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Plasma discharge in supercritical fluids

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Parallel plate discharge of a CO_2 fluid under the supercritical condition is known to exhibit a peculiar Paschen's law [1,2]; the breakdown voltage is significantly lower at the critical point than that under the equivalent normal (i.e., non critical) conditions. In the present work a theory to account for this phenomenon is proposed, which attributes the increase of ionization rates to the formation of micro cavities (i.e., electron channels) due to the cluster formation of fluid atoms (or molecules) under supercritical conditions.

I. Introduction When the pressure and temperature of a fluid are sufficiently high, the difference between the gas and liquid phases no longer exist. The point in the phase space at which the phase boundary between the gas and liquid phases disappears is called the critical point and the fluid that has slightly larger pressure and temperature than those of the critical point is called supercritical fluid [3]. For example, the critical point of carbon dioxide (CO_2) is given by the critical temperature T_c = 304K, critical pressure $p_c = 74\,\text{bar} = 7.4\,\text{MPa}$ (72.9atm), and critical mass density $n_m = 0.468$ g/cm^3 (molecular number density $n = 6.40 \times 10^{21}/\text{cm}^3$) [4,5]. Supercritical fluids typically possess combined characteristics of gas and liquid such as gas-like large transport coefficients (e.g., viscosities and thermal conductivities) and liquid-like large densities. For industrial applications, supercritical fluids are often used as solvents for enhanced chemical reactions.

Ito and Terashima [1] have shown using direct current (DC) parallel plate discharges in CO_2 supercritical fluids that the breakdown voltage of the fluid is significantly lower near the critical point than what one would expect from the ordinary Paschen's law [1,2]. In the present work, we attempt to explain this abnormality of the breakdown voltage as a function of the product of the pressure and electrode gap distance.

II. Model Before discussing our supercritical discharge model, we briefly outline the Townsend discharge model for an ordinary fluid (gas). Let us consider a one-dimensional parallel plate discharge, where the distance between the two electrodes and the charge-neutral gas density are given by d and N_g . When a voltage is applied to the electrodes, a constant electric field E appears in the inter-electrode space. In what follows, we assume the charge density is sufficiently low, so that no space-charge effects need to be considered. The electron density n_e as a function of the distance x measured from the cathode satisfies the relation

$$\frac{dn_e}{dx} = \alpha n_e \qquad (1)$$

where α , defined as

$$\alpha(E) \equiv N_g \left\langle v\sigma_{\text{ion}} \right\rangle / v_{\text{ed}} , \qquad (2)$$

is called as the first Townsend coefficient and generally a function of the local electric field E . In Eq. (2), σ_{ion} is the differential cross section for ionization, v is the electron velocity, v_{ed} is the electron drift velocity, and $\langle \; \rangle$ represents the average over the velocity space. The solution to Eq. (1) leads to $n_e(x) = n_0 \exp(\alpha x)$. The condition that a discharge be maintained between these electrodes is that positive ions created in the ionization process reach the cathode and produce a sufficient number of electrons to replenish the electrons that are lost to the anode. This condition may be written as

$$\gamma\left[\exp(\alpha d) - 1\right] = 1 \qquad (3)$$

where γ represents the secondary electron emission coefficient at the cathode.

For an ordinary gas, it is usually assumed that the first Townsend coefficient is given by $\alpha(E) = AN_g \exp(-BN_g / E)$ with A and B being some constants, as given by the blue curve in Fig. 1. (In Fig.1, $\alpha(E)/E$ is plotted as a function of the gas density normalized by the electric field N_g/E .) For supercritical fluids, we expect the dependence of this coefficient on E changes due to the following reasons. Under supercritical conditions, it is known that the atoms (or molecules) constituting the fluid form micro clusters, which may also be considered as nano-scale liquid droplets, due to the attractive interactions among fluid atoms (or molecules). The formation of micro clusters with little change of the total fluid volume naturally creates some extra inter-cluster space (micro cavities) [6]. We note that atoms forming such a cluster exchange themselves rapidly, typically in the time scale of pico seconds [7]. The micro cavities created by cluster formation also presents open space where electrons are accelerated to higher energies by the electric field E, which then leads to higher ionization rates. For this reason, we also call the micro cavities "electron channels". Due to the limited page space here, we are unable to present the details of how the increase of ionization rates will alter the dependence of the first Townsend coefficient on the applied electric field, but let us assume that it is given by the red curve in Fig. 1 with the increase of $\alpha(E)$ at the critical density (which is given at $N_g/E \simeq 3$ in this case). Based on this curve, we solve Eq. (3) with respect of E numerically and plot the breakdown voltage $V = Ed$, which is given by the red curve in Fig. 2. (The blue curve is the well known Paschen's law for an ordinary gas.)

It should also be noted that, near the critical point, the density and pressure is not proportional for a given temperature. For example, the blue line in Fig. 3 represents the equation of state for an ideal gas whereas the red curve represents a typical equation of state for a fluid near the critical point. With this equation of state, we redraw the breakdown voltage curves given in Fig. 2 with respect of $p_g d$, instead of $N_g d$ with p_g being the fluid pressure, which are given in Fig. 4. The red curve in Fig. 4 qualitatively reproduces the experimentally observed breakdown voltage curves of supercritical CO_2 fluid given in Ref. 1 and 2.

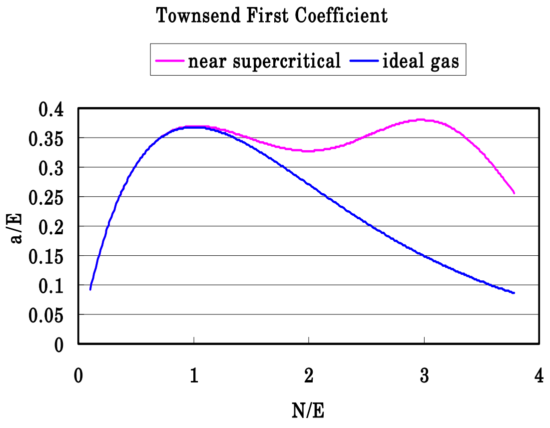


Fig. 1: The first Townsend coefficients as functions of the fluid density. (Values are all normalized.) The red curve is the one in the neighbourhood of the critical point.

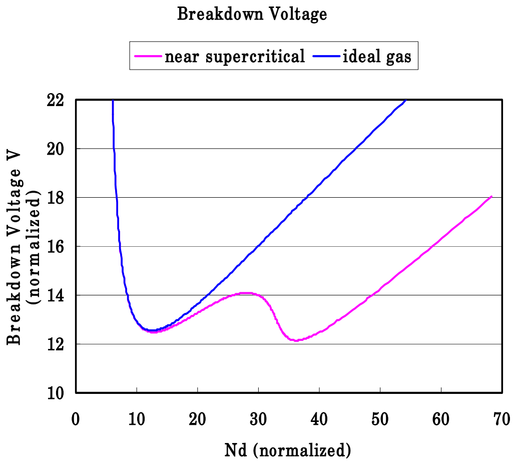
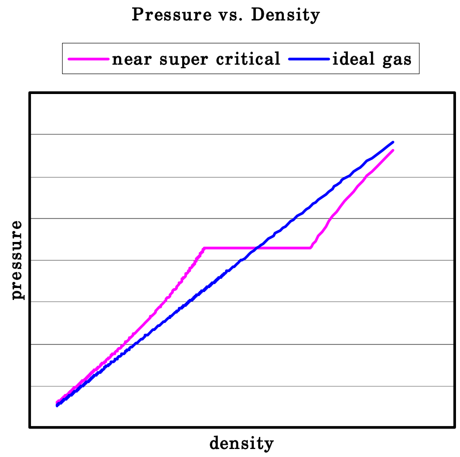


Fig. 2: The normalized breakdown voltages as functions of the product of fluid density and gap distance. The red curve is the Paschen curve for a fluid near its critical point.



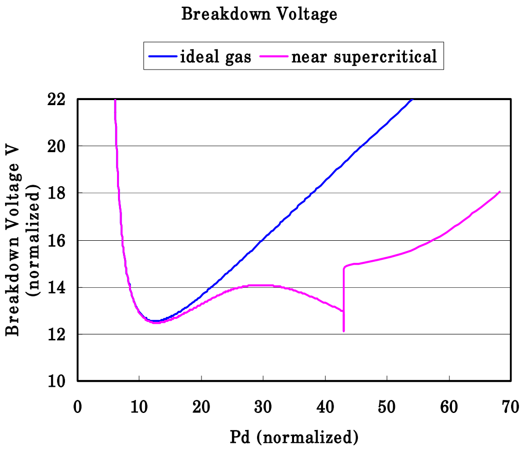


Fig. 3: Models of the equations of state for an ideal gas (blue) and a fluid near the critical point (red) for a constant temperature. Note that, near the critical point, the density varies significantly with small variation of the pressure.

Fig. 4: Normalized breakdown voltage *V* as a function of the normalized pressure-distance product. The blue and red curves represent the cases for the ideal gas and a fluid near supercritical conditions. At the critical pressure ($Pd \simeq 45$ in this case), the breakdown voltage is shown to be lowered.

III Summary In the present work, we have outlined our theory to account for the breakdown voltage drop under supercritical conditions. The central issue regarding supercritical fluid discharge is the formation of micro clusters of fluid molecules. The formation of such clusters creates micro cavities (i.e., electron channels), where electrons gain higher kinetic energies from the applied electric field than those in a normal liquid under similar conditions. This effectively increases the ionization rate and therefore reduces the breakdown voltage.

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