Theoretical Modeling and Experimental Testing on the Electrical Breakdown in Supercritical Fluids

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***Abstract*- Supercritical fluids (SCFs) have been recently considered to be used as insulating media due to properties that show exceptional dielectric strength, high heat transfer capability, and low viscosity. This paper reports the result of breakdown experiments on carbon dioxide (CO_2) from gaseous to supercritical state. Experiments are performed under the isothermal condition of 310 K (37°C). The dielectric strength test is conducted in a 0.1 mm gap under uniform dc electric field. To interpret the result, a theoretical model that combines the thermodynamic calculation and existing data from the structure analysis by small angle x-ray scattering is developed. Our experiments suggest that the dielectric behavior of supercritical CO_2 shows a discontinuity of the dielectric strength near the critical point. This phenomenon can be well explained by the theoretical model, which calculates the molecular cluster size and considers the local fluid structure.**

I. Introduction

Supercritical fluids (SCFs), i.e., matter in a state that is achieved when temperature and pressure are above the critical temperature (T_c) and the critical pressure (P_c) as shown in Fig. 1, have been extensively investigated and involved in industrial applications, including chemical processing, mass transfer processes, and nanostructured materials [2-4]. In addition to chemistry, SCF-related researches have also been expanded to the electrical energy topic, such as using SCFs as dielectric media for power applications [5, 6]. For example, Zhang *et al.* developed a versatile supercritical medium switch and presented the breakdown voltage as a function of the pressure, gap distance, and the medium flow rate through the gap of electrodes [7, 8]. Kiyan *et al.* investigated the electrical breakdown voltage of a negative DC (direct current) un-uniform gap in supercritical carbon dioxide at 200 μm [9, 10]. Wei *et al.* conducted experimental investigations on supercritical fluid mixtures, such as supercritical carbon dioxide-ethane (CO_2-C_2H_6) and supercritical carbon dioxide-trifluoroiodomethane (CO_2-CF_3I) mixtures [11-13].

Theoretical models have also been developed to describe the electrical breakdown in SCFs. Tian *et al.* and Haque *et al.* investigated the electron scattering cross sections of supercritical CO_2, supercritical He, and supercritical Xe of different cluster sizes based on the Boltzmann analysis [14-17]. 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 [18]. 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. Established gas discharge theories [19, 20] are proved to be inaccurate in the electrical breakdown characteristics, especially in the uniform electric field.

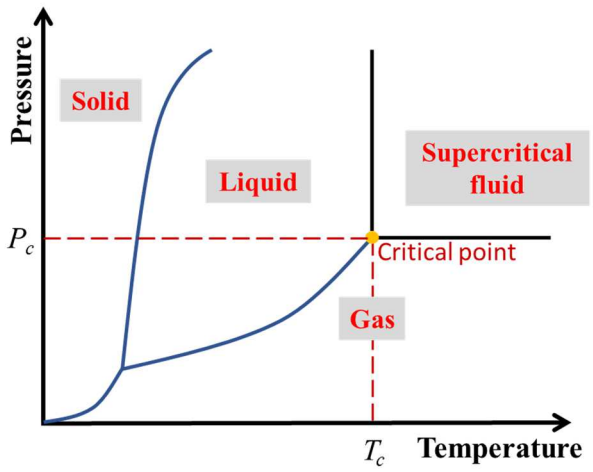


Fig. 1 A pressure-temperature (*P-T*) phase diagram that divides a substance into four thermodynamic phases: solid, liquid, gas, and supercritical fluid.

In this paper, we demonstrate, to the best of our knowledge, the first theoretical modeling 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.

II. Theoretical Modeling

The ideal gas law does not take the interaction between molecules into consideration. Thus, it cannot explain the change of kinetic energy during collisions. The van der Waals

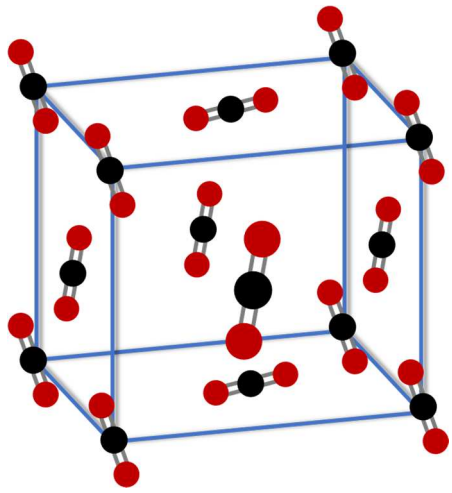


Fig. 2 The crystal structure of CO_2: a face-centered-cubic structure. It has a coordination number of twelve and contains four molecules per unit cell. Red circles indicate the oxygen atom, and black circles indicate the carbon atom.

equation, as a generalized equation based on the ideal gas law, is given by:

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

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 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 exists, which defines the critical point as in [21]:

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

Solving (1) and (2):

$$Vc = 3b$$

$$Pc = \frac{a}{27b^2}$$

$$Tc = \frac{8a}{27N_A k_B b}$$

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 [22]:

$$I(s) = \frac{I(0)}{1 + \xi^2 s^2} \tag{3}$$

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:

$$s = \frac{4\pi \sin\theta}{\lambda} \tag{4}$$

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

Data obtained from the small angle x-ray scattering experiment are related to density fluctuation F_D:

$$F_D = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} = \frac{I(0)}{N}\frac{1}{Z^2} = \frac{(n_s V)^2}{n_{ave} V} = \frac{k_T}{k_T^0} \tag{5}$$

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.

The equation of isothermal compressibility k_T is defined in the following equation, with $V = N_A/n$, where n is the number density.

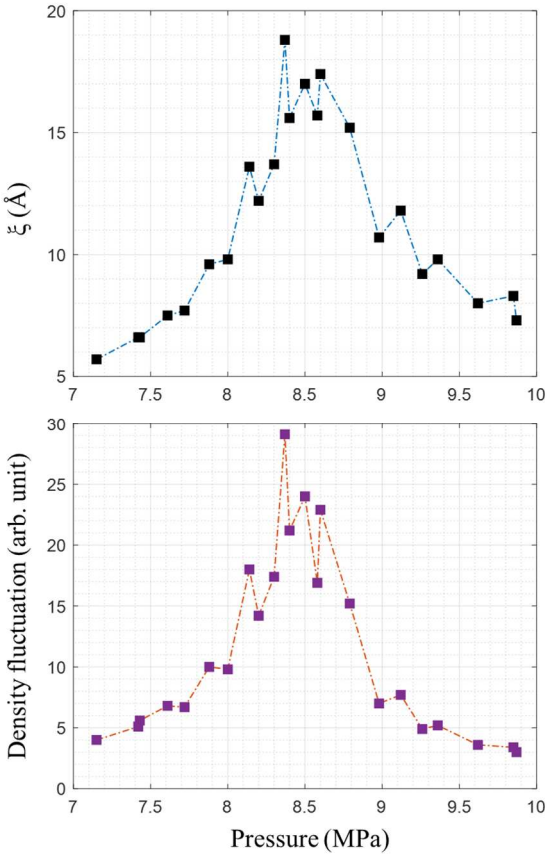
$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{n}\left(\frac{\partial n}{\partial P}\right)_T \tag{6}$$

The Ornstein–Zernike is an integral equation for defining the direct correlation function. It describes how the correlation between two molecules can be calculated.

In the present study, CO_2 has a face-centered-cubic crystal structure as shown in Fig. 2, which means it has a coordination number of twelve and contains four molecules per unit cell. The corresponding length of the crystallographic axes of CO_2 is measured from 4.330 Å to 5.963 Å [23]. According to the cell edge length, the cluster size of supercritical CO_2 at different thermodynamic conditions can be calculated as presented in Section III.

III. Results

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* [1]. Their results are plotted as shown in Fig. 3. Fig. 3 (above) shows the Ornstein-Zernike correlation length ξ of supercritical CO_2



obtained from scattering experiments as a function of the pressure, at the temperature of 310 K. Fig. 3 (below) shows density fluctuation values of supercritical CO_2 obtained from scattering experiments as a function of the pressure, at the temperature of 310 K.

Fig. 3 The Ornstein-Zernike correlation length ξ (above) and density fluctuation values (below) obtained from small angle x-ray scattering experiments in supercritical CO_2 as a function of pressure at 310 K. The figure is plotted based on measurement data from [1].

The breakdown voltage measurements of CO_2 are carried out at the same temperature as the small angle x-ray scattering experiment at 310 K, from the gaseous phase to supercritical condition. Fig. 4 shows the measured breakdown voltage as a function of the pressure. 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 of Fig. 4 shows the calculated result of the cluster size at different thermodynamic conditions of supercritical CO_2, based on the cell edge length. As shown in the left y-axis of Fig. 4, the measured breakdown voltage values increase with the density of CO_2 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.

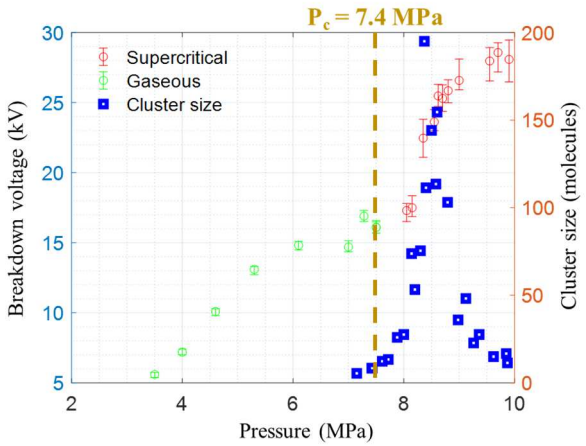


Fig. 4 Experimental results for the breakdown voltage of supercritical CO_2 up to 10 MPa. The experiment is conducted in a uniform electric field at 0.1 mm.

IV. Conclusions

In this study, we conducted DC breakdown measurements of CO_2 from gaseous to supercritical phase at the isothermal of 310 K. We also developed a theoretical 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 ξ, 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 behavior 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.

Acknowledgment

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