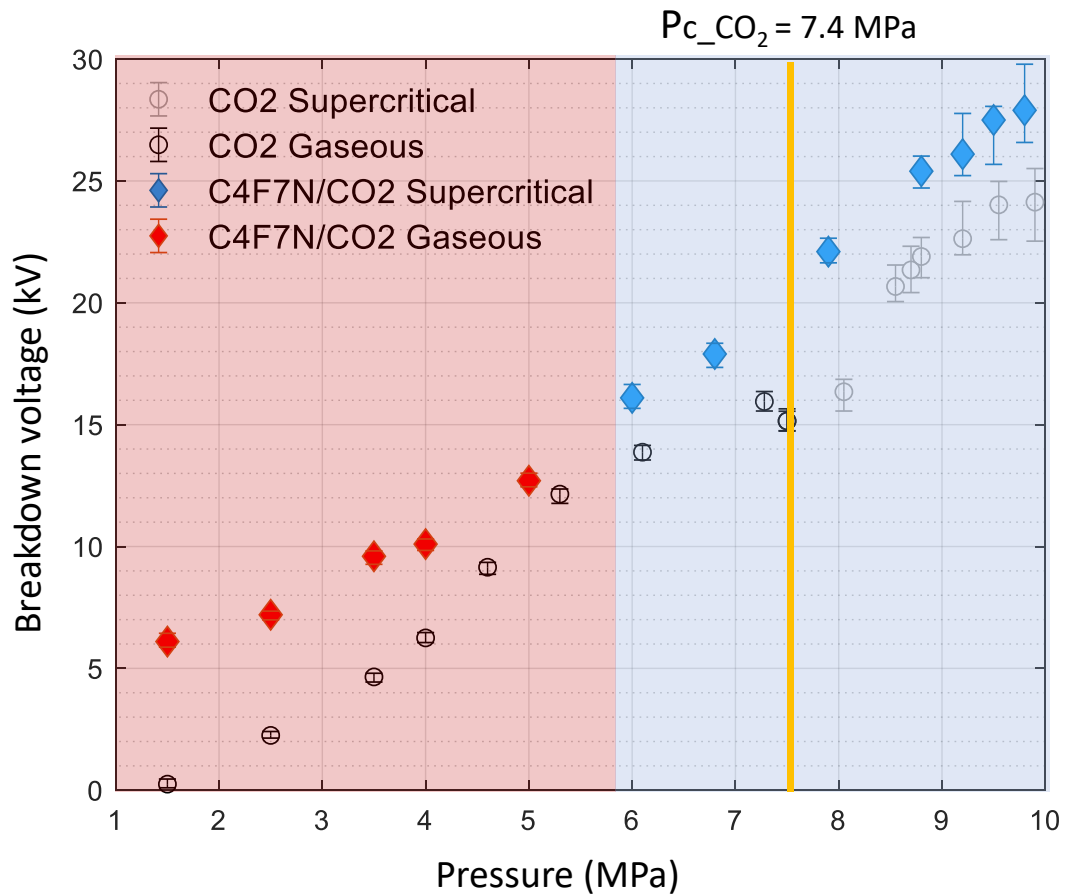


Figure 22 – The breakdown voltage of CO_2 - C_4F_7N fluid mixture at 40% C_4F_7N mass fraction. Breakdown voltages of pure CO_2 have been shown in black and gray markers. The solid yellow line indicates the critical pressure of pure CO_2 at 7.4 MPa.

Breakdown voltage measurements of the CO₂-C₄F₇N mixture are conducted in a uniform electric field formed between a 0.1 mm gap from the gaseous phase to the supercritical phase. The same experimental setup has been used, as illustrated in Appendix B. The C₄F₇N mass fraction of 40% is chosen to be tested during the experiments. To identify the thermodynamic phase inside the high-pressure chamber, we first confirmed the critical points of this mixture in an optical chamber, as shown in Figure 11. The binary mixture scatters visible light in the region around the critical point, the optical pressure vessel is built to observe the phase transition and to measure the critical points of this mixture. This critical opalescence indicates that there are significant density fluctuations over distances equal to the wavelength of visible light. In the situation that the density fluctuations reach to the size of the wavelength of light, the light is effectively scattered [17].

Table 14 – Experimental condition and optical observation of the critical point of the CO₂-C₄F₇N mixture at the mass fraction of 40%.

Substance	Mass fraction of C ₄ F ₇ N	Molar fraction of C ₄ F ₇ N	Critical temperature T_c (K)	Critical pressure P_c (K)	Experimental temperature T_e (K)
CO ₂ -C ₄ F ₇ N	40%	18%	335	5.90	338

As illustrated before, SCFs on the density-pressure (ρ - P) diagram show that ρ changes rapidly at around the critical pressure P_c . The change is less dramatic and moves to higher pressures as the temperature T is increased. Thus, it is difficult to precisely control the density near the critical temperature T_c . Another consideration lies in the fact that the scale and magnitude of the density fluctuation F_D achieve maxima on the Widom line [27,

128], where the correlation length and the thermodynamic response functions have maximum values. It sets the boundaries of the liquid-like and the gas-like regions, even though no physically observable difference between liquid and gas exists in the SCF phase [128, 129]. So, in the study of the CO₂-C₄F₇N mixture, to avoid the drastic change of fluid properties near the critical point, experiment temperature T_e is selected slightly above the observed critical temperature T_c . The experimental condition is listed as shown in Table 14.

Figure 22 shows the experimental results for the dielectric strength of the CO₂-C₄F₇N mixture up to 10 MPa. The mass fraction of C₄F₇N is selected to be 40%. The average breakdown voltage of fifteen measurements is represented by the diamond, and their scattering data are represented by a vertical error bar. The breakdown voltage figure can be divided into two regions: the red region on the left indicates the breakdown strength is measured with the medium being gaseous; the blue region on the right shows the breakdown voltage measured in SCF. To make the comparison clearer, the dielectric strength of pure CO₂ has also been added into the figure with black and gray open circles and vertical bars. In the gaseous region, especially when the pressure is below 4 MPa, the dielectric strength of CO₂-C₄F₇N shows an average of around 200% improvement than pure CO₂. The dielectric strength improvement is less pronounced when the medium enters the supercritical state. The experimental result shows an average of around 18% dielectric strength improvement than pure CO₂.

5.5 Dielectric strength investigation on the supercritical fluid mixture with oxygen

In this section, the dielectric strength of gaseous and supercritical CO_2/O_2 mixture is investigated. Many previous works have been conducted on gaseous CO_2/O_2 mixture, and the main advantage of adding O_2 is that it helps avoid carbon deposits thus increase stability of medium after repeated dissociation [140, 141]. Although experimental investigations have been conducted on the gaseous CO_2/O_2 mixture [97, 142], the dielectric strength of supercritical CO_2/O_2 mixture is unknown. Therefore, the present work is focused on the dielectric strength of supercritical CO_2/O_2 mixture in a 0.1 mm uniform electric field.

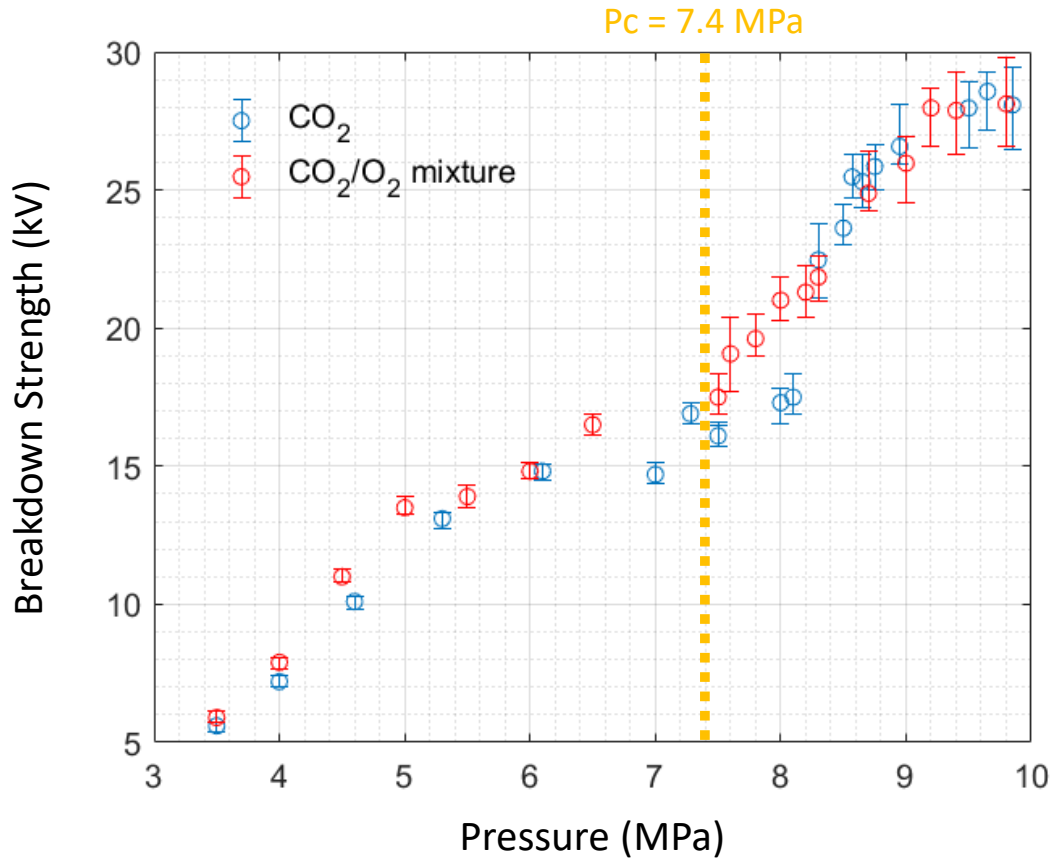


Figure 23 – The breakdown voltage of $\text{CO}_2\text{-O}_2$ fluid mixture at 25% O_2 mass fraction. Breakdown voltages of pure CO_2 have been shown in blue markers. The dashed yellow line indicates the critical pressure of pure CO_2 at 7.4 MPa.

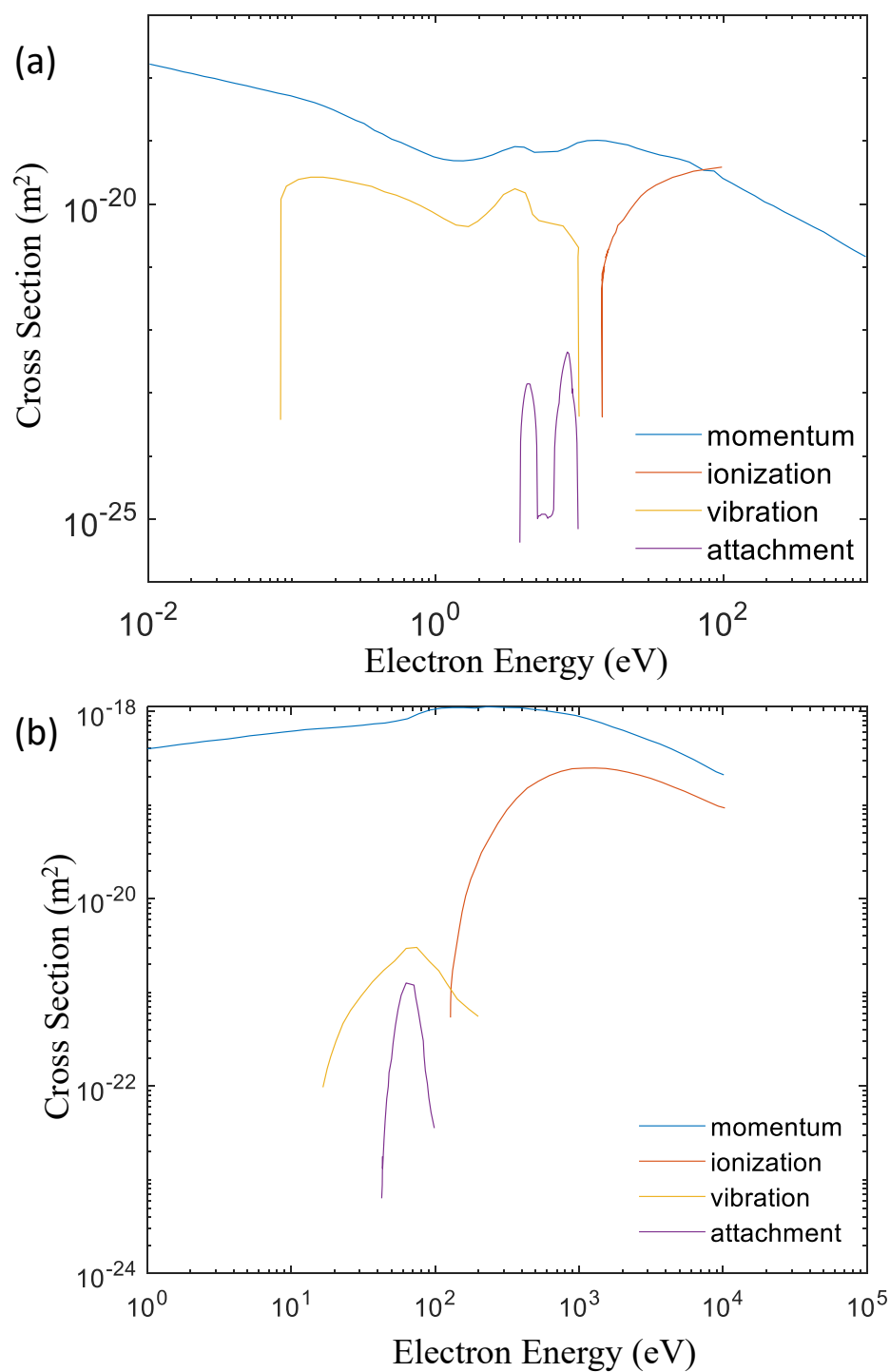


Figure 24 – (a) The electron-scattering cross section of CO₂, (b) the electron-scattering cross section of O₂. The y-axis scales differently in (a) and (b).

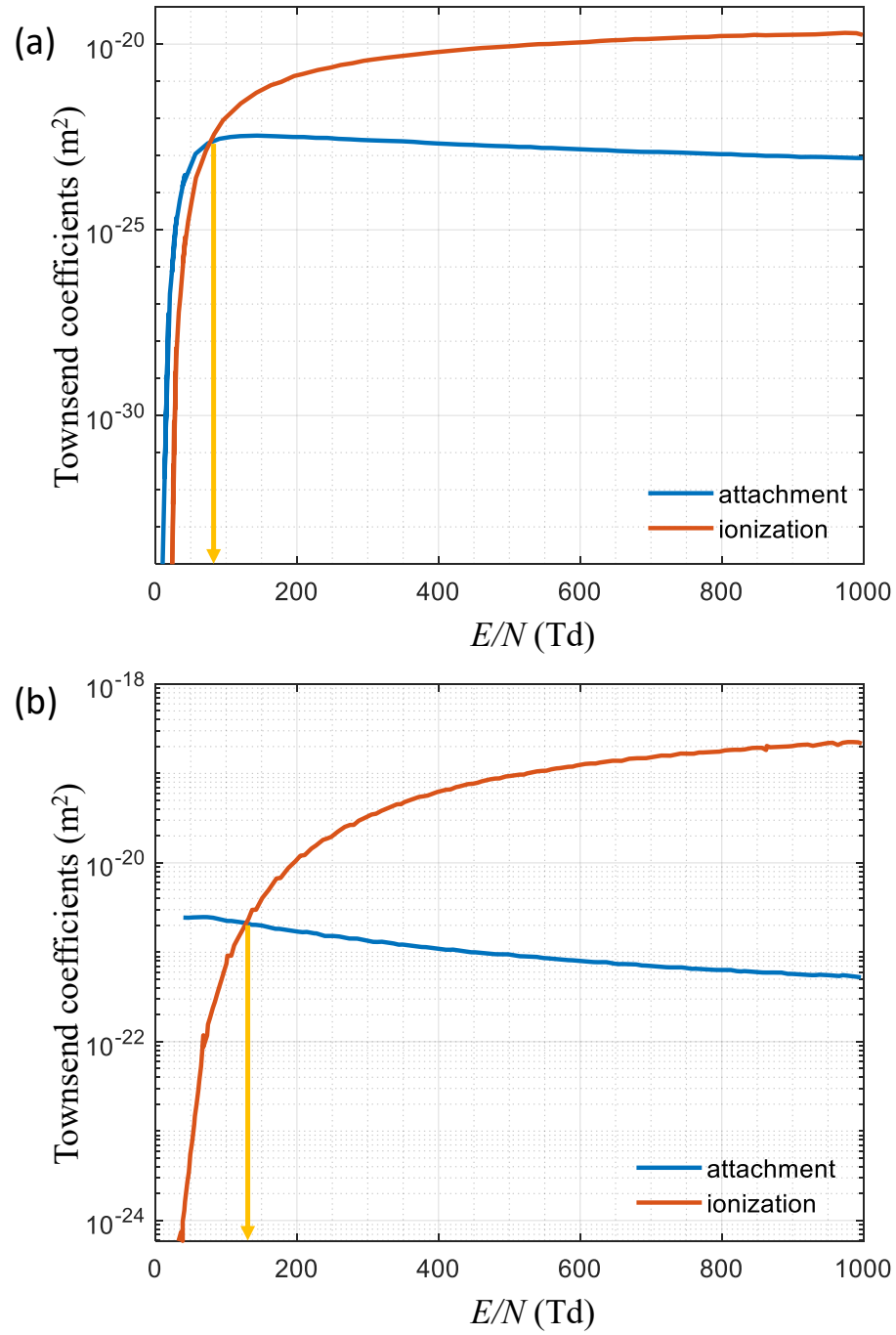


Figure 25 – The density-reduced ionization coefficient (α/N) and the density reduced attachment coefficient (η/N) of CO_2 (a) and O_2 (b). The density-reduced critical electric field ($(E/N)_{cr}$) of O_2 reaches around 130 Td, and pure CO_2 reaches around 80 Td.

The breakdown voltage measurements of CO₂/O₂ mixture are conducted at the temperature of 310 K from the gaseous phase to supercritical condition. The mass fraction of O₂ is about 25%, which is equivalent to 30% molar fraction. Figure 23 shows the measured breakdown voltages as a function of pressure. The average breakdown voltage of fifteen measurements and their scattering data at one experimental condition are represented by an open circle and a vertical error bar. To make a comparison, the breakdown strength of pure CO₂ is also included in the figure. In general, the dielectric strength of this mixture shows a more obvious improvement at the lower pressure region (lower than 7 MPa). When the pressure reaches the critical pressure, there is no obvious increase of breakdown strength in the supercritical fluid state.

To interpret the experimental result, electron kinetics and Boltzmann analysis are conducted. Figure 24 shows the electron-scattering cross section of CO₂ and O₂. The cross section data are collected from numerous datasets available in the LXCat project [101]. Cross section data of CO₂ and O₂ are extracted from the SIGLO database [102]. The dielectric strength of CO₂ and O₂ can be estimated based on the electron kinetic processes represented by the density-reduced ionization coefficient (α/N) and the density-reduced attachment coefficient (η/N). Figure 25 presents α/N and η/N values calculated based on EEDFs of CO₂ and O₂, as a function of E/N . The density-reduced critical electric field ($(E/N)_{cr}$) is defined as the density-reduced electric field (E/N), in which the rates of ionization and attachment processes are equal, that is, E/N corresponding to $(\alpha - \eta)/N = 0$. For gaseous CO₂, this value is about 80 Td, while for gaseous O₂, the value is about 130 Td. The result indicates that gaseous O₂ is supposed to have a higher dielectric strength than gaseous CO₂, which agrees with the experimental result.

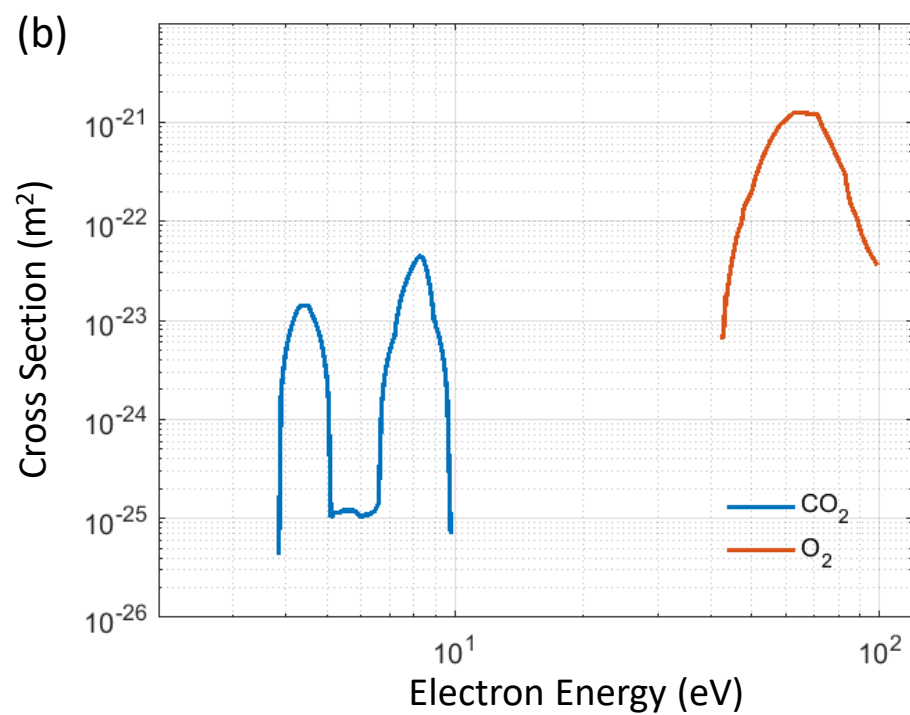
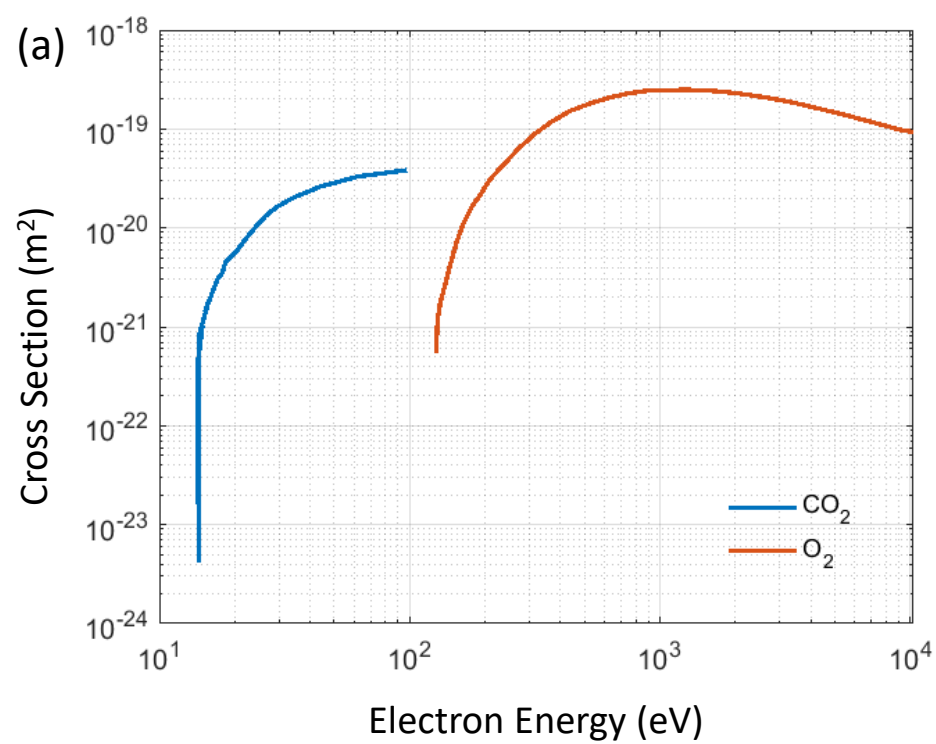


Figure 26 – (a) The ionization cross section of CO_2 and O_2 , (b) The attachment cross section of CO_2 and O_2 .

Although a 10% dielectric strength improvement is observed in the gaseous phase, the CO₂/O₂ mixture shows almost the same breakdown voltage above the critical pressure. One possible reason for this phenomenon is that the density of the medium is much higher in SCF than in gas. The mean free path of electron in SCF is shorter than the mean free path in gaseous. Therefore, the cross section of the substance is more impactful at the lower electron energy region when it comes to SCF state. Figure 26 compares the ionization cross section and the attachment cross section of CO₂ and O₂. It can be seen that the cross section of CO₂ dominates the lower electron energy region, while the cross section of O₂ is more pronounced at the higher electron energy region.

In conclusion, the experimental result shows that the CO₂/O₂ mixture manifests a 10% dielectric strength improvement over pure CO₂ in the gaseous phase. The breakdown strength maintains the same level of pure CO₂ when the medium enters the supercritical state. Since O₂ can oxidize free carbon generated in CO₂ discharges and arcs, this mixture is suitable for power applications that require carbon control during arc quenching activities.

5.6 Summary

Extensive research has been carried out on the electric discharge generated in supercritical CO₂ and N₂, yet there is no consideration of many other highly promising supercritical substances or their mixtures. This is especially true for power applications, where there has not been any investigation of SF₆ alternatives in the supercritical phase. Similarly, although numerous research efforts have focused on the insulation performance of CF₃I and its mixtures with CO₂ and N₂ over the past few years [75, 76, 118], these

studies are all conducted in the gaseous phase, which lacks the heat transfer and dielectric strength provided by SCFs. In this chapter, theoretical and experimental investigations are conducted on supercritical carbon dioxide and different supercritical fluid mixtures. Experimental investigation on pure CO₂ has been conducted to explore the breakdown characteristics of SCFs. The result shows a close correlation between the dielectric strength and the density fluctuation of the fluid. The materials added to CO₂ range from highly electronegative substances to azeotropic constituents, such as C₄F₇N, CF₃I, O₂, and C₂H₆. The result from this chapter fills the gap in the dielectric strength research by providing breakdown strength data on different SCF substances. Furthermore, the result indicates that the anomalous breakdown characteristics discovered in the pure SCF are also observable in binary mixtures of supercritical fluids. The similar behavior suggests that the unstable molecular clustering could significantly affect the discharge phenomenon observed in both pure SCFs and supercritical mixtures. The results show that some SCF binary mixtures, such as CO₂-CF₃I and CO₂-C₄F₇N, exhibit a dielectric strength of up to 300-350 kV/mm, which is much higher than what could ever be achieved by a dielectric gas. Thus, this study indicates the suitability of using SCF mixtures as dielectric and insulating media for applications that require strong electric fields. Meanwhile, the low viscosity and high heat transfer capability of SCFs also make it possible to utilize SCFs in applications that need effective heat dissipation and high-speed motion. For example, ultra-fast switchgear can benefit from such a dielectric medium by reducing the required contact separation, thereby allowing faster switching operation [109]. Graber *et al.* proposed a new generation direct-current circuit breaker, with SCFs as a new switching medium. Such a circuit breaker could play an enabling role for the materialization of the widespread use of more reliable and

resilient DC power applications in microgrids, shipboard power systems, wind collector systems, and railway applications [130]. Similarly, electrostatic rotating machines need to spin at high speed to develop power. However, gaseous or vacuum dielectric media enable limited torque due to the low dielectric strength. Liquid dielectrics, on the other hand, introduce drag, which limits the speed of the machine. SCFs, which provide both high dielectric strength as well as low viscosity, are ideal for this application [110]. Moreover, linear particle accelerators equipped with Van de Graaff generators that generate high-voltage DC for supplying ions can benefit from SCF insulation as it enables the reduction of size, cost, and ultimately allow more widespread use.

CHAPTER 6. UNDERSTANDING THE BREAKDOWN STRENGTH ANOMALY OF SUPERCRITICAL FLUIDS NEAR THE CRITICAL POINT

The investigation of electrical discharge in SCFs has been a continuing effort for decades, yet most studies are related to the generation of electric plasmas in SCFs for chemical synthesis and nanomaterials fabrication [22, 23]. There are few reports on utilizing SCFs as dielectric media for insulating purposes. As a relatively new field of research, the feasibility of SCFs to replace conventional dielectric and insulating media came into public notice only a few years ago [1, 46]. In addition, although experimental investigations on the electrical discharge in SCFs have been carried out mostly in the non-uniform electric field, theoretical analysis is less explored. Specifically, there is no broadly accepted theory describing the breakdown mechanism in SCFs, and the breakdown characteristics of SCFs in the uniform field is mostly unknown.

Theoretical models have been developed to describe the electrical breakdown in SCFs. Tian *et al.* and Haque *et al.* developed models to describe the mechanism of electrical breakdown in supercritical CO₂, He, and Xe with molecular clusters formation based on electron scattering cross sections. By analyzing the cross-section data of clusters, it has been confirmed that the cross-section data of clusters decrease from those of gases, especially near the critical point [53-55, 143]. Muneoka *et al.* presented an investigation of the breakdown behavior of micrometer gap DC discharges in supercritical helium and developed a discharge model to reproduce the breakdown behavior by using an improved gas-like and liquid-like breakdown mechanism [38]. Even though extensive research has

been conducted on this topic, the discharge behavior of highly-pressurized media, especially during the transition from gaseous to supercritical phase, is not fully understood. The gas discharge theory developed by Townsend's and Paschen's work [28, 29] is found to be inaccurate in estimating the breakdown behavior [1]. In addition, it cannot explain the critical anomaly in the dielectric strength in supercritical fluids, especially near the critical point [22, 23].

This chapter demonstrates a new numerical method that combines the effect of local density fluctuation and the structural analysis by small angle X-ray scattering to interpret data obtained from the electrical breakdown test. Since the properties of traditional dielectric media have been a major limiting factor impacting the design and operation of many applications spanning from particle accelerators over X-ray radiography and radiotherapy to electrical power systems, the research in SCFs as dielectric media could serve as a key to unlock the design of numerous applications that require high power density.

6.1 Structure analysis by small angle X-ray scattering

Small angle X-ray scattering is an analytical technique that measures the intensities of X-rays scattered by a sample as a function of the scattering angle. It is used to measure the intensity at large distances, or small angles. Small angle X-ray scattering has been used to study nanoparticles since the 1950s [144]. Since then, it has been a powerful method to determine an object's size, size distribution, shape, and surface structure. Furthermore, it has also been used to measure the relative positions of particles [145]. Small angle X-ray scattering has increased its popularity in recent years due to the rapid development of

synchrotron X-ray sources with high flux and high energy. This technique has two major advantages: it is nondestructive, and provides structural data averaged over macroscopic sample volumes. Small angle X-ray scattering is also able to characterize structural information in realistic sample conditions due to the tunable flux and energy at modern synchrotrons [146].

Small angle X-ray scattering technique has also been used to characterize the structural composition of SCFs. Density fluctuation and correlation length are the most suitable parameters to quantitatively evaluate the inhomogeneity of SCFs. The density fluctuation quantifies the inhomogeneity from the number of molecules, and the correlation length describes the inhomogeneity from the size of aggregates of molecules. These two parameters can be obtained by small angle X-ray scattering experiments, small angle neutron scattering experiments, and static light scattering experiments [147-149]. Among all the methods, small angle X-ray scattering has been most frequently used to study the structural inhomogeneity of SCFs.

6.2 Theoretical analysis based on the van der Waals equation and density fluctuation

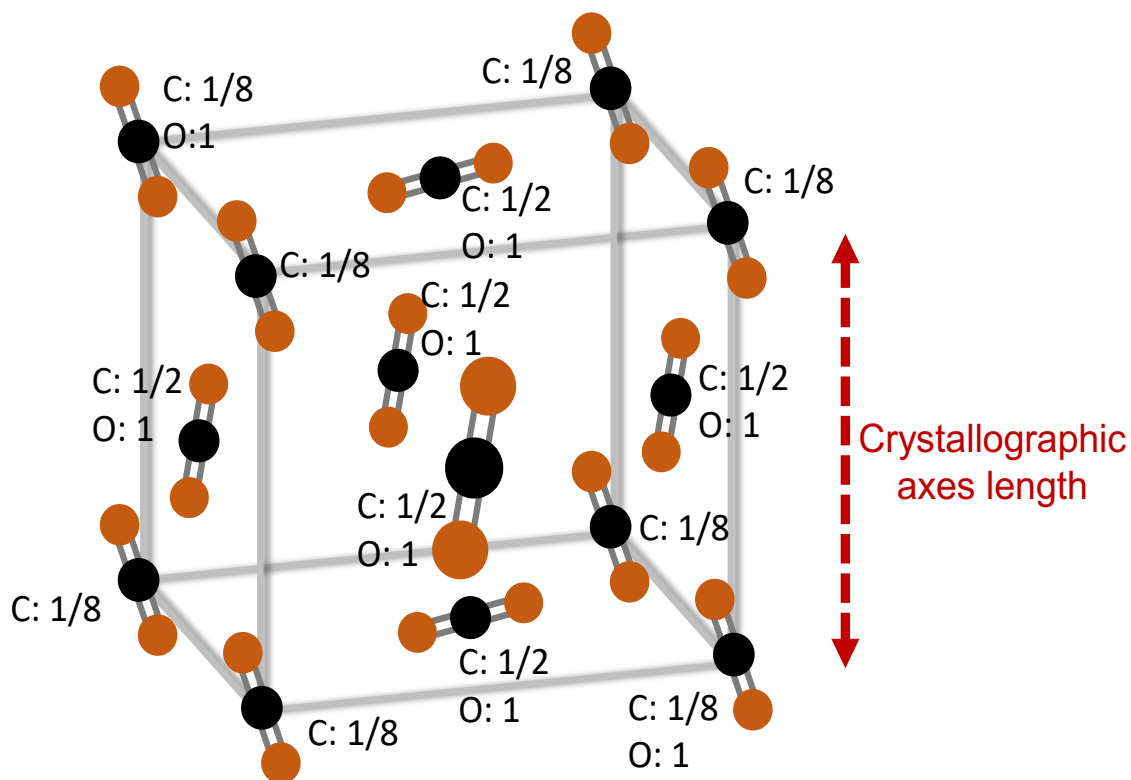


Figure 27 – The crystal structure of CO₂: a face-centered-cubic structure. It has a coordination number of twelve and contains four molecules per unit cell. Red circles indicate the oxygen atom, and black circles indicate the carbon atom.

The numerical calculation and derivation of the van der Waals equation and density fluctuation is demonstrated in Appendix E. The Ornstein–Zernike is an integral equation for defining the direct correlation function. It describes how the correlation between two molecules can be calculated.

According to the crystallographic axes L_s and the number of molecules (or atoms) per unit cell k , the cluster size of supercritical fluid (number of molecules or atoms in a cluster) can be calculated as follows:

$$N = \left(\frac{\xi}{L_s}\right)^3 k \quad (33)$$

In the present study, CO₂ has a face-centered-cubic crystal structure as shown in, which means it has a coordination number of twelve and contains four molecules per unit cell. The corresponding length of the crystallographic axes of CO₂ is measured from 4.330 Å to 5.963 Å [150]. According to the cell edge length, the cluster size of supercritical CO₂ at different thermodynamic conditions can be calculated as presented in the following section.

6.3 Experimental testing on the dielectric strength

The complete SCF breakdown testing setup is described as shown in Appendix B. The experiments are conducted under DC voltage (Spellman SL60PN1200, rated 60 kV and 20 mA). The voltage is ramped up at 0.5 kV/s, and the gap between the two electrodes is set to be 0.1 mm. The gap length is adjusted and controlled by a stainless steel feeler gauge. The breakdown voltage is then measured and recorded fifteen times at each thermodynamic condition. The average breakdown voltage and the corresponding scattering data are calculated based on these fifteen measurements. The average time interval between two successive breakdown events is about two minutes to minimize the effect of the medium state variation caused by the arc discharge. In addition, the time interval allows discharge byproducts to move away from the zone of the highest electric field.

6.4 Results and discussions

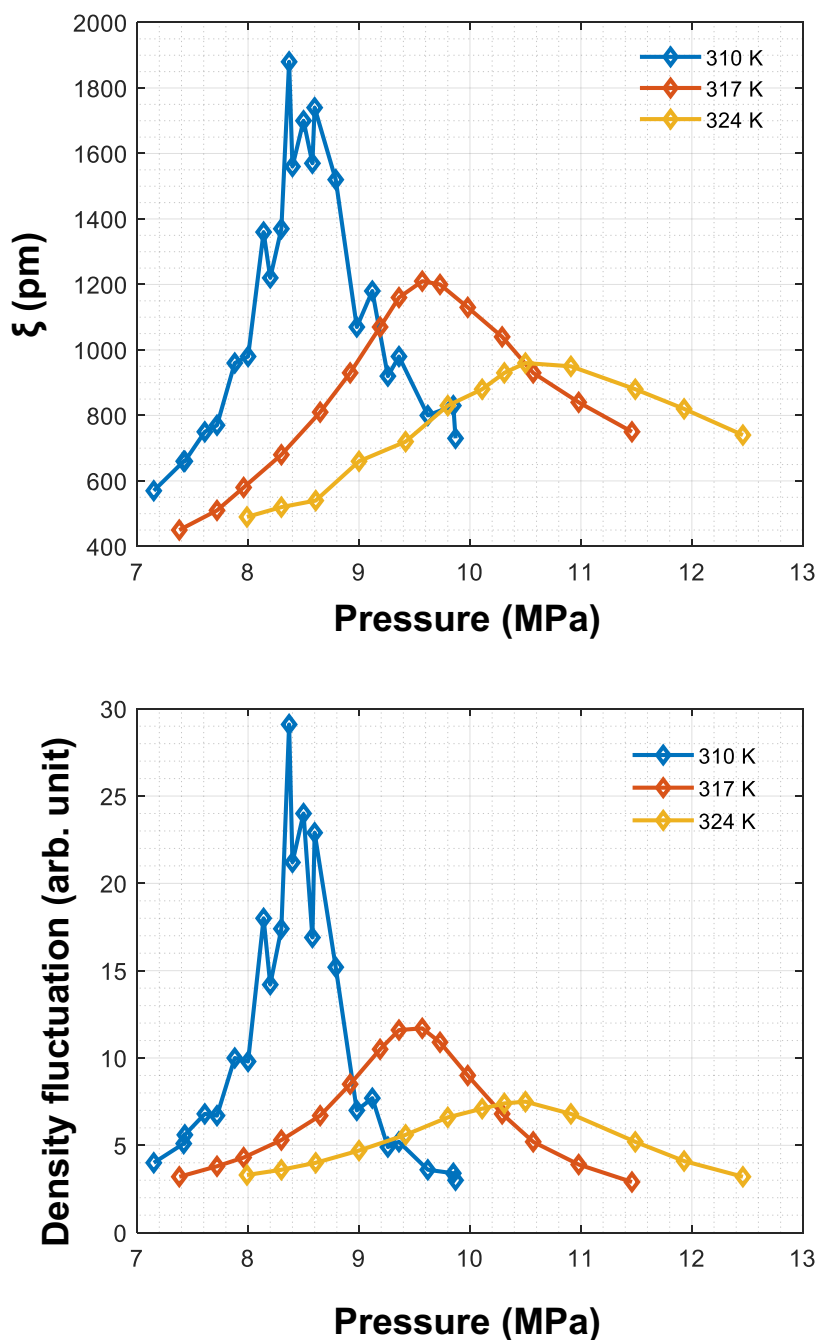


Figure 28 – The Ornstein-Zernike correlation length ξ (above) and density fluctuation values (below) obtained from small angle X-ray scattering experiments in supercritical CO₂ as a function of pressure [123]. The temperature values of the experiment is 310 K, 317 K, and 324 K.

The Ornstein-Zernike correlation length ξ and the density fluctuation values are obtained from the small-angle x-ray scattering experiments reported by Nishikawa *et al.*[123] Their results are plotted as shown in Figure 28. They show the Ornstein-Zernike correlation length ξ of supercritical CO₂ obtained from scattering experiments as a function of the pressure, at the temperature of 310 K, 317 K, and 324 K. Figure 28 also shows density fluctuation values of supercritical CO₂ obtained from scattering experiments as a function of the pressure, at the temperature of 310 K, 317 K, and 324 K. A detailed discussion about the correlation length and density fluctuation is presented in Appendix E.

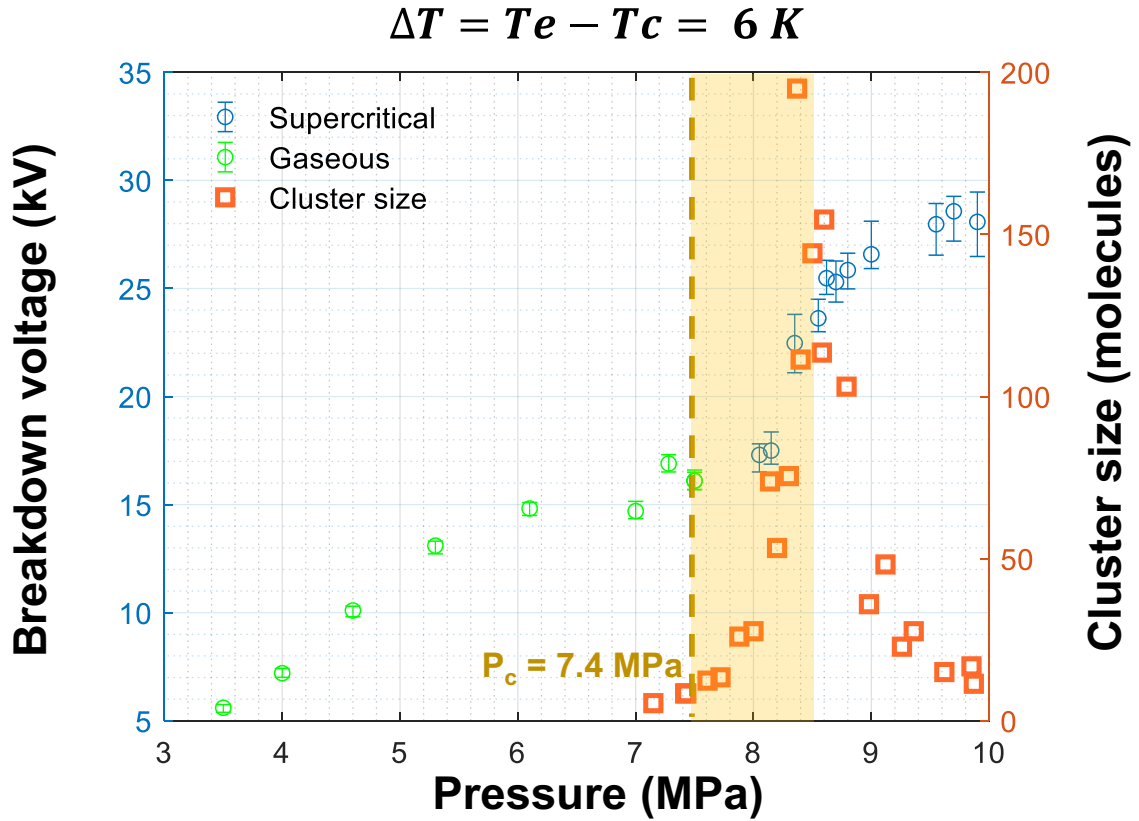


Figure 29 – The experimental result of the breakdown voltage of supercritical CO₂ at 310 K. Experiments are conducted in a uniform electric field at 0.1 mm. The average breakdown strength values are indicated by circles, with their scattering values indicated by the horizontal error bars. The right y-axis indicates the cluster size

calculated by the numerical model. The shaded area highlights the area from the critical pressure T_c to the maximum cluster size.

The breakdown voltage measurements of CO₂ are carried out at the same temperature as the small-angle x-ray scattering experiment at 310 K, 317 K, and 324 K from the gaseous phase to supercritical condition. Figure 29, Figure 30, and Figure 31 show the measured breakdown voltage as a function of the pressure at these three temperature values, respectively. The average breakdown voltage of fifteen measurements and their scattering data under one experimental condition is represented by an open circle and a vertical error bar, respectively. The right y-axis shows the calculated result of the cluster size at different thermodynamic conditions of supercritical CO₂, based on the cell edge length. As shown in the left y-axis, the measured breakdown voltage values increase with the density of CO₂ and scatter more in the supercritical region. An obvious discontinuity of the slope can be observed near the critical point where the substance experiences a phase change.

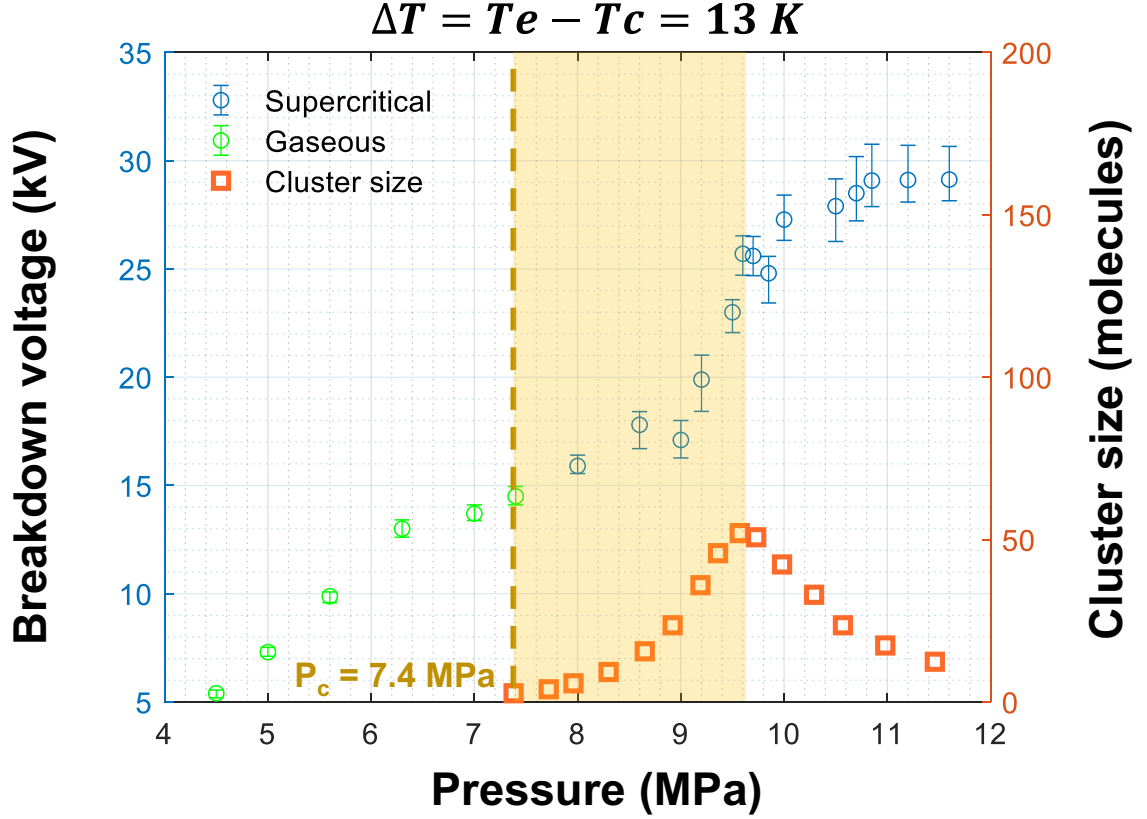


Figure 30 – The experimental result of the breakdown voltage of supercritical CO₂ at 317 K. Experiments are conducted in a uniform electric field at 0.1 mm. The average breakdown strength values are indicated by circles, with their scattering values indicated by the horizontal error bars. The right y-axis indicates the cluster size calculated by the numerical model. The shaded area highlights the area from the critical pressure T_c to the maximum cluster size.

The cluster size achieve maxima on the Widom line, where the correlation length has maximum values. Therefore, for an isothermal process, the number of clusters reaches maximum at the critical pressure P_c only if the temperature is at the critical temperature T_c . In the present study, since all the experimental temperatures (310 K, 317 K, and 324 K) are chosen above the critical temperature T_c , the maximum value of cluster size appears at the position higher than the critical pressure.

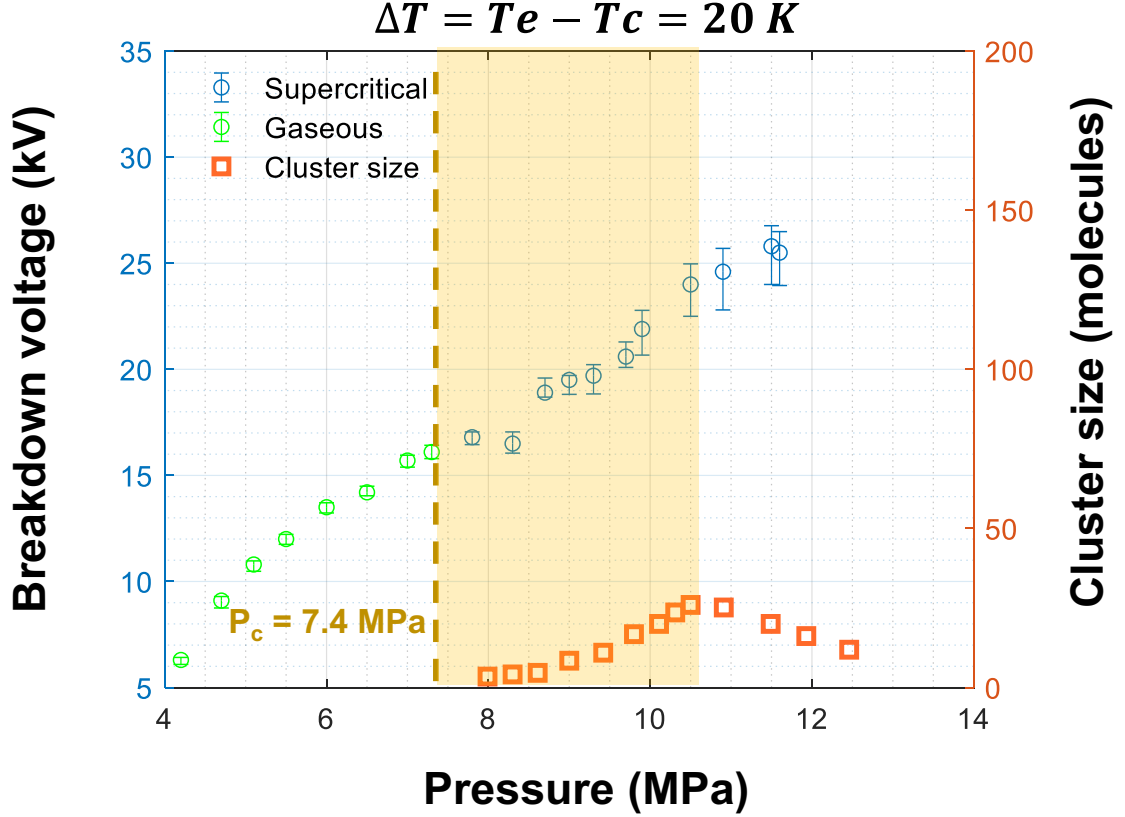


Figure 31 – The experimental result of the breakdown voltage of supercritical CO₂ at 324 K. Experiments are conducted in a uniform electric field at 0.1 mm. The average breakdown strength values are indicated by circles, with their scattering values indicated by the horizontal error bars. The right y-axis indicates the cluster size calculated by the numerical model. The shaded area highlights the area from the critical pressure T_c to the maximum cluster size.

The density inhomogeneity is caused by the clustering effect, which forms a large mean free path where electrons could gain enough energy and ionize particles. Although the phenomenon of the discontinuity in breakdown versus density near the critical point in the experiment is pronounced, the decrease in breakdown voltage near the critical point reported by Ito *et al.* is not observed.[35, 36] This is expected because the gap length in this study is relatively large, even the discharges happen under the condition of being close to the critical point, clustering and density fluctuation F_D decrease due to the local increase

of the temperature caused by discharges. If the gap length is smaller than 1 μm , the cluster structure can be preserved because more effective heat dissipation is enabled by the large specific surface area. Thus, a reduction of breakdown voltage can be observed.

6.5 Summary

In this chapter, DC breakdown measurements of CO_2 from gaseous to supercritical phase at different isothermals of 310 K, 317 K, and 324 K are conducted. We also develop a numerical model which considers the local fluid structure and calculates the molecular cluster size. The model takes the data obtained from small-angle x-ray scattering, specifically the Ornstein-Zernike correlation length ζ , as the input. According to the crystal structure and the length of crystallographic axes of the molecule, the model calculates the molecular cluster size (the number of molecules inside one cluster) at different thermodynamic conditions. By comparing with data measured from the dielectric strength experiment, we prove that the breakdown characteristics of SCFs also exhibit a similar critical anomaly phenomenon as observed in other transport properties of SCFs. The direct comparison between the calculated cluster size and the breakdown voltage measurement manifests a strong correlation, which implies the anomalous dielectric strength of SCFs is caused by long mean free paths in the highly fluctuating fluid that accelerate electrons. This work provides theoretical foundations to understand the electrical breakdown characteristics of supercritical fluids.

CHAPTER 7. CONCLUSION

This dissertation is focused on furthering the fundamental understanding of the dielectric properties of supercritical fluids and their mixtures, especially near the critical point. To identify the most promising SCF candidates, the dissertation discusses the criteria and specifications the SCF candidates must exhibit. The dissertation analyses on the electron kinetics of different SCF substances, which indicates the suitability of using these SCFs as dielectric media. Electrical breakdown experiments show that the dielectric strength of pure supercritical CO₂ reaches about 250 kV/mm. For supercritical CO₂-CF₃I and CO₂-C₄F₇N mixtures, the breakdown strength reaches up to 300 kV/mm, which is much higher than what could ever be achieved by a dielectric gas. The supercritical CO₂-O₂ mixture manifests a similar dielectric strength as pure supercritical CO₂. Since O₂ can oxidize free carbon generated in CO₂ discharges and arcs, this mixture is also proved to be suitable for power applications that require carbon control during arc quenching activities. Experimental investigations also demonstrate that the anomalous breakdown characteristics discovered in the pure SCF are also observable in binary mixtures of SCFs at various mixing ratios. This similar behavior suggests that the unstable molecular clustering significantly affects the discharge phenomenon observed in pure SCFs and supercritical mixtures. A theoretical method that combines the thermodynamic calculation and data from the structure analysis by small-angle X-ray scattering is developed to interpret the breakdown characteristics of SCFs. The method calculates the molecular cluster size (the number of molecules inside one cluster) at different thermodynamic conditions. The comparison between the calculated cluster size and the breakdown voltage

measurement manifests a correlation, which implies the anomalous behavior dielectric strength of SCFs is caused by long mean free paths in the highly fluctuating fluid that accelerate electrons.

This dissertation fills a gap in the SCF research by providing the theoretical and experimental validation of breakdown strength variations due to the density fluctuation in SCF binary mixtures. The unique breakdown characteristics of SCFs are expected to attract interest for a wide range of applications. Besides the applications in power and energy, where they could be used for switchgear and electrostatic machines, SCF mixtures could also enable affordable van de Graaff generators for particle accelerators used in high energy physics and medical applications, such as radiation therapy.

CHAPTER 8. FUTURE WORK

There are several research directions that could be further explored based on the results presented in this work:

1. Investigation on the development of a new law with experimentally proved empirical coefficients that works better at predicting the dielectric strength of SCFs;
2. Development of a thorough understanding of the ionization, attachment, excitation, and avalanche processes of SCFs;
3. Investigation of the breakdown characteristics of more promising candidates, especially the candidates that can form an azeotropic mixture for reduced critical temperature and enhanced dielectric strength;
4. Investigation of a method to experimentally measure molecular cluster sizes in supercritical fluids. Previous research has been conducted using small-angle X-ray scattering and Raman spectroscopy;
5. Investigation of an optical experimental method to accurately measure the critical point of binary supercritical fluid mixtures at different mixing ratio;
6. Investigation of the breakdown characteristics modeling work in binary and ternary SCF mixtures.

APPENDIX A. LIST OF PUBLICATIONS

Journal Papers

- J1. **J. Wei**, C. Park, and L. Graber, "Breakdown characteristics of carbon dioxide–ethane azeotropic mixtures near the critical point," *Physics of Fluids*, vol. 32, no. 5, p. 053305, 2020, doi: 10.1063/5.0004030. **(Published)**
- J2. **J. Wei**, A. Cruz, F. Haque, C. Park, and L. Graber, "Investigation of the dielectric strength of supercritical carbon dioxide–trifluoroiodomethane fluid mixtures," *Physics of Fluids*, vol. 32, no. 10, p. 103309, 2020, doi: 10.1063/5.0024384. **(Published)**
- J3. F. Haque, **J. Wei**, L. Graber, and C. Park, "Modeling the dielectric strength variation of supercritical fluids driven by cluster formation near critical point," *Physics of Fluids*, vol. 32, no. 7, p. 077101, 2020, doi: 10.1063/5.0008848. **(Published)**
- J4. F. Haque, **J. Wei**, A. Cruz, L. Graber, and C. Park, "Modeling cluster formation driven variations in critical electric field of He and Xe near critical point based on electron scattering cross sections," *Physics of Fluids*, vol. 32, no. 12, p. 127106, 2020. **(Published)**

Conference Papers

- C1. **J. Wei**, A. Cruz, F. Haque, C. Park, and L. Graber, "Electrical Breakdown Characteristics of Supercritical Trifluoroiodomethane-Carbon Dioxide ($\text{CF}_3\text{I}-\text{CO}_2$) Mixtures," in *2020 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP)*, 2020: IEEE, pp. 427-430. **(Published)**
- C2. **J. Wei**, A. Cruz, C. Xu, F. Haque, C. Park, and L. Graber, "A Review on Dielectric Properties of Supercritical Fluids," in *2020 IEEE Electrical Insulation Conference (EIC)*, 2020: IEEE, pp. 107-113. **(Published)**
- C3. **J. Wei**, A. Cruz, A. West, F. Haque, C. Park, and L. Graber, "Theoretical Modeling and Experimental Testing on the Electrical Breakdown in Supercritical Fluids," in *IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP)*, 2021. **(Accepted)**
- C4. C. Xu, **J. Wei**, and L. Graber, "Compatibility Analysis of Piezoelectric Actuators in Supercritical Carbon Dioxide," in *2020 IEEE Electrical Insulation Conference (EIC)*, 2020: IEEE, pp. 171-174. **(Published)**
- C5. F. Haque, **J. Wei**, L. Graber, and C. Park, "Electron Scattering Cross Section Data of Supercritical CO_2 Clusters," in *2020 IEEE Electrical Insulation Conference (EIC)*, 2020: IEEE, pp. 144-147. **(Published)**
- C6. A. West, **J. Wei**, A. Cruz, F. Haque, Z. Jin, C. Park, and L. Graber, "Characterization of the Viscosity of Gaseous and Supercritical CF_3I as a Dielectric Medium," in *IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP)*, 2021. **(Accepted)**

- C7. Y. Tian, **J. Wei**, C. Park, Z. Wang, and L. Graber, "Modelling of electrical breakdown in supercritical CO₂ with molecular clusters formation," in *2018 12th International Conference on the Properties and Applications of Dielectric Materials (ICPADM)*, 2018: IEEE, pp. 992-995. **(Published)**
- C8. L. GRABER, T. DAMLE, C. XU, **J. WEI** *et al.*, "EDISON: A New Generation DC Circuit Breaker," in CIGRE Session 2020, Paris (Virtual), 2020: CIGRE, pp. A3-0012. **(Published)**

APPENDIX B. EXPERIMENTAL SETUP DESCRIPTION

The electrical breakdown experimental setup is built to measure the breakdown voltage of SCFs in uniform field. The setup is also able to be used to conduct experiments on the breakdown strength of gaseous and liquid dielectric media. A complete setup with the high pressure chamber (A), a temperature-controlled water bath (B), pressure gauges (C), a thermal control system (D and E), high precision scale, and control valves is assembled and built as shown in Figure 33(c). The body of the high pressure chamber is made of a stainless steel pipe with an outer diameter of 89 mm and an inner diameter of 66 mm, with internal threads at both ends as shown in Figure 33(b), and two stainless steel plugs are attached with Viton O-rings to provide the high pressure seal. The high voltage bushing consists of a brass conductor and an insulator body made of polyetherimide (PEI). PEI is an amorphous thermoplastic with a high glass transition temperature, frequently used for machining insulators of bushings. Epoxy resin is used to bond the stainless steel plug with the PEI insulator, and the PEI insulator with the brass conductor. Reltek A3 primer is used to promote moisture resistance chemical bonding. Reltek B-45TH is applied to bond parts together. The electrode on the high voltage side is attached to the brass conductor, and the grounded electrode is clamped by a stainless steel plate which is supported and electrically grounded by three stainless steel rods (F) as shown in Figure 33(a). The clamp adjusts the gap length between these two electrodes within a range of 0 to 6 mm. The gap is measured by a steel feeler gauge. Hydrostatic pressure testing is performed up to 12 MPa to ensure safety. Uniform and constant temperature control inside the high pressure chamber is achieved by immersing the chamber into a temperature-

controlled bath (B) as shown in Figure 33(c). A 1 kW heater with thermostat and stirrer (D) allows to precisely control and measure the temperature of the bath. The temperature rating of the chamber is limited by the epoxy resin, which gives the range from 0 °C to 130 °C. A 6.35 mm stainless steel tube which is attached to needle and ball valves, pressure gauges, and a pressure relief valve allows evacuating and filling the pressure chamber.

The electrodes (G) are made of copper with a diameter of 20 mm. Before installing into the high pressure chamber, the electrodes are cleaned by an ultrasonic cleaner and conditioned by isopropyl alcohol to minimize the effects of contamination and oxide layers on the electrode surface. The whole test setup is evacuated for about 30 minutes. The chamber is then filled with liquid testing substances up to the desired amount to perform the breakdown experiment. The mass of substance in the chamber is measured by a scale with a resolution of 5 g (Pennsylvania 7600 Series Bench Counting Scale).

The experiments are conducted under DC voltage (Spellman SL60PN1200, rated 60 kV and 20 mA). The voltage is ramped up at 0.5 kV/s, and the gap between the two electrodes is set to be 0.1 mm. Five breakdowns are performed initially to season the electrodes before collecting the data. The breakdown voltage is then measured and recorded fifteen times at each condition. The time interval between two successive breakdown events is about two minutes to reduce the effect of the density fluctuation caused by the arc discharge.

A static equilibrium apparatus is built to replicate the experimental conditions considering mixing ratios and densities to conduct the optical diagnostics for the critical point of mixtures. The body of this optical apparatus is made out of aluminum, and two-

layer transparent view-port. The inner layer of the view-port is chemically strengthened alkali-aluminosilicate glass (Corning Gorilla Glass), which provides material compatibility for many organic chemical compounds including hydrocarbon-refrigerants such as C_2H_6 and propane (C_3H_8). The outer layer of the view-port is polycarbonate, which is a durable material with a high tensile modulus (modulus rupture $F_a = 2,200$ MPa).

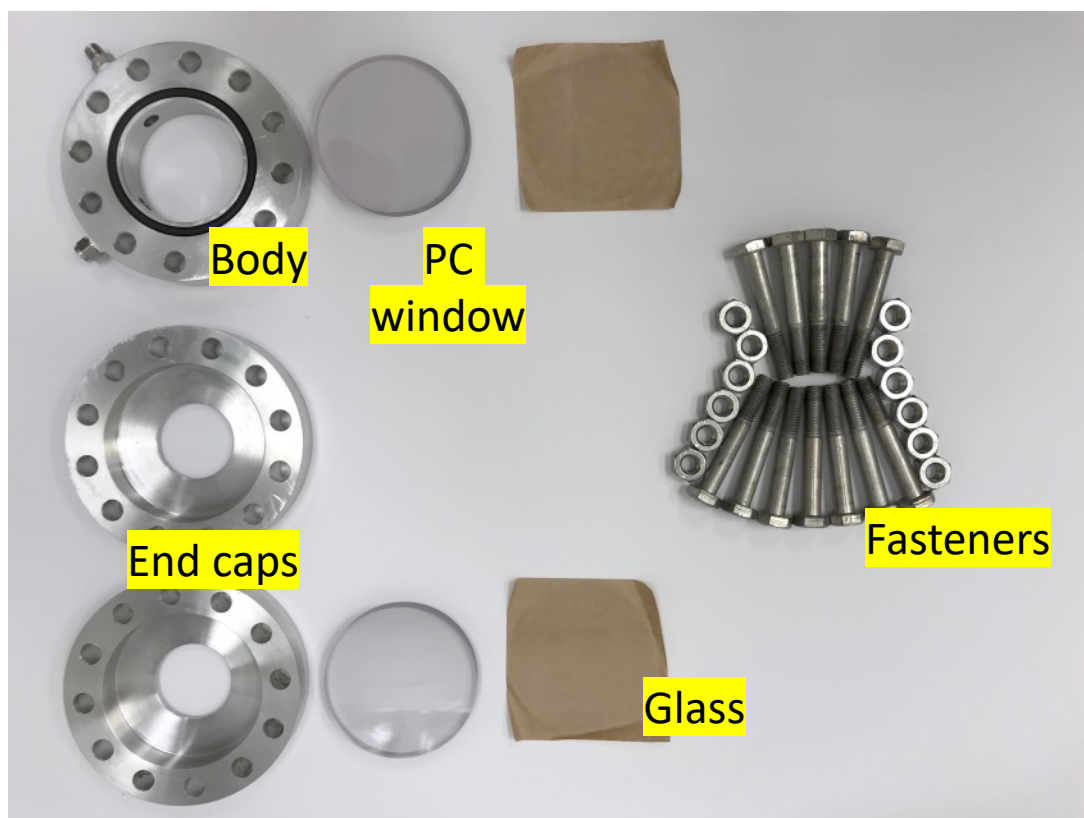


Figure 32 – The optical chamber: the body is made of aluminum 6061, the window layers consist Corning Gorilla Glass to provide material compatibility and polycarbonate to provide high tensile strength.

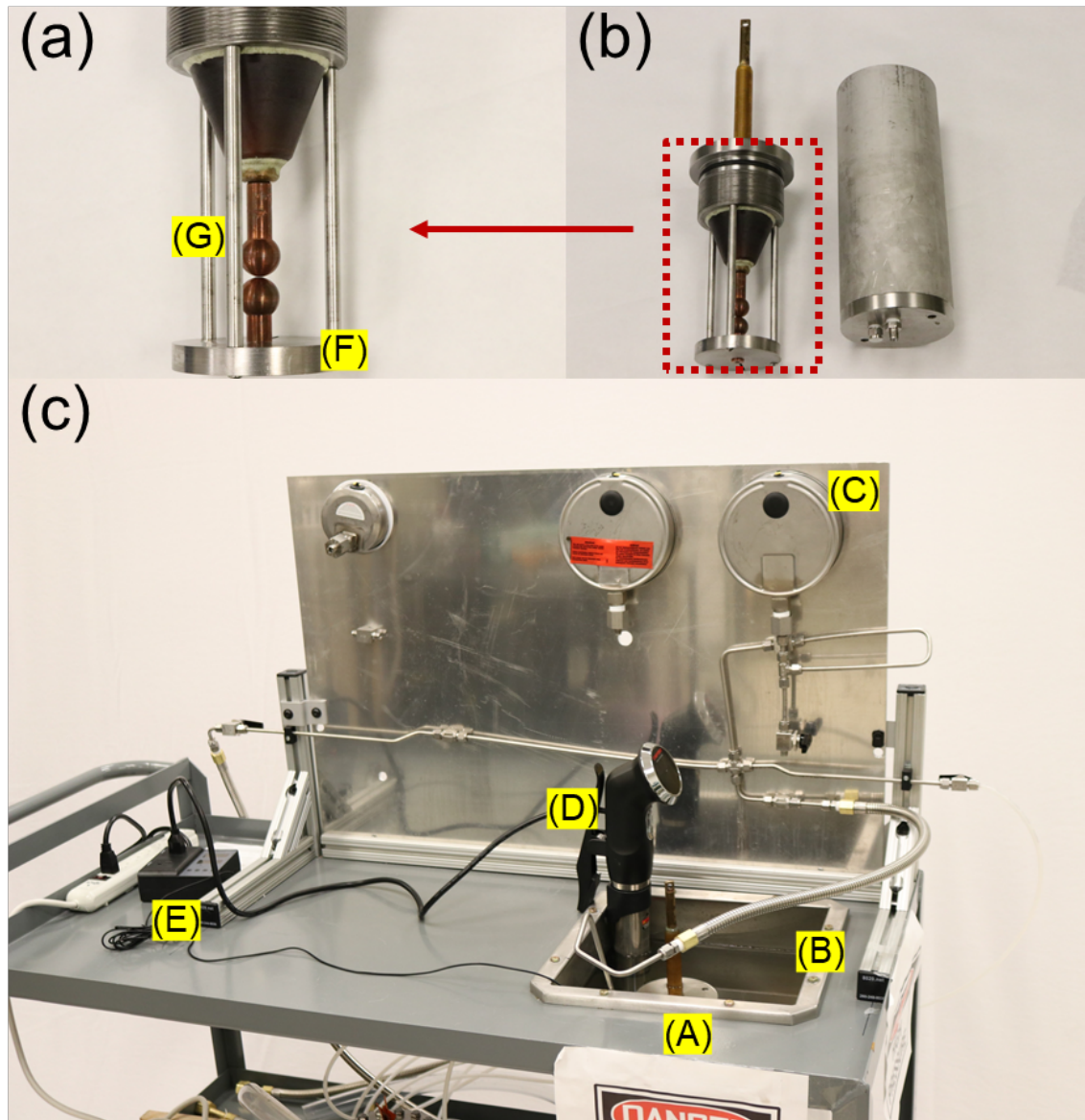


Figure 33 – The electrical breakdown experimental setup. Upper-left: the internal configuration of the chamber. Upper-right: the external view of the high pressure bushing and the body of the high pressure chamber. Lower: the testbed for the SCF breakdown experiment, which contains a temperature-controlled bath, pressure gauges, and a thermal control system.

APPENDIX C. THE HISTORY OF CIRCUIT BREAKERS

Circuit breakers are critical components in electricity generators, transmission lines, and distribution grids. They normally serve two functions: switching of lines during normal operation for control purposes, and protection of valuable assets by clearing faults. As one of the most important components in circuit breakers, an arc-quenching medium is used that allows cool the arc and eventually break the fault current. Over the past 100 years, the dielectric media for circuit breakers have evolved dramatically with the increasing capacity rating of circuit breakers. Figure 34 shows an overview of the evolution of dielectric media in circuit breakers [151].

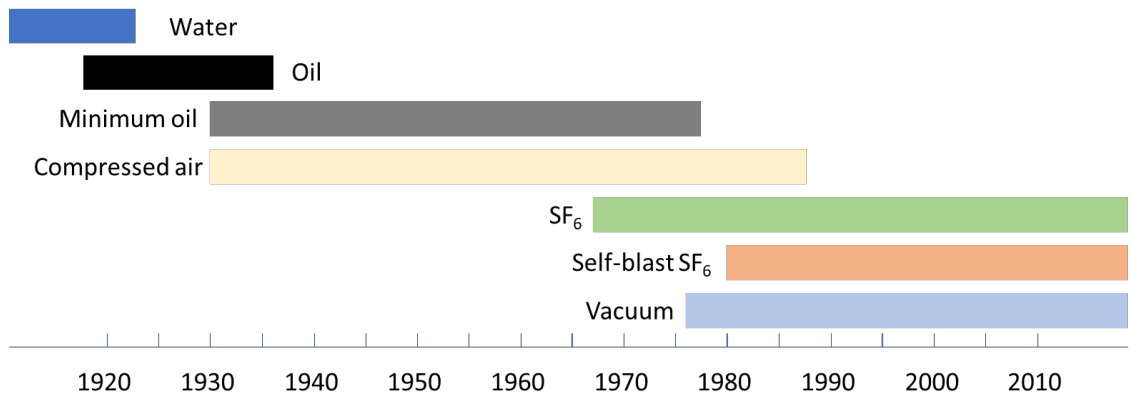


Figure 34 – The evolution of dielectric media in circuit breakers [151].

As the earliest circuit breakers in the history, water and oil circuit breakers are often used initially. Disadvantages of using water and oil as the arc-quenching medium are obvious: devices are usually bulky since they required a large volume of the dielectric medium, and oil posed a significant risk of fire and explosion. Moreover, water get contaminated quickly since it is a good solvent for ionic substances, which increases the electrical conductivity by orders of magnitudes. Water and bulk oil circuit breakers are

soon replaced by minimum oil circuit breakers and compressed air circuit breakers. As a relatively new dielectric medium around the 1930s, compressed air quickly dominated the design of circuit breakers and took over the market. This is not only because compressed air fulfilled all the technical requirements, but also it satisfied environmental demands. However, compressed air also had its drawback: compressed air circuit breakers required powerful compressors and are very noisy during switching operation. This is also the reason why compressed air is gradually replaced by SF₆ and vacuum breakers starting in the 1970s [152, 153]. Disadvantages of SF₆ are its decomposition products are corrosive and toxic, and SF₆ is a potent greenhouse gas with a long atmosphere lifetime. Similarly, vacuum insulation also exhibits non-negligible weaknesses: the only mechanism to cool the arc is through radiation. Vacuum insulation limits heat transfer to radiation and conduction through the conductors. Furthermore, ultra-high vacuum (UHV) conditions are difficult to maintain.

With the current trend towards direct current (DC) power systems, a DC circuit breaker is required for protection and control. In the meantime, the development of DC circuit breakers also brings more requirements and challenges to the arc-quenching medium. Conventional insulating and switching media are not able to provide low viscosity, high dielectric strength, and efficient heat transfer at the same time. What is needed is a new dielectric fluid with improved properties.

APPENDIX D. EVALUATION OF POTENTIAL HIGH POWER DENSITY APPLICATIONS OF SUPERCRITICAL FLUIDS AS DIELECTRIC MEDIA

Many applications that require strong electric fields, efficient heat dissipation, and fast motion could benefit from such a new dielectric fluid. Three potential applications that can be made more feasible, efficient, and cost-effective are discussed in this section.

Ultra-fast switchgear provides opportunities for DC circuit breakers, which enable the use of meshed DC power systems such as those required for power distribution on all-electric ships and electric aircraft [154] as well as multi-terminal high voltage DC power transmission [155]. Transcontinental exchange of renewable energy can eventually be achievable by enabling the new design of DC circuit breakers with supercritical fluids as dielectric media. Non-arcing disconnect switches with a new operating mechanism such as piezoelectric actuators also can be integrated with a new type of insulating medium for enhanced performances [156, 157]. Supercritical fluids as new dielectric media with high dielectric strength and low viscosity allow reducing the contact travel, therefore allowing much faster switching operation. Figure 35 shows the schematic diagram of two potential applications: a high speed disconnect switch and a circuit breaker.

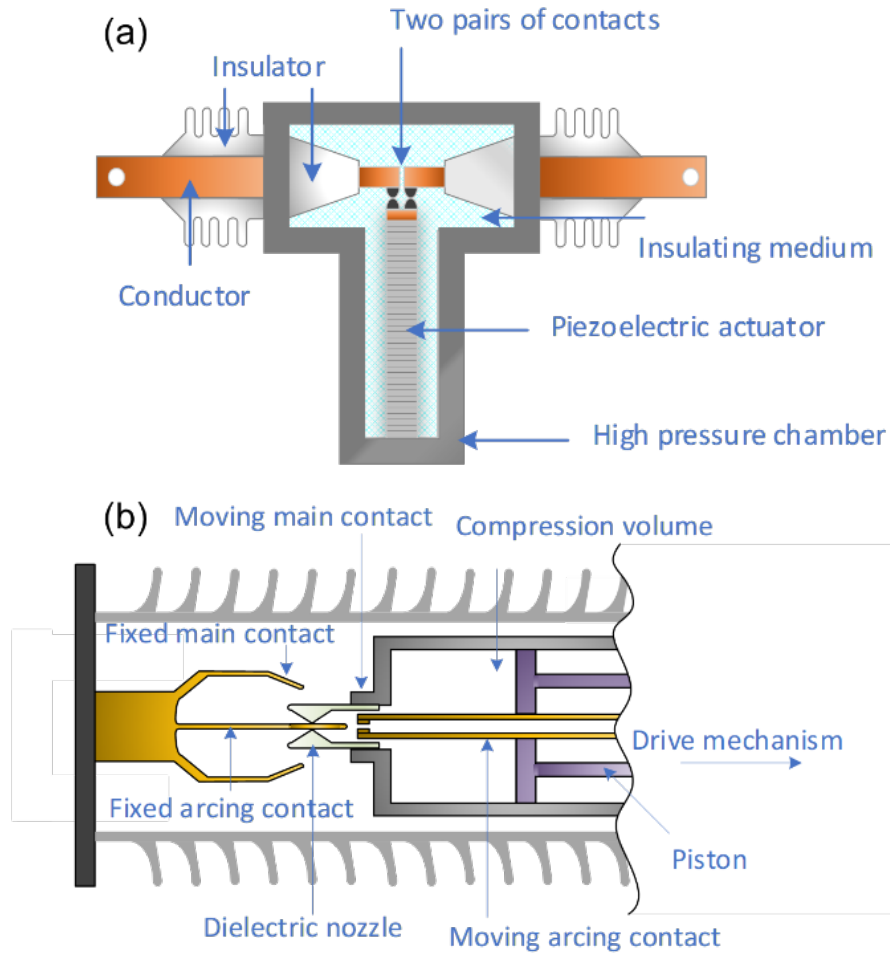


Figure 35 – Conceptual drawings of applications for ultra-fast switchgear that could benefit from using SCFs as dielectric media: (a) the high speed disconnect switch, and (b) the circuit breaker.

For certain applications, electrostatic machines are preferred over electromagnetic machines due to their relatively simple structures, manufacturability, and higher power density. Ge *et al.* investigated and compared ultra-high vacuum, dielectric gas, and liquid dielectrics for electrostatic motors. Ultra-high vacuum and gaseous dielectrics can only provide limited torque, and the machines have to spin at a very high speed to develop power. Viscosity is the main issue for liquids since it determines the drag losses which influence the speed range of the machine [110, 111]. A dielectric medium which combines

high dielectric strength as well as low viscosity is ideal for this application. Figure 36 shows a schematic diagram of an electrostatic motor.

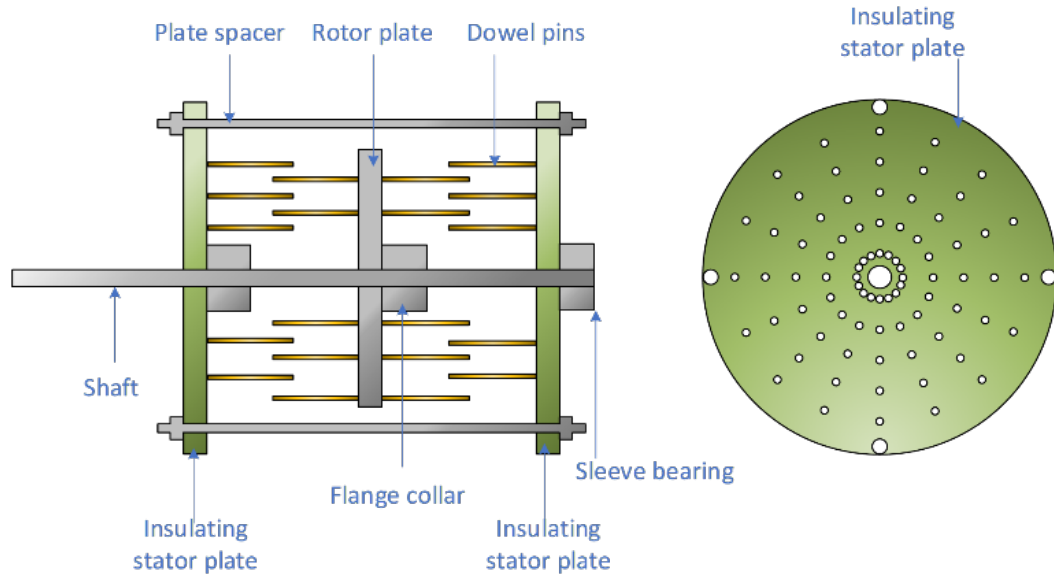


Figure 36 – A prototype electrostatic machine built by Ge et al. [111]. Such a machine can achieve a higher force because the voltage across micro-scale distances produces strong electric fields. Electrostatic machines would neither require heavy permanent magnets nor iron rotor/stator systems.

Linear accelerators often rely on van de Graaff generators to provide ultra-low ripple DC voltage to supply ions. The limited dielectric strength of the insulation gas in which the generators operate increases the size of the installation. SCFs could shrink the size of such accelerators, potentially reducing their cost, and ultimately allow more widespread use. The use of SCFs would benefit high energy research as well as medical applications [113, 158]. Figure 37 shows a van de Graaff generators in a linear particle accelerator.

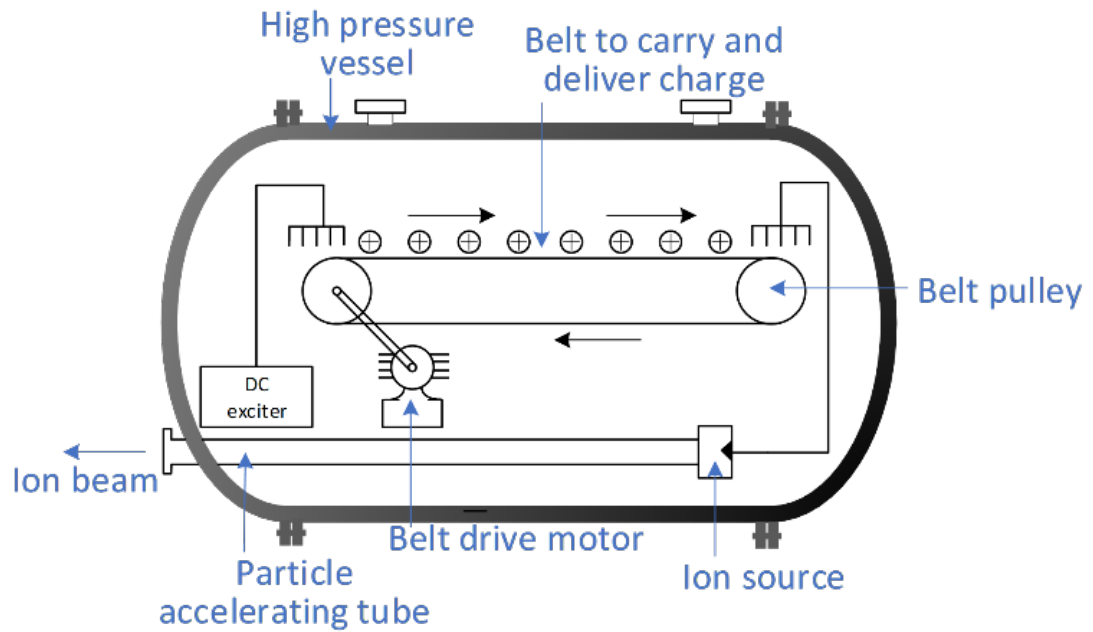


Figure 37 – Schematic diagram for a tandem Van de Graaff generator in a linear particle accelerator. Using SCFs as insulating media enables a more compact design so that it can be widely adopted.

APPENDIX E. THE CALCULATION OF THE DENSITY FLUCTUATION AND CONVERSION FROM THE CORRELATION LENGTH TO THE CLUSTER SIZE BASED ON THE ORNSTEIN- ZERNIKE THEORY

The van der Waals equation is given by:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = N_A k_B T \quad (1)$$

where V_m is the molar volume, b is the volume that is occupied by one mole of the molecules, N_A is the Avogadro number, k_B is the Boltzmann constant, T is temperature, P is pressure, and V is volume, and a is a constant whose value depends on the molecular interaction. This equation accounts for the intermolecular attraction from molecules.

At the critical point, the heat of vaporization reaches zero. A stationary inflection point in the isothermal lines on a P-V phase diagram can be observed, which defines the critical point as in [2]:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad (2)$$

Solving the above two equations, we get:

$$V_c = 3b \quad (3)$$

$$P_c = \frac{a}{27b^2} \quad (4)$$

$$T_c = \frac{8a}{27N_A k_B b} \quad (5)$$

By use of the reduced variables:

$$P_r = \frac{P}{P_c} \quad (6)$$

$$T_r = \frac{T}{T_c} \quad (7)$$

$$V_r = \frac{V}{V_c} \quad (8)$$

Equation (1) can be rewritten as:

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \quad (9)$$

The volume V can be substitute by the number density:

$$n = \frac{N_A}{V} \quad (10)$$

With the reduced number density:

$$n_r = \frac{n}{n_c} = \frac{1}{V_r} \quad (11)$$

Equation (9) can be rewritten as follows:

$$(P_r + 3n_r^2)(3 - n_r) = 8T_r n_r \quad (12)$$

Thermodynamically, the density fluctuation is given by:

$$F_D = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} = nk_B T k_T \quad (13)$$

where isothermal compressibility, k_T , is defined by:

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{n} \left(\frac{\partial n}{\partial P} \right)_T \quad (14)$$

From equation (13) and the equation (14), the density fluctuation can be written as:

$$\frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} = \frac{T_r}{Z_c} \left(\frac{\partial n_r}{\partial P_r} \right)_{T_r} \quad (15)$$

where Z_c is the compressibility ratio at the critical point defined by:

$$Z_c = \frac{P_c V_c}{k_B N_A T_c} \quad (16)$$

Equation (12) and equation (15) can be combined in the following form:

$$\frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} = \frac{4T_r (3 - n_r)^2}{9(4T_r - n_r (3 - n_r)^2)} \quad (17)$$

According to equation (12), the van der Waals equation is defined in the region of:

$$0 \leq n_r \leq 3.0, T_r \geq 1.0 \quad (18)$$

The density fluctuation diverges into infinity at the critical point where:

$$n_r = 1.0, \text{ and } T_r = 1.0 \quad (18)$$

Equation (17) also shows that the density fluctuation of the van der Waals fluid is a function of n_r and T_r only. It is proved that the law of corresponding states applies to the density fluctuation.

The cluster size and the number of molecules in an SCF cluster can be calculated from the Ornstein-Zernike correlation length ξ . According to the Ornstein-Zernike theory, the correlation length ξ can be determined from the characterization of the material using small angle X-ray scattering [11]:

$$I(s) = \frac{I(0)}{1 + \xi^2 s^2} \quad (19)$$

where $I(s)$ is the scattering intensity, and $I(0)$ is the zero-angle scattering intensity at $s = 0$. s is a measure of the scattering angle defined as:

$$s = \frac{4\pi \sin \theta}{\lambda} \quad (20)$$

where θ is the scattering angle, and λ is the X-ray source wavelength.

According to the crystallographic axes L_s and the number of molecules (or atoms) per unit cell k , the cluster size of supercritical fluid (number of molecules or atoms in a cluster) can be calculated as follows:

$$N = \left(\frac{\xi}{L_s} \right)^3 k \quad (21)$$

F_D values are calculated based on the following definition [11]:

$$F_D = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} = \frac{(n_s V)^2}{n_{ave} V} = \frac{k_T}{k_T^0} \quad (22)$$

where N is the total number of particles in a given volume V , $\langle N \rangle$ is the average of N , k_T is the isothermal compressibility, k_T^0 is the value of k_T for an ideal gas, n_s is the standard deviation of the local number density, and n_{ave} is the average number density.

A larger F_D means larger density fluctuations, and F_D reaches local maxima at the critical point. $F_D = 1$ represents an ideal gas situation. The isothermal compressibility k_T is defined by [159]:

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (23)$$

where V is volume and P is pressure.

To numerically calculate the density fluctuation F_D , we consider the ideal gas law:

$$PV = nRT \quad (24)$$

where P, V and T are the pressure, volume and temperature; n is the amount of substance; and R is the ideal gas constant. Solving equation (23) and equation (24) gives:

$$k_T^0 = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} nRT \left(-\frac{1}{P^2} \right) = \frac{1}{P} \quad (25)$$

The specific heat ratio γ is defined as [160]:

$$\gamma = \frac{C_P}{C_V} = \frac{k_T}{k_s} \quad (26)$$

where C_P is the heat capacity at constant pressure, C_V is the heat capacity at constant volume, and k_s is the isentropic compressibility. k_s is defined by [160]:

$$k_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_s = \frac{1}{\rho u^2} \quad (27)$$

Using the results in equations (25), (26), and (27) and comparing with equation (18), the density fluctuation can be numerically calculated by:

$$F_D = \frac{k_T}{k_T^0} = \frac{C_P}{C_V} \frac{P}{\rho u^2} \quad (28)$$

where ρ is the density, and u is the speed of sound.

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