Study of electron energy distribution function and transport parameters for CF_4 and Ar gases discharge by using the solution of Boltzmann equation-*Part I*

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Abstract

The Boltzmann transport equation is solved by using two-terms approximation for pure gases . This method of solution is used to calculate the electron energy distribution function and electric transport parameters were evaluated in the range of E/N varying from $1\times10^{-17}V\ cm^2 \le E/N \le 5\times10^{-15}V\ cm^2$.

From the results we can conclude that the electron energy distribution function of CF_4 gas is nearly Maxwellian at (1,2)Td, and when E/N increase the distribution function is non Maxwellian. Behavior of electrons transport parameters is nearly from the experimental results in references. The drift velocity of electron in carbon tetraflouride is large compared with other gases

Keywords
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دراسة دالة توزيع طاقة الإلكترون ومعلمات الأنتقال لتفريغ مزيج غازات Ar,CF_4 بواسطة استخدام حل معادلة بولتزمان

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الخلاصه

تم حل معادلة بولتزمان للغازات النقية والمزيجات باستخدام التقريب ذي الحدين. استخدمت هذه الطريقة لحساب دالة توزيع طاقة الإلكترون ومعلمات الانتقال الالكترونيK حسبت في مدى متغير من E/N $1\times10^{-17}V\ cm^2 \le E/N \le 5\times10^{-15}V\ cm^2$.

أظهرت تلك النتائج أن دالة توزيع طاقة الإلكترون لغاز CF_4 قريب من التوزيع الماكسويلي عند (1،2) تاوسند، بعد ذلك عندما تزداد E/N التوزيع يصبح غير ماكسويلي، سلوك معلمات الانتقال قريب من النتائج التجريبية في المصادر. سرعة انجراف الإلكترون في غاز رباعي فلوريد الكاربون كانت كبيره مقارنة مع بقية الغازات .

Introduction

The electron –velocity distribution function plays a central role in defining the physical properties of plasma. The statistical behavior of electrons is governed by the electron energy distribution function (EEDF). Transport properties of electron are directly dependent on EEDF. Theoretically EEDF can be obtained by solving Boltzmann equation. The EEDF is determined by the balance between the gain of the electrons from acceleration electric field and losses of electrons through the collisions [1].

The electron transport parameters of pure gas and gas mixtures have been studied for a wide range of applied electric field. These parameters: such as the drift velocity, mobility, diffusion coefficient, ionization coefficient, and mean electron energy are defined in collision cross section and EEDF represent the backbone of the electron swarm behavior of pure gas

and gas mixtures in discharge of plasma [2].

Solution of transport Boltzmann equation for the electron –velocity distribution function $f\ (\vec{r},\vec{v},t)$ in spherical harmonics is given by [3].

$$f\ (\vec{r},\vec{v},t)=\sum_{\ell=0}^{\infty} f_{\ell}(\vec{r},\vec{v},t)\,p_{\ell}(\cos\theta) \quad \ldots.(1)$$

where $f_{\ell}(\vec{r},\vec{v},t)$ represent coefficient of expansion and $p_{\ell}(\cos\theta)$ is Legendre Polynomials. By using two–terms approximation, the equation form become

$$f\ (\vec{r},\vec{v},t)=f_0(\vec{r},\vec{v},t)+f_1(\vec{r},\vec{v},t)\cos\theta \ \ldots(2)$$

$$f\ (\vec{v}) = f_0\ (\vec{v}) + \frac{\vec{v}}{v} f_1\ (\vec{v}) \qquad (3)$$

The first term $f_0(\vec{v})$, is isotropic distribution in velocity space. This occurs in elastic collisions, where the electrons could be expected to suffer large directional changes of velocity but relatively small energy losses because of mass difference between electrons and molecules. The second term $\frac{\vec{v}}{v} f_1(\vec{v})$, the distribution is anisotropic because of large energy losses of electron in inelastic collisions $f1 \ll f2$.

The electron energy distribution function in CF_4 gas discharge was numerically calculated for *E/N=15-300 Td* using Boltzmann kinetic equation in 2006 by Masek [4]. The momentum transfer and vibration cross-section were derived from available experimental swarm parameters while the cross section for inelastic electron-molecule collisional processes were taken from the literature. The two terms spherical harmonic expansion of the distribution function was used in the calculations.

Niktovic and Potrovic in 2008 [5] are obtained results by using simple solution for Boltzmann equation in mixture of CF_4 with its radicals for ratios of the electric field to the gas number density *E/N* from (1Td – 1000 Td) . The analysis of non – conservative collisions revealed a range of *E/N* where electron attachment introduced by radicals significantly changes electron kinetics obtained for pure CF_4 gas.

The Aim of this work is to study theoretically the electron energy distribution function and electron transport parameters in DC electric discharge processes for CF_4 , Argon gases and its mixtures from different ratios from solution of Boltzmann equation by using two terms approximation.

1.Theory

The fundamental equation governing the electron distribution function is the Boltzmann equation. For spatially uniform gas in the presence of steady electric field. The Boltzmann equation for electrons in collisions state is given by [6]:

$$\frac{\partial f}{\partial t} + v\ \frac{\partial f}{\partial r} - \frac{e\vec{E}}{m}\frac{\partial f}{\partial v} = \left(\frac{df}{dt}\right)_c \qquad (4)$$

where $\left(\frac{df}{dt}\right)_c$ represents the rate of change of $f\ (\vec{r},\vec{v},t)$ due to collision, thus, when collisions are considered. The total derivative $\frac{df}{dt}$ represents all particles moving in the phase space, where, the partial derivative $\frac{\partial f}{\partial t}$ represents the change in the number of electrons at a given point in the phase space.

Now one considers the case of spatially uniform gas, also, $f\ (\vec{r},\vec{v},t)$ function of velocity only, where $\nabla_r f = 0$ and thus equation (4) becomes:

$$\frac{\partial f}{\partial t} - \frac{e\vec{E}}{m}\nabla_v f = \left(\frac{df}{dt}\right)_c \qquad (5)$$

In weakly ionized gases, the most collisions occurrence between electrons and neutral atoms, the collisions between electron –electron and electron – ion are rare.

Consider now only neutral atoms collision. The contribution of collision of each kind to the change the distribution function can be quite simply added together. One will divide collisions into elastic and inelastic collisions :

$$\left(\frac{df}{dt}\right)_c = \left(\frac{df}{dt}\right)_{elastic} + \left(\frac{df}{dt}\right)_{inelastic} \quad (6)$$

The first part of equation (6) represents the change of function due to elastic collisions and the second part of equation represents the change of function because the inelastic collisions. The class of inelastic collisions do not include excitation process of atoms or molecules but also the creation of new electrons as a result of ionization .
After the compensation (two- terms approximation), we obtain two equations:

$$\frac{\partial f_0}{\partial t} - \frac{e\vec{E}}{m}\frac{1}{3\mathrm{v}^2}\frac{\partial}{\partial \mathrm{v}}\left(\mathrm{v}^2 f_1\right) = \left(\frac{df_0}{dt}\right)_c \quad (7)$$

(8)

When the electron collision frequency for momentum- transfer is much larger than the electron collision frequency for excitation, the necessary condition for the two terms expansion for distribution function to be valid , the momentum-transfer collisions play the major role in reducing the asymmetry in the distribution function .the function change in elastic collisions state is given by [7] :

$$\left(\frac{df_1}{dt}\right)_c = -\upsilon_e(\mathrm{v}) f_1(\vec{\mathrm{v}}) \quad (9)$$

where υ_e is the electron momentum transfer collision frequency where

$$\upsilon_e(\mathrm{v}) = N Q_m(\mathrm{v})\,\mathrm{v}$$

$$\left(\frac{df_1}{dt}\right)_c = -N Q_m(\mathrm{v})\,\mathrm{v} f_1(\vec{\mathrm{v}}) \quad (10)$$

v represented electron velocity and $Q_m(\mathrm{v})$ is momentum transfer cross section. From the solution of equation (8), we will find $f_1(\mathrm{v})$ value, where all quantities are assumed to independent of time, is given by:

$$\frac{\partial f_0}{\partial t} - \frac{2e}{mv}\frac{\partial}{\partial \varepsilon}\left[\frac{\vec{E}^2\varepsilon}{3NQ_m}\frac{\partial f_0}{\partial \varepsilon} + \frac{2m}{M}NQ_m\varepsilon^2 f_0 + \frac{2mK_BT}{Me}NQ_m\varepsilon^2\frac{\partial f_0}{\partial \varepsilon}\right] = \left(\frac{df_0}{dt}\right)_c$$

(11)

The change of function in elastic collisions is given by:

$$f_1(\vec{\mathrm{v}}) = \frac{e\vec{E}}{\mathrm{v}\,m\,N\,Q_m(\mathrm{v})}\frac{\partial f_0}{\partial \mathrm{v}} \quad (12)$$

The right hand side of equation (12) represented the combined effect on the distribution function of elastic and inelastic electron –neutral collisions only, assuming that the electron-electron collisions and electron-ion are negligible.
The change of the function $\left(\frac{df}{dt}\right)_c$ in inelastic collisions is given by:

$$\frac{\partial f_1}{\partial t} - \frac{e\vec{E}}{m}\frac{\partial f_0}{\partial \mathrm{v}} = \left(\frac{df_1}{dt}\right)_c \quad (13)$$

The energy gain from electric field in superelastic collisions is given by [6].

(14)

Now, the sum of function change in two state (ground state and excitated state), after the equations compensation (12) , (13) and (14), we obtain on work equation [7]:

$$\left(\frac{m\varepsilon}{2e}\right)^{1/2}\frac{\partial f_0}{\partial t} = \frac{E^2}{3}\frac{\partial}{\partial \varepsilon}\left(\frac{\varepsilon}{NQ_m}\frac{\partial f_0}{\partial \varepsilon}\right) + \frac{2m}{M}\frac{\partial}{\partial \varepsilon}\left(\varepsilon^2 NQ_m f_0\right) + \frac{2mk_BT}{Me}\frac{\partial}{\partial \varepsilon}\left(\varepsilon^2 NQ_m\frac{\partial f_0}{\partial \varepsilon}\right) +$$
$$\sum_j\left[\left(\varepsilon+\varepsilon_j\right)f_0\left(\varepsilon+\varepsilon_j\right)N_0Q_j\left(\varepsilon+\varepsilon_j\right) - \varepsilon f_0(\varepsilon)N_0Q_j(\varepsilon)\right] +$$
$$\sum_j\left[\left(\varepsilon-\varepsilon_j\right)f_0\left(\varepsilon-\varepsilon_j\right)N_jQ_{-j}\left(\varepsilon-\varepsilon_j\right) - \varepsilon f_0(\varepsilon)N_jQ_{-j}(\varepsilon)\right]$$

(15)

In right hand side of equation (15), the first part accounts for the gain of energy result from electric field. The second part of equation accounts for gain in energy (KT) and elastic losses by 2m/M. Also , in third part of the equation , few energy losses occur because of elastic scattering of electron due to electron collision with molecule . These, processes all occurs in

ground state of molecules. The first term of excitation state, accounts energy losses of electrons result the inelastic collisions. The last part of equation (15), is the energy gain of electrons given by the electric field electrons to compensation the energy loss of electrons because the collisions.

When the left hand side of equation (15), equal zero, the function $f(\varepsilon)$ becomes isotropic.Equation (15) is used in pure gases state, if the gas is mixture of different species. The momentum transfer cross section, excitation cross section and super elastic for molecules of species (k) in inelastic processes are represented by Q_m^k, Q_j^k, Q_{-j}^k respectively. Also, the electron collision frequency in elastic collisions state for molecules of species k (mixtures) become:

$$\upsilon_e^k(\mathrm{v}) = N_K Q_m^K(\mathrm{v})\,\mathrm{v} \quad (16)$$

where N_K is the number of molecules of species k.

Transport coefficients

The drift velocity is nonlinear function with electric field, and the mobility depends on strength field. at sufficiently low E/N, where an electron loses all equal to the gain from the electric field at one elastic collision , the drift velocity is proportional to E/N.

The relation between drift velocity and distribution function of electron energy is given by [8]:

$$\mathrm{v}_d = -\frac{E}{3}\left(\frac{2e}{m}\right)^{1/2}\int_0^\infty \frac{u}{N Q_m(u)}\frac{df_0}{du}du \quad (18)$$

The mobility is defined as the proportionally coefficient between the drift velocity of a charged particle and electric field. The mobility of electrons is:

$$\mu_e = \frac{e}{m\upsilon_m} = \frac{\mathrm{v}_d}{E} \quad (19)$$

Where υ_m represent the electron momentum- transfer collision frequency. The electron mobility decreased with E/N increase, this occur energy loss result of electron through the collisions between electrons and neutral molecules.

From the relation between the drift velocity and mobility with EEDF, we can be calculate the electron mobility equation [9]:

$$\mu_e = -\frac{1}{3}\left(\frac{2e}{m}\right)^{1/2}\int_0^\infty \frac{u}{\sum \delta_s Q_m(u)}\frac{df_0}{du}du \quad (20)$$

where δ_s represents fractional concentration of the s species ($\delta_s = \frac{N_s^j}{N_s}$) and N_s^j is the number of molecules of species s in the excited state j.

when the density of charged particles is very low, the charges of opposite signs diffuse independently of each other, This is known as free diffusion.

In a weakly ionized gas discharge, the ambipolar diffusion coefficient is simplified by noting that $\mu_e \gg \mu_i$ usually The relation between diffusion coefficient and electron energy distribution function is given by [10]:

$$D_T = \frac{1}{3}\left(\frac{2}{m}\right)^{1/2}\int \frac{u^{1/2}}{N Q_m(u)} f(u)du \quad (21)$$

An electron colliding with a neutral atom can produce a negative ion in a process termed electron attachment. Dissociative and non dissociative electron attachment reactions depend strongly on the electron energy

The primary ionization coefficient is a basic parameter in discharge physics and is defined as the number of ionizing collisions made by an electron in moving 1cm in the direction of the applied electric field. The coefficient is used in describing the behavior of a swarm of electrons traveling through a gas [11].the ionization coefficient is calculate from the relation:

$$\frac{\alpha}{N} = \frac{1}{\mathrm{v}_d}\left(\frac{2e}{m}\right)^{1/2}\sum_k \int_{uik}\frac{N_K}{N}Q_{ik}(u)uf_0(u)du \quad (22)$$

$\frac{\alpha}{N}$ is called ionization coefficient. N_K represent the number of atoms of type k .

method of calculation

The work deals with the theoretical studies about electron energy distribution function and electron transport parameters in DC electric discharge processes for CF_4, Ar gas and its mixtures with different ratios at low temperature of the plasma.

The search dependent on solving the equation of Boltzmann for collisions by two-terms approximation method in gas discharge processes at regular uniform electric field by using NOMAD computer program in Fortran language.

The electron energy distribution function and transport parameters was calculated for range (1 -500) Td with NOMAD program by input data for this program such as collision cross section, the number density of gases, number and types of gases, concentration of gas, distribution density, E/N represent the ratio between electric field intensity to the number density of gas, molecular weight , gas temperature, electron density, as well as the program contain other condition must be taken into account this work like, electron energy distribution function dependent of collision cross sections.

The number density of gas was calculated theoretically depended on weight density and molecular weight, the relation between these rewrite [12] :

$$N = \frac{\rho N_A}{\omega} \qquad (23)$$

where ρ represent weight density ω is molecular weight, N_A represent Avogadro constant. The table (1) shown that the number density of gases and mass density in pure gases (CF_4, Ar) at room temperature.

Gas Mixtures	Mass density (10^{-3}gm /cm^3)	Number of density (10^{19}atom/ c m^3)
90%CF_4+10 %Ar	3.650	1.718
75%CF_4+25 %Ar	3.339	1.572
50%CF_4+50 %Ar	2.820	1.328
25%CF_4+75 %Ar	2.742	1.293
10%CF_4+90 %Ar	1.990	0.937

Table (1): the number densities values and mass density of pure gases

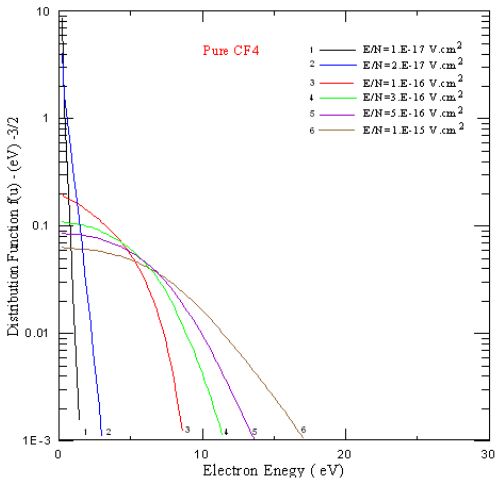
Table (2): The number of density for mixtures calculated in this work.

Results and Discussion

Gas	Mass density (10^{-3}gm /cm^3)	Number of density(10^{19}atom/ cm^3)
CF_4	3.85	2.640161 [13]
Ar	1.783	2.68772 [14]

Pure Carbon tetrafluoride

Five types of cross section (vibration, electronics excitation, attachment, ionization and momentum- transfer cross section) in pure carbon tetrafluoride are used in the analysis. The cross sections data is input data for NOMAD computer program. Equation (17) is solved numerically for range of E/N values (1-500) Td. The distribution function of electron energy is Maxwellian when the condition ($\frac{eD}{\mu} = \frac{2}{3}\langle \varepsilon \rangle$) is to be realized, this means an isotropic distribution (the distribution in thermal equilibrium state between electrons and atoms or molecules of gas). The results are shown in figures(1 to 6)



Figure(1): The electron energy distribution function as a function of electro energy for several values of E/N in pure CF_4 gas.

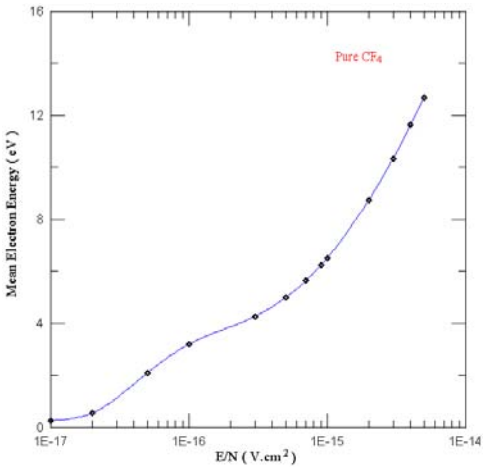
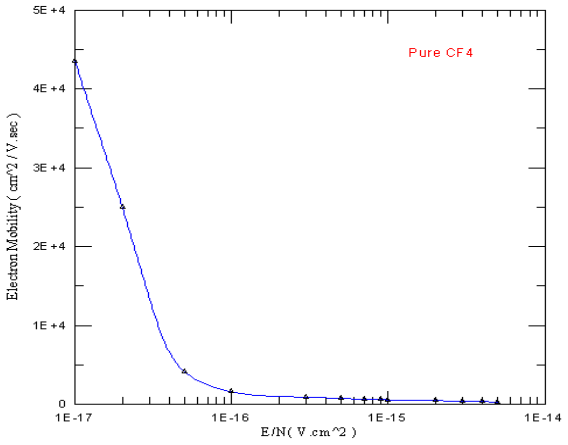


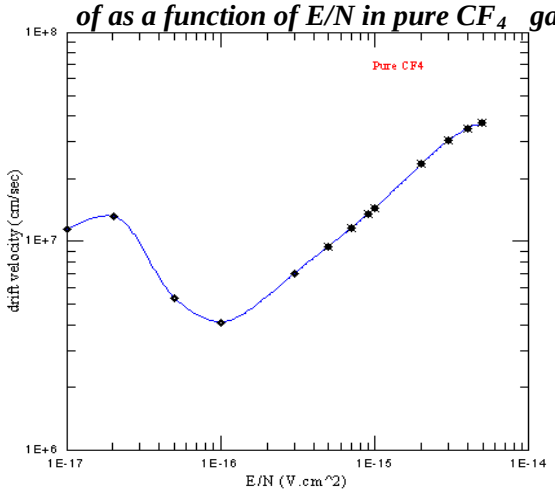
Figure (2): The mean electron energy as a function of E/N in pure CF_4 gas.

Figure (1) represents electron energy distribution function as a function of electron energy in pure CF_4. The EEDF normally non- Maxwellian because the characteristic energy $\frac{eD}{\mu}$ is greater than $\frac{2}{3}\langle\varepsilon\rangle$. The EEDF decreased when E/N increase, it is attributed to the electron collisions number that will increase with neutral molecules or atoms, this cause the electron energy losses. Also, some of electrons have very weak energy and this increases the probability of attachment with neutrals atoms to create negative ions. Therefore EEDF decrease . The electron energy distribution function at E/N values $(1\times10^{-17}$ - 2×10^{-17} V.cm^2) has isotropic distribution and nearly of thermal equilibrium state, thereafter, at electric field density increase, the electron energy distribution function is non Maxwellian , $\frac{eD}{\mu}\neq\frac{2}{3}\langle\varepsilon\rangle$ with energy losses due to inelastic collisions in discharge processes, as shows in figure (1). Also, the agreement point occurs for electron energy distribution functions at approximately electron energy of (7eV) for different values of E/N. At this point the system in thermal equilibrium state.

Figure (2) shows the mean electron energy in range (0.27 – 12.68) eV for different values of E/N (1-500) Td. The change of mean electron energy is progressive exponential, the electrons gain energy from electric field.



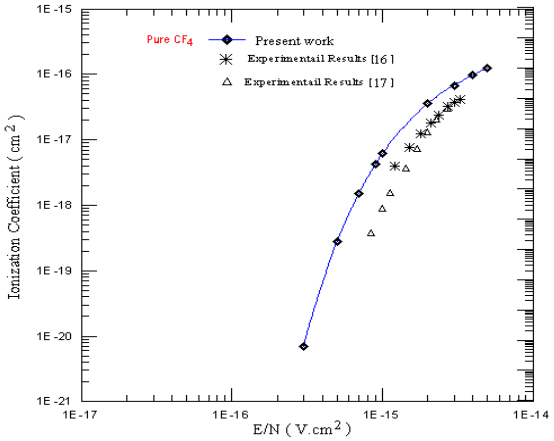
Figure(3): The mobility of electron as a function of as a function of E/N in pure CF_4 gas.



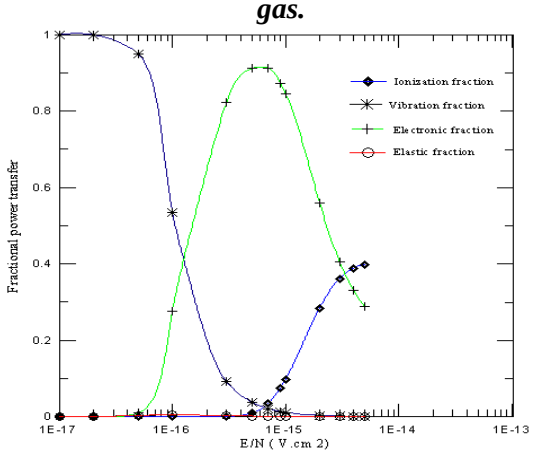
Figure(4) The drift velocity of electron E/N in pure CF_4 gas

The figure (3) shows the electron mobility exponential decrease when electric field density increase , this occurs because that the electrons obtained kinetic energy by acceleration from electric field to produce increased number of collisions to contribute to the decrease of mean free path therefore the electron mobility is decreased.

Figure (4) shows the behavior of the drift velocity as a function of E/N: firstly in range (1 – 2) Td the drift velocity increases due to elastic collisions, secondly in range(2-10) Td
the inelastic collisions occurs to attain critical value at 10 Td, thirdly the region in range(10-500) Td the drift velocity increases due to the electron gain from electric field and momentum transfer from molecule to electrons after collision.



Figure(5): The ionization coefficient of electron as a function of E/N in pure CF_4 gas.



Figure(6): Fractional electron power transfer as a function of E/N in pure CF_4 gas.

The values of ionization coefficient have been calculated for CF_4 gas over the range $4\times10^{-16} \le E/N \le 5\times10^{-15}$ $V.cm^2$ as shown in figure (5). The values of ionization coefficient in the present work are in agreement with pervious measurement of Naidu in 1972 [16]and Lucas in 1973 [17].

The elastic and inelastic collision processes are clarified in figure (6) and indication of energy losses of electrons. The vibration fraction in weakly electric field (1Td) has high value and it is vanished at strong electric field (200Td). The electronic fraction in the range (5-70Td) is increasing and electronic excitation maximum at (70 Td). The ionization fraction above (40 Td) increases. These values of E/N represented low energy for excitation.

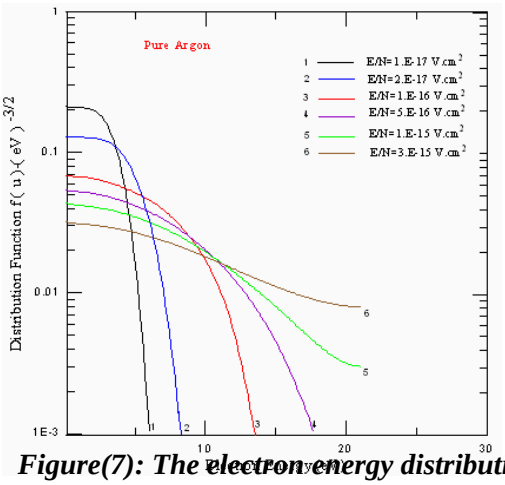
4.2- Pure Argon gas

A set of the cross sections were used in Argon analysis. The cross sections were determined on basis experimental values taken from set of papers, these represent electronic excitation, ionization and momentum transfer cross sections. The excitation cross section of Argon has onset energy of (11.62) eV, also, the threshold energy of ionization is (15.759) eV.

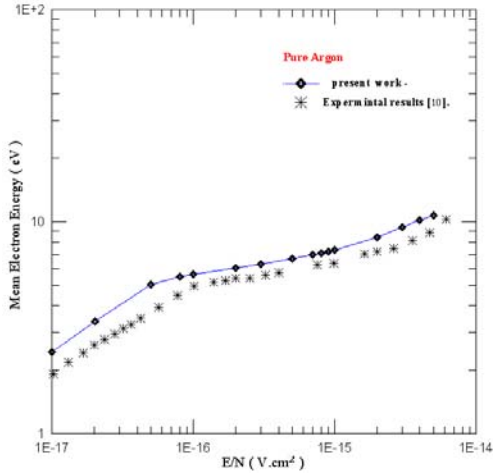
The E/N values are chose as input data in range (1Td - 500Td). The electron energy distribution function decreases with the increase of E/N as shown in figure(7). At low E/N value (1Td), the electron energy distribution function is non Maxwellain and the lose of electron energy increase at high E/N, therefore the distribution function is anisotropic.

The mean electron energy for pure Argon discharge in the range (2.43-10.7) eV is shown in figure (8). The mean electron energy increases linearly with E/N from $(1\times10^{-17} - 5\times10^{-17})$ $V.cm^2$. The mean electron energy increase is slow from $(5\times10^{-17} - 1\times10^{-15})$ $V.cm^2$ because of the energy losses in inelastic collision processes. Thus, the mean energy of

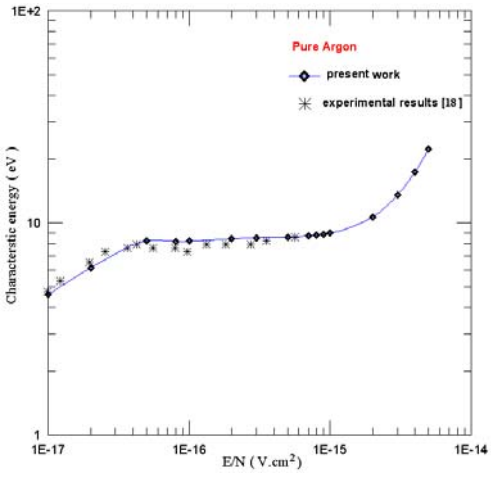
electron is in good agreement experimental results of Makabe [10].



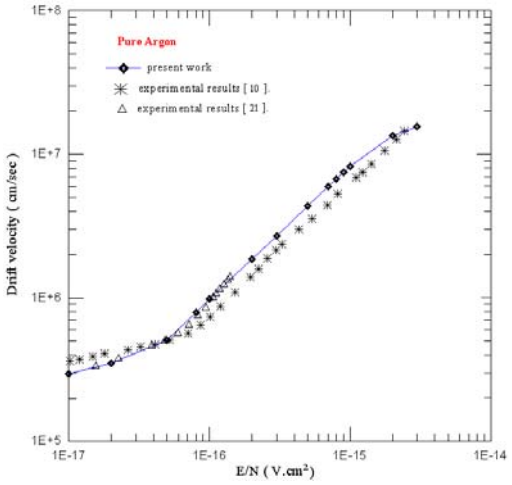
Figure(7): The electron energy distribution function several values of a function of E/N in pure Argon



Figure(8): The mean electron energy as as a function of electron energy for E/N in pure Argon.



Figure(9): The characteristic energy of electron as a function of E/N in pure Argon gas.



Figure(10): The drift velocity of electron as a function of E/N in pure Argon.

Figure (9) shows the behavior of characteristic energy which increases with increase of E/N by the effect of the angular scattering of the inelastic collision. But at low E/N the differential scattering cross section is same for both inelastic and elastic collisions. The values of characteristic energy in this work are in agreement with experimental results of Dutton in 1975 [18].

The drift velocity of electrons as a function of E/N of Argon is represented in figure (10). It is compared with experimental results of Makabe and Nielsen in references [10] respectively. The drift velocity increases with increase of E/N and our results are in good agreement with experimental results of Makabe and Nielsen.

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