

Electron Scattering Cross Section Data of Supercritical CO₂ Clusters

Farhina Haque

*Department of Electrical and Computer Engineering
Mississippi State University
Mississippi State, MS, USA
fh317@msstate.edu*

Lukas Graber

*School of Electrical and Computer Engineering
Georgia Institute of Technology
Atlanta, GA, USA
lukas.graber@ece.gatech.edu*

Jia Wei

*School of Electrical and Computer Engineering
Georgia Institute of Technology
Atlanta, GA, USA
jia.wei@gatech.edu*

Chanyeop Park

*Department of Electrical and Computer Engineering
Mississippi State University
Mississippi State, MS, USA
chanyeop.park@ece.msstate.edu*

Abstract—Density fluctuations caused by clustering occurs during phase transition near the critical point, beyond which is the supercritical phase. Supercritical phase is the intermediate state where fluids show both liquid and gas properties. The high dielectric strength provided by the high density of supercritical fluid exhibits a steep degradation at the phase change due to the so-called clustering effect. In this paper, the dielectric properties of SC CO₂ have been studied. Based on the dielectric strength analysis method used for gas mixtures, the electron-scattering cross section data of SCF CO₂ clusters is utilized, which are modified from those of gaseous CO₂ assuming various cluster sizes, to estimate the density-fluctuation-dependent dielectric strength of SCF CO₂. The electron energy loss models of distinct electron energy levels have been utilized to determine the geometrical electron scattering cross section data of SCF CO₂ clusters with various cluster sizes and impinging electron energies.

Keywords—Supercritical fluids, collision cross section, dielectric strength, density fluctuation

I. INTRODUCTION

Supercritical fluids (SCF) are substances above their critical temperature and pressure condition, in which the substance is neither liquid nor gaseous. SCFs generally show densities comparable to liquids and viscosities comparable to gases [1]. Owing to their high densities and low viscosities, SCFs are utilized as a working fluid that reduce radiative and convective heat loss in energy production, used as environmentally-friendly refrigerants for air-conditioning applications, and used in chemical processes, in which high reaction rate can be achieved by the high density of the medium [1, 2]. SCFs have high dielectric strength provided by their high density and therefore short mean free electron path. These beneficial dielectric properties of SCFs enable them to be utilized in various high voltage applications that require high power density. The use of SCF as an insulation material has started to draw the attention by the researchers in recent years [3]. Though there are not enough known data on this regard.

At and near the critical point, SCFs experience the formation of clusters that causes an increase in spatial density fluctuation. It has been experimented that density fluctuation driven by the clustering effect of CO₂ molecules during SCF phase transition causes a steep degradation in the dielectric strength of SCF CO₂ during phase transition [1, 4-6]. In this paper, based on the dielectric strength analysis method used for gas mixtures, we utilized the electron-scattering cross section data of SCF CO₂ clusters, which are modified from those of gaseous CO₂ [7] assuming various cluster sizes, to estimate the density-fluctuation-dependent dielectric strength of SCF CO₂.

Specifically, the cross-sectional data of SCF CO₂ are obtained by the product of geometrical cross section of a cluster and the probability for an electron colliding with the cluster to make at least one ionizing collision inside it [8]. The geometrical cross section accounts for the energy losses inside the cluster of electrons. The energy loss of electrons inside the cluster can be modeled depending on initial electron energy. For high energy electrons, Borns approximation [8] is utilized for the application of Bethe's formula [8], which fails at low energy level. The energy loss rate at low energy level is evaluated by summing all possible energy-loss mechanisms including ionization, momentum transfer, and excitation collisions of an electron impinging atomic or molecular particles. At very low energy levels, electrons lose energy mainly by rotational and vibrational excitation modes, which are taken into account in the model that determines electron energy loss in the cluster.

In this paper, we utilize the electron energy loss models of distinct electron energy levels to determine the geometrical electron scattering cross section data of SCF CO₂ clusters with various cluster sizes and impinging electron energies. In short, the electron-scattering cross section data of SCF CO₂ derived from those of gaseous CO₂ are used to model the dielectric strength variation caused by density fluctuation in SCF CO₂ near its critical point solving the Boltzmann equation with the two term approximation [9]. From the solutions, the density-

reduced critical electric field of CO₂ cluster can be estimated which then be compared with the density-reduced critical electric field of free CO₂ gas molecule to understand the steep degradation of dielectric properties near critical point.

II. SUPERCRITICAL FLUID AND CLUSTERING NEAR CRITICAL POINT

A. Supercritical Fluid

Supercritical fluid is the state of a substance at which the temperature and pressure of the fluid are above the critical point showing viscosity and diffusivity compared to gas state and density and solvating property compared to liquid state. These properties enable its use in high power application. Near the critical point, any change in pressure or temperature of CO₂ can cause variation in the physical properties including density, dielectric strength, and heat capacity. However, near the critical point, some of the properties of SCFs, e.g., thermal conductivity, specific heat, and compressibility, have higher values compared to gaseous and liquid states rather having values in between liquid and gaseous states. The high pressure of SCFs help them to be used in chemical synthesis processes where high reaction rate is achieved by the high-pressure media. SCFs has density higher than gaseous phase which enables higher dielectric strength.

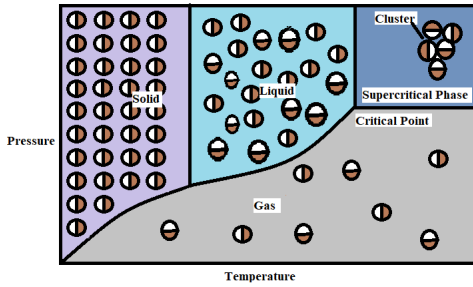


Fig. 1: Phase diagram

B. Effect of Clustering near Critical Point

Supercritical fluids are historically called “cluster fluid” [4] because of the nature of formation of cluster of different size having weak intermolecular forces near the critical point as shown in phase diagram as function of pressure and temperature in Fig. 1. The formation of clusters causes higher density fluctuation in the substances which influences the dielectric strength of materials. Due to the increased density fluctuation near the critical point, the breakdown voltage of the material becomes lower compared with the gas discharge theory described by Paschen’s law.

III. MODELING

A. Electron Scattering Cross Section

Near the critical point of CO₂, which is at $T_c = 304.1$ K and $P_c = 7.39$ MPa, the gas molecules of CO₂ forms clusters of various sizes. The dielectric property, which can be determined by Boltzmann analysis, changes with the formation of cluster.

To perform Boltzmann analysis to estimate the critical electric field, the electron scattering cross section data of clusters are needed. However, the electron scattering cross section for CO₂

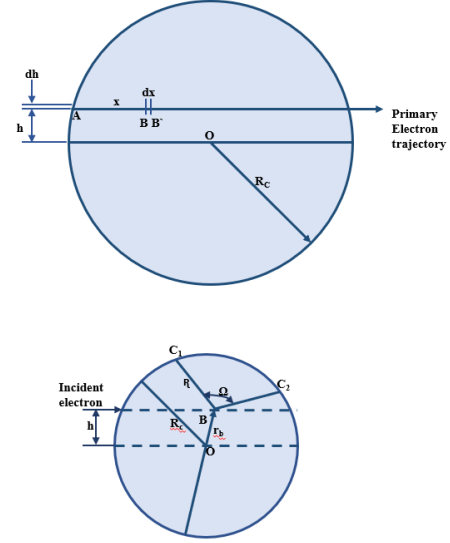


Fig. 2: Electron colliding with a cluster

clusters are not directly available but could be derived from the CO₂ gas molecule cross section data.

Clusters formed by CO₂ near the critical point are considered spheres with radius R_c as represented in Fig. 2. When an electron with energy W_e impinge the spherical cluster at point A, it will follow an electron trajectory that has a distance h from the center of the cluster and a number of collisions happens between B and B'. The distance between the electron trajectory and cluster center is called cluster impact parameter. The total scattering cross section is the integration of the product of two terms, which are the geometrical cross section of a cluster containing a certain number of molecules and the probability of an electron colliding with the cluster to make at least one collision inside the cluster. The above physical phenomena can be represented by the following equation [8]:

$$\sigma(N, W_{e0}) = 2\pi \int_0^{R_c} h \{1 - \exp[-n_0 \int_0^{2\sqrt{(R_c^2 - h^2)} \sigma_0(1, We(x)) F(W_{s0}(x), x) dx]\} dh, \quad (1)$$

where N is the cluster size defined as the number of molecules contained in a cluster, W_{e0} is the initial impact energy by an electron, $\sigma(N, W_{e0})$ is the total scattering cross section, h is the distance between the cluster center and primary electron trajectory, n_0 is the molecular density of the crystal, $\sigma_0(1, We(x))$ is the geometrical cross section of CO₂ gas molecule, $F(W_{s0}(x), x)$ is the probability for a secondary electron produced by the collision of a molecule to escape out the cluster, and R_c is the radius of the cluster. R_c is dependent on the size of the cluster determined by the following equation:

$$R_c = \sqrt[3]{\frac{3NM}{4\pi\rho}}, \quad (2)$$

where M is mass of the molecule, ρ is the specific mass of the cluster.

B. Energy Loss Model

The geometrical cross section of cluster includes the electron energy which reduces as the electron travels through the cluster. The electron energy at any position can be determined by the following equation:

$$W_e = W_{e0} - \int_0^x \left(\frac{dW_e}{ds} \right) ds, \quad (3)$$

where W_{e0} is the initial electron impact energy and $\frac{dW_e}{ds}$ is the energy loss rate by an electron traversing in a cluster. The energy loss by an electron can be modeled based on the initial electron impact energy level. When the energy is high, greater than 80 eV, Bethe's formula is taken into account to determine the energy loss while the electron is traversing in the cluster. Then the total energy loss can be written as,

$$\frac{dW_e}{ds} \cong -\frac{\alpha_1 z}{W_e} \ln \left(\frac{\alpha_2 W_e}{z} \right) \text{ eV m}^{-1}, \quad (4)$$

where $\alpha_1 = k_1 q^2 n / (8\pi\epsilon_0)$, W_e is the electron energy, n is the density of the cluster and k_1 is the empirical factor of correction, z is the atomic number, q is the charge of an electron. For CO_2 , k_1 is taken equal to unity.

The possible electron energy loss mechanisms of an electron interacting with a molecule are ionization, excitation, and momentum transfer. When the electron impact energy falls lower than 80 eV, Bethe's formula is no longer applicable to evaluate electron energy loss rate. Thus, all the energy loss mechanisms of an electron should be summed together to determine the energy loss rate:

$$\frac{dW_e}{ds} \cong -n\sigma_\tau \left((V_i + W_{s0})\alpha_i + \sum_{m,n} V_{m,n}^* a_{m,n} + 2 \frac{m_e}{M} W_e \alpha_d \right) \text{ eV m}^{-1}, \quad (5)$$

here σ_τ is the total collision cross section, $\alpha_i \sigma_\tau$ is the ionization cross section, W_{s0} is the mean initial energy of the electron expelled in an ionization collision, $\alpha_{m,n} \sigma_\tau$ is the excitation cross section, $\alpha_d \sigma_\tau$ is the momentum cross section, V_i is the ionization potential energy, $V_{m,n}$ is the excitation energy, m_e is the mass of electron and M is the mass of the cluster molecule.

The computed attachment, elastic, excitation, and ionization cross section of SCF CO_2 with cluster size 25 using (1) is plotted with the cross section data of CO_2 gas molecule in Fig. 3, Fig. 4, Fig. 5, and Fig. 6, respectively. The total cross section of a cluster computed from (1) is averaged by the number of molecules that a cluster contains to compare the values with a gas molecule. From the behavior represented in Fig. 3-6, the influence of clustering on the cross section values can be observed. The differences of cross section data of CO_2 cluster from free CO_2 gas molecule have influences on the dielectric properties of SCF CO_2 . We observed the clustering effects on the dielectric properties of SCF CO_2 by solving Boltzmann

equation based on the scattering cross section data of cluster and free gas molecule.

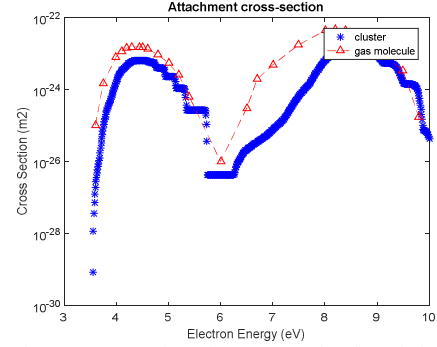


Fig. 3: Attachment cross section of CO_2 gas molecule and cluster of size 25

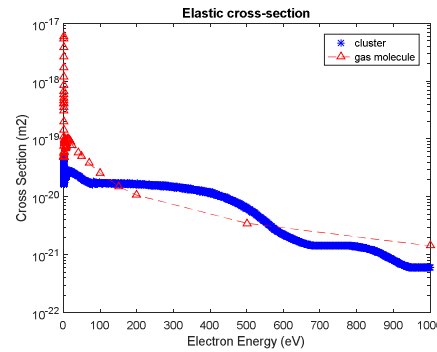


Fig. 4: Elastic cross section of CO_2 gas molecule and cluster of size 25

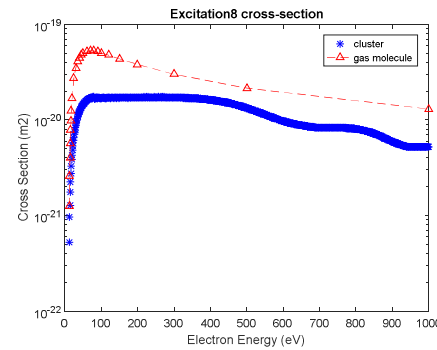


Fig. 5: Excitation cross section of CO_2 gas molecule and cluster of size 25

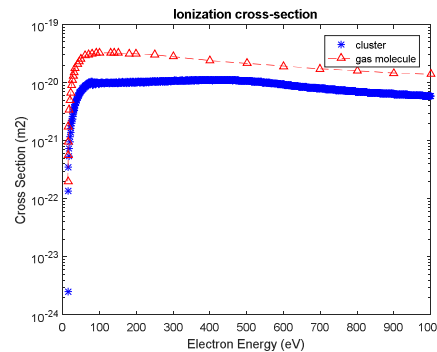


Fig. 6: Ionization cross section of CO_2 gas molecule and cluster of size 25

C. Dielectric Strength Modeling Using Boltzmann Analysis

The Boltzmann equation method is a widely used tool used for describing the kinetic processes of electrons for the effect of collisions [10–13]. To be more specific, the transport coefficients and rate coefficients due to the occurrence of collision by electron in molecule can be calculated as a function of the reduced electric field E/N by solving the electron Boltzmann equation [9]:

$$\frac{\partial f}{\partial t} + \vartheta \cdot \Delta f - \frac{e}{m} E \cdot \nabla_v f = C[f], \quad (6)$$

where f is the electron distribution function in phase space, ϑ is the velocity vector, e is the elementary charge, m is the mass of electron, E is the electric field, ∇_v is the velocity gradient, and $C[f]$ is the rate of change in f due to collision.

The dielectric strength of supercritical CO_2 is estimated based on the density-reduced ionization (α/N) and density-reduced attachment (η/N) coefficients. In this paper, we solve the Boltzmann equation with the electron scattering cross section data of CO_2 clusters of various cluster sizes and electron impact energies. Fig. 7 represents the Townsend coefficient as a function of density-reduced electric field (E/N). The dielectric properties of CO_2 gas molecules and CO_2 cluster can be compared by the density-reduced critical electric field $(E/N)_{cr}$ defined as the point, in which the density-reduced ionization and attachment coefficients are equal. From Fig. 7, it is observed that $(E/N)_{cr}$ for CO_2 gas molecules is 77.78 Td while for cluster size 25 of CO_2 cluster, $(E/N)_{cr}$ is as low as 27.27 Td. The reduced critical electric field observed in the cluster is due to density fluctuation causing dielectric breakdown at lower electric fields than in gas defined by Paschen's law.

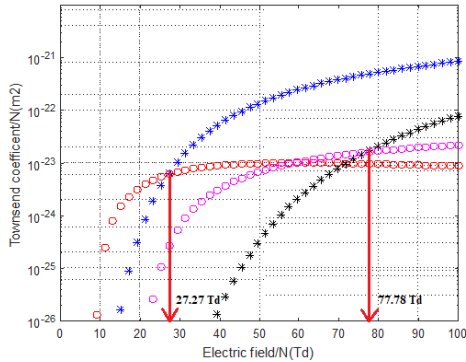


Fig. 7: Density-reduced Townsend Coefficient for CO_2 gas molecule and CO_2 cluster

IV. CONCLUSION

In this paper, electron scattering cross section data of supercritical CO_2 cluster of different cluster size is modeled utilizing the cross section data of CO_2 gas molecule utilizing the energy loss model. Further, the scattering cross section data CO_2 cluster and free gas molecule are employed for Boltzmann analysis to determine the density reduced critical electric field

for cluster and free gas molecule. The results show the effect of clustering on the dielectric properties of supercritical CO_2 fluids by giving a lower critical electric field than of free gas molecule. In this study, we investigate the dielectric properties of SC CO_2 with the goal of using this fluid in high voltage application as insulating medium. Therefore, further studies on the dielectric properties SC CO_2 could be beneficial for using SC CO_2 as insulating and dielectric medium in various high voltage application.

REFERENCES

- [1] S. Stauss, H. Muneoka, K. Urabe, and K. Terashima, "Review of electric discharge microplasmas generated in highly fluctuating fluids: Characteristics and application to nanomaterials synthesis," *Phys. Plasmas*, vol. 22, no. 5, p. 057103, May 2015, doi: 10.1063/1.4921145.
- [2] Ž. Knez, E. Markočič, M. Leitgeb, M. Primožič, M. Knez Hrnič, and M. Škerget, "Industrial applications of supercritical fluids: A review," *Energy*, vol. 77, pp. 235–243, Dec. 2014, doi: 10.1016/j.energy.2014.07.044.
- [3] Y. Tian, J. Wei, C. Park, Z. Wang, and L. Graber, "Modelling of electrical breakdown in supercritical CO_2 with molecular clusters formation," in *2018 12th International Conference on the Properties and Applications of Dielectric Materials (ICPADM)*, Xi'an, 2018, pp. 992–995, doi: 10.1109/ICPADM.2018.8401205.
- [4] T. Ito and K. Terashima, "Generation of micrometer-scale discharge in a supercritical fluid environment," *Appl. Phys. Lett.*, vol. 80, no. 16, pp. 2854–2856, Apr. 2002, doi: 10.1063/1.1470695.
- [5] T. Ito, H. Fujiwara, and K. Terashima, "Decrease of breakdown voltages for micrometer-scale gap electrodes for carbon dioxide near the critical point: Temperature and pressure dependences," *J. Appl. Phys.*, vol. 94, no. 8, p. 5411, 2003, doi: 10.1063/1.1611283.
- [6] M. Sawada, T. Tomai, T. Ito, H. Fujiwara, and K. Terashima, "Micrometer-scale discharge in high-pressure H_2O and Xe environments including supercritical fluid," *Journal of Applied Physics*, vol. 100, no. 12, p. 123304, Dec. 2006, doi: 10.1063/1.2400802.
- [7] Y. Itikawa, "Cross Sections for Electron Collisions With Carbon Dioxide," *Journal of Physical and Chemical Reference Data*, vol. 31, no. 3, pp. 749–767, Sep. 2002, doi: 10.1063/1.1481879.
- [8] F. Bottiglion, J. Coutant, and M. Fois, "Ionization Cross Sections for H_2 , N_2 , and CO_2 Clusters by Electron Impact," *Phys. Rev. A*, vol. 6, no. 5, pp. 1830–1843, Nov. 1972, doi: 10.1103/PhysRevA.6.1830.
- [9] G. J. M. Hagelaar and L. C. Pitchford, "Solving the Boltzmann equation to obtain electron transport coefficients and rate coefficients for fluid models," *Plasma Sources Sci. Technol.*, vol. 14, no. 4, pp. 722–733, Nov. 2005, doi: 10.1088/0963-0252/14/4/011.
- [10] C. Park, L. Graber, and S. Pamidi, "The dielectric properties of gaseous cryogenic mixtures of He , H_2 , Ne , and N_2 in a temperature range of 50–80 K at pressures up to 2.0 MPa," *Journal of Applied Physics*, vol. 121, no. 8, p. 083304, Feb. 2017, doi: 10.1063/1.4976565.
- [11] C. Park, S. Pamidi, and L. Graber, "Boltzmann Analysis of Cryogenic He-H_2 Gas Mixtures as Dielectric Media for High-Temperature Superconducting Power Devices," *IEEE Trans. Appl. Supercond.*, vol. 27, no. 4, pp. 1–6, Jun. 2017, doi: 10.1109/TASC.2016.2637319.
- [12] C. Park, S. Pamidi, and L. Graber, "The critical electric field of gas mixtures over the extended range of cryogenic operating conditions," *Journal of Applied Physics*, vol. 122, no. 15, p. 153301, Oct. 2017, doi: 10.1063/1.4995663.
- [13] C. Park, S. Pamidi, and L. Graber, "The dielectric strength of dissociated cryogenic gas media," *Journal of Applied Physics*, vol. 124, no. 10, p. 104104, Sep. 2018, doi: 10.1063/1.5051769.