Generalized Einstein relation in disordered organic semiconductors: Influence of the acoustic phonons–charge carriers scattering

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Abstract

In this work, we analyze the generalized Einstein relation for disordered organic semiconductors with a non–equilibrium Druyvesteyn–type distribution function. The Druyvesteyn behavior of hot electrons in a solid state is associated with the acoustic phonons–charge carriers scattering. Such a case has been experimentally demonstrated in electroluminescent inorganic rare–earth–doped zinc chalcogenides. Therefore, we can assume that, in a part of organic materials used in organic light–emitting diodes (OLEDs), we can also find the Druyvesteyn–type distribution of charge carriers under external electric fields. It looks that the electric–field–dependent diffusion coefficient, which is observed in the phonon–induced hopping electron transport, plays a key role here. The theoretical analysis of the Einstein relation shows that for lower concentrations of charge carriers, the diffusivity–mobility ratio (D/μ) reaches a value lower than 1 (in kT/q units). The temperature dependencies of D/μ are similar to the tendencies reported for the equilibrium conditions. The obtained satisfactory agreement between experimental results and calculations based on the Druyvesteyn–type distribution function confirms the usefulness of the presented model.

Keywords: Organic light emitting diodes, Organic semiconductors, Einstein relation

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1. Introduction

Nowadays, organic semiconductors are treated as promising materials for electronic and optoelectronic systems. Therefore, a great attention is currently paid to the recognition of physical effects which can lead to a better efficiency of such devices. So far, mostly organic light–emitting diodes (OLEDs) have found commercial applications. In OLEDs, we observe an emission of light occurring in an external electric field (the electroluminescence process). It means that these diodes work under non–equilibrium conditions.

One of the most important parameters in the description of electrical and photoelectrical phenomena is the diffusivity–mobility ratio for charge carriers. In a simple case, this ratio can be written using the Einstein relation

$$\frac{D}{\mu} = \frac{kT}{q}, \tag{1}$$

where D is the diffusion coefficient, μ represents the mobility of charge, k denotes the Boltzmann constant, T is the temperature and q represents the elementary charge.

Most organic semiconductors are amorphous or polycrystalline materials. The disorder existing in such structures causes that equation (1) should be replaced by the generalized Einstein relation known from the theory of degenerate semiconductors [1, 2]

$$\frac{D}{\mu} = \frac{1}{q}\frac{n}{\frac{dn}{dE_F}}, \tag{2}$$

where n is the carrier concentration and E_F represents the energy of a quasi–Fermi level. Recently, a generalized form of the Einstein relation has been intensively studied for molecular and disordered semiconductors used in electronic devices [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23].

In the solid state theory, the occupancy probability of electrons and holes is described by the quantum Fermi–Dirac distribution function. For non–degenerate semiconductors, this function can be approximated by the classical Maxwell–

Boltzmann equation. Both these functions are valid only for a thermal equilibrium. However, they are often applied also for smaller perturbation states, such as low and intermediate electric fields regimes. Therefore, most researchers try to describe the generalized Einstein relation using the Fermi–Dirac function. However, electronic devices predominantly work in higher electric fields. Thus, it is required to apply non–equilibrium distribution functions in such studies.

Generally, there are no accurate analytical equations to describe the distribution of charge carriers under non–equilibrium conditions in a condensed matter. One can find only approximated formulas [24]. It should be also mentioned that equation (2) has been derived for a thermal equilibrium. Thus, its usefulness is approximately valid only for lower and intermediate electric fields. Therefore, different methods based on Monte–Carlo simulations, the hopping transport or the statistical physics were used to model the diffusivity–mobility relationship [18, 19, 25]. However, it has been analytically proved that the Einstein relation can be applied also for a non–equilibrium analysis of semiconductor devices [26, 27].

For the electroluminescent inorganic rare–earth–doped zinc chalcogenides, it has been theoretically considered [28, 29] and also experimentally confirmed [30] that the non–equilibrium Druyvesteyn distribution function describes the behavior of hot electrons in such structures. The Druyvesteyn function is often used in plasma physics to depict the distribution of electrons in ionized gases under electric field [31, 32, 33, 34]. This type of function has been also considered for a solid state [35, 36, 37, 38, 39, 40]. For example, Yamashita and Watanabe [35] have derived the Druyvesteyn–type formula for the case of the acoustic phonons–charge carriers scattering (see supplementary material). It means that the role of acoustic phonons becomes dominant, if this type of distribution function is observed in materials. We should note that the influence of phonons is currently of a great interest in different electronic devices [41]. Thus, the impact of acoustic phonons has been previously studied in organic materials [42, 43, 44, 45].

The Druyvesteyn–type behavior of electrons in electroluminescent inorganic materials leads to the conclusion that also in some organic systems this type of distribution function can be valid. So far, there was no experimental evidence of such a case in molecular structures. However, we cannot exclude a dominant role of the acoustic phonons–charge carriers scattering in a part of organic materials used in OLEDs. In these devices, electrons and holes are injected from opposite electrodes and move toward the area where they recombine radiatively. For amorphous molecular materials, one can expect the phonon–induced hopping transport of electrons. The aim of this work is to examine the generalized Einstein relation with the Druyvesteyn distribution function in disordered organic semiconductors.

2. Methodology

We can calculate the concentration of charge using a formula

$$n = \int_{-\infty}^{+\infty} g(E) f(E) dE, \tag{3}$$

where E is an energy of particles, $g(E)$ represents the density of states (DOS) and $f(E)$ denotes the distribution function.

For organic semiconductors, the DOS is often described with a Gaussian distribution of states

$$g(E) = \frac{N_v}{\sqrt{2\pi} \cdot \sigma} \exp\left[-\left(\frac{E - E_0}{\sqrt{2} \cdot \sigma} \right)^2 \right], \tag{4}$$

where N_v represents the effective DOS, σ is a width of the energy distribution in the DOS and E_0 denotes the energy of a Gaussian center.

In this work, we adopt the Druyvesteyn–type distribution function with a chemical potential (a quasi–Fermi energy) in the form (see supplementary material)

$$f_D = \exp\left[-\frac{(E - E_F)^2}{2pk^2T^2} \right]. \tag{5}$$

Here, p represents an electric–field–dependent parameter [35]

$$p = \frac{(qFl)^2}{6m^* u^2 kT}, \tag{6}$$

where F is the electric field, l denotes the mean free path in a weak electric field, m^* represents the effective mass of charge carriers and u is the velocity of a sound in a material.

We should remind that the position of a quasi–Fermi level changes with an electric field. Therefore, we use the replacement

$$E_F \rightarrow E_F - qFx, \tag{7}$$

where x is a distance from the electrode.

Thus, the diffusivity–mobility ratio with the Druyvesteyn–type function can be written as

$$\frac{D}{\mu} = \frac{kT}{q} \frac{\int\limits_{-\infty}^{+\infty} \exp\left[-\left(\frac{E-E_0}{\sqrt{2}\cdot\sigma}\right)^2\right] \exp\left[-\frac{(E-E_F+qFx)^2}{2pk^2T^2}\right] dE}{\int\limits_{-\infty}^{+\infty} \exp\left[-\left(\frac{E-E_0}{\sqrt{2}\cdot\sigma}\right)^2\right] \exp\left[-\frac{(E-E_F+qFx)^2}{2pk^2T^2}\right] \frac{(E-E_F+qFx)}{pkT} dE}. \tag{8}$$

It will be convenient to compare D/μ calculated from equation (8) with the diffusivity–mobility ratio obtained with the Fermi–Dirac function

$$f_{FD} = \frac{1}{1+\exp\left(\frac{E-E_F}{kT}\right)}. \tag{9}$$

In an electric field, this ratio has a form

$$\frac{D}{\mu} = \frac{kT}{q} \frac{\int\limits_{-\infty}^{+\infty} \exp\left[-\left(\frac{E-E_0}{\sqrt{2}\cdot\sigma}\right)^2\right] \frac{1}{1+\exp\left(\frac{E-E_F+qFx}{kT}\right)} dE}{\int\limits_{-\infty}^{+\infty} \exp\left[-\left(\frac{E-E_0}{\sqrt{2}\cdot\sigma}\right)^2\right] \frac{\exp\left(\frac{E-E_F+qFx}{kT}\right)}{\left[1+\exp\left(\frac{E-E_F+qFx}{kT}\right)\right]^2} dE}. \tag{10}$$

In this work, all integrals have been calculated numerically using the Gauss–Hermite quadratures.

3. Results and discussion

First, we will discuss the values of physical parameters used in calculations. It is known that the velocity of a sound in polymers depends on many physical quantities, like a temperature, a frequency or a pressure. Its value can be found in a wide range, usually 700 – 2800 m/s and is around two times greater for longitudinal waves than for transverse ones [46]. The mean free path of charge carriers increases with a kinetic energy of these particles in polymers [47]. If we consider typical electric fields applied in organic electronic and optoelectronic devices, then the mean free path should not be greater than 1 nm.

In general, the effective masses of electrons and holes depend on the energy of a particle at the wavevector in the band. For polymers with a simple structure, the effective mass is around $0.1m_e$, where m_e represents a free electron mass [48]. However, we can also find a higher order of magnitude for this quantity in the literature [49]. It has been confirmed for polymers that the value of an effective mass increases for a charge transport along a π–stacking direction [48, 50]. In the case of $\mathrm{Alq_3}$ electroluminescent compound, which is widely used in OLEDs, the effective masses are of a few times of the bare electron mass [51]. Therefore, we will use a value $1.5m_e$ in these calculations.

Fig. 1 and Fig. 2 show the diffusivity–mobility ratio drawn as a function of a relative Fermi energy, which can be defined as an energetic distance between a quasi–Fermi level and the Gaussian DOS center ($E_F - E_0$). In this work, the D/μ relationship is presented in kT/q units. Here, we have decided to choose a greater value of the sound velocity (2000 m/s) associated with the longitudinal acoustic wave. Fig. 1 illustrates a comparison between the ratios D/μ obtained with the Druyvesteyn and the Fermi–Dirac distribution functions calculated for three different electric fields (8×10^6 V/m, 1×10^7 V/m and 2×10^7 V/m). These values are lower than typical electric fields applied in OLEDs during the electroluminescence process ($\sim 10^8$ V/m). Therefore, the diffusivity–mobility ratio can be calculated for this perturbation state using the generalized Einstein relation given by equation (2).

Fig. 1 demonstrates that the D/μ relationship with the Druyvesteyn function increases with a field F, while it is field–independent with the Fermi–Dirac function. We can also see that the diffusivity–mobility ratio strictly increases for all relative Fermi energies when the acoustic phonons–charge carriers scattering dominates (the Druyvesteyn case). If we use the Fermi–Dirac function, then D/μ has a constant value equal to 1 (in kT/q units) for almost all $E_F - E_0$ and starts to rise close to the energy center of the Gaussian DOS (E_0). This fact can be clearly interpreted based on the results presented in Fig. 2. Here, the factor D/μ is drawn for three values of the width σ (0.05 eV, 0.1 eV and 0.15 eV). For a narrower DOS (the case of a lower σ), we describe conditions which are closer to non–degenerate ones because the quasi–Fermi level is farther from the Gaussian DOS. Then D/μ tends to 1 (in kT/q units) for a longer range of $E_F - E_0$. The increasing of σ causes that charge carriers in the states of DOS approach to the E_F. It leads to the degenerate conditions which are characterized by the ratio $D/\mu > 1$ (in kT/q units).

We should note that results presented in Fig. 1 and Fig. 2 depict an unusual tendency for D/μ obtained with the Druyvesteyn distribution function. It is seen that the diffusivity–mobility ratio is sometimes lower than 1 (in kT/q units). Such a tendency does not correspond to the known Einstein relation for degenerate or non–degenerate semiconductors. Fig. 1 shows that this effect depends on the electric field. If F increases, then $D/\mu < 1$ (in kT/q units) for greater energetic distances between E_0 and E_F. Usually, the mobility of charge is an electric–field–dependent parameter, while a diffusion coefficient does not change with F. However, in disordered organic materials, a hopping transport of electrons occurs between states localized among the quasi–Fermi energy and the transport energy level [52]. Thus, one can find theoretical models, where D depends on F. According to one of them, the total diffusion coefficient D includes also an additional electric–field–dependent term D_F when a multiple trapping transport dominates [23, 53]. It has been confirmed that the ratio D_F/μ can be lower than 1 (in kT/q units). Such a case was observed for higher charge concentrations in amorphous silicon with a combination of exponential and Gaussian mobility–gap states [23]. However, it seems that we should not use this interpretation here, which will be discussed in the following.

Fig. 3 shows the ratio D/μ obtained with the Druyvesteyn distribution function versus the concentration of charge carriers drawn for two electric fields. Solid and dashed lines represent results for $\sigma = 0.05$ eV and $\sigma = 0.15$ eV, respectively. We can see that a decreasing of F or σ causes a decreasing of D/μ. It is visible that values of D/μ lower than 1 (in kT/q units) can be obtained only for lower charge carrier concentrations. Thus, the multitrapping transport should not be dominant here. However, we think that a concept of the non–equilibrium electric–field–dependent diffusion coefficient (different than the previous one) is still valid.

Fig. 4 presents the diffusivity–mobility ratio calculated with the Druyvesteyn–type function versus the square of an electric field drawn for several sound velocities (1000 m/s, 1500 m/s, 2000 m/s and 2500 m/s). Here, we have decided to use the position of a quasi–Fermi level equal to -4.2 eV, which is 1.4 eV lower than an energy of the Gaussian DOS center (-2.8 eV). A band gap between HOMO and LUMO for organic electroluminescent materials often takes a value around 2.5 – 3 eV, so we have chosen the level E_F around a mid–gap. It is observed that an increasing of the sound velocity leads to a visible decreasing of D/μ. Thus, in general, we should consider separately independent diffusion coefficients and mobilities of charge for longitudinal and transverse acoustic waves. Additionally, it is clearly seen that the diffusivity–mobility ratio is a linear function of F^2. Such a linear tendency has been previously demonstrated for a non–equilibrium case in disordered organic semiconductors using an analytical model based on the hopping transport theory [19]. We should also mention that a quadratic growth of the diffusion coefficient has been reported for the hopping transport in disordered materials [54]. It validates the concept that the electric–field–dependent diffusion coefficient plays a key role here.

Fig. 5 shows the factor D/μ obtained with the Druyvesteyn distribution drawn as a function of the charge concentration for two temperatures. Solid and dashed lines represent results for $T = 200$ K and $T = 300$ K, respectively. We can see that an increasing of temperature lowers values of D/μ. This effect has been reported in the literature of organic semiconductors for the equilibrium conditions [4, 7, 22]. In addition, the diffusivity–mobility ratio is plotted versus the reciprocal of kT in Fig. 6. We observe a linear tendency of D/μ. It is seen that a rise of the DOS width σ leads to an increasing of D/μ values, which causes that slopes of the linear functions increase. This behavior looks similarly to the literature results obtained with the Fermi–Dirac distribution [8].

The conclusion is that a lowering of the ratio D/μ below 1 (in kT/q units) can be explained qualitatively that an interaction between the optical phonons and charge carriers has not been taken into account. If we consider both types of phonons, then a jump rate for the phonon–induced hopping transport reaches different values than for a pure acoustic phonons–charge carriers scattering [55]. It is known that the average jump rate influences the diffusion coefficient in disordered systems [56]. Thus, such an interpretation should be in an agreement with a concept of the electric–field–dependent diffusion coefficient.

The final step is to compare the presented theoretical model with real experimental results. We have decided to find the literature data where the diffusion coefficient changes with an electric field. As a consequence, such results obtained for the donor–doped bisphenol–A–polycarbonate [57] have been used in this paper. For an analysis, the mobility μ and the diffusion coefficient D were taken from figures 2 and 3, respectively (both numbers of figures from [57]). The experimental D/μ ratios drawn versus a square of the electric field are presented by triangle symbols in Fig. 7. We have chosen data measured for three values of the donor dipole moment. It is visible that D/μ increases with both the electric field and the dipole moment. Here, this ratio can have values lower than 1 (in kT/q units) which was not reported before. Therefore, the selected experimental data are good for a comparison with the theoretical model based on the Druyvesteyn distribution function.

In order to fit these data, we need reasonable parameters for the model. It is well known that the dipole moment of a dopant changes the width σ, which can be written in the form [58]

$$\sigma = \sqrt{\sigma_{vdv}^2 + \sigma_{dip}^2}. \tag{11}$$

Here, σ_{vdv} and σ_{dip} represent the van der Vaals and the dipole components, respectively. The latter may be found from an expression

$$\sigma_{dip} = \frac{Ac^b d}{a^2 \varepsilon_r}, \tag{12}$$

where c is the dipoles concentration, d denotes the dipole moment, a represents the intersite distance in the lattice and ε_r is a dielectric constant of a material. We should notice that when we write d in the debye unit and a in angstroms, then the parameter σ_{dip} will be given in electronvolts. The coefficients A and b depend on the theoretical model. It can be found in the literature that $A = 3.06$, $b = 2/3$ [59], $A = 7.03$, $b = 1/2$ [60] and $A = 8.35$, $b = 2/3$ [57]. In this paper, we have decided to use values from [57], because we have chosen experimental results from this paper. To determine σ_{dip}, an average intermolecular distance (12 Å), a doping concentration (26.3%) and the permittivity (3.0) were also taken from [57]. The obtained dipole components are equal to 0.022 eV, 0.025 eV and 0.037 eV for 2.79 debye, 3.13 debye and 4.65 debye, respectively. We assume that the van der Vaals component $\sigma_{vdv} = 0.1$ eV. Then, the DOS widths calculated from equation (11) have values $\sigma = 0.102$ eV (for 2.79 debye), $\sigma = 0.103$ eV (for 3.13 debye) and $\sigma = 0.106$ eV (for 4.65 debye).

The energy of a Gaussian center E_0 = -0.625 eV (the LUMO position) has been estimated from theoretical studies of the electronic structure of bisphenol–A–polycarbonate [61]. The calculated value of the HOMO–LUMO gap is 5.365 eV [61]. It has been demonstrated that the work function (an energetic distance between the Fermi energy and the vacuum level) changes its value with a dipole moment [62]. If we consider a donor–doping material, one can expect that a quasi–Fermi energy should be above the level of a mid–gap. Here, E_F is treated as a fitting parameter. The determined values E_F = -1.85 eV (for 2.79 debye), E_F = -1.55 eV (for 3.13 debye) and E_F = -1.35 eV (for 4.65 debye) show that the work function decreases with an increasing of the donor dipole moment.

The thicknesses of samples were 6–8.5 μm [57]. When we consider the bulk of a material, we can assume that $x = 3.5$ μm. The temperature used in our calculations ($T = 293$ K) has the same value as in the experiment [57]. Other parameters are equal for all samples: $N_0 = 10^{26}$ m^{-3}, $l = 0.5$ nm and $m^* =$

$2.5m_e$. The velocity of a sound can be treated as a numerical parameter. The obtained values $u = 2800$ m/s (for 2.79 debye), $u = 2720$ m/s (for 3.13 debye) and $u = 2500$ m/s (for 4.65 debye) should be associated with longitudinal acoustic phonons. It is seen that this velocity decreases when the dipole moment of a donor increases.

Fig. 7 illustrates the comparison between our calculations and experimental data. The ratios D/μ obtained with the Druyvesteyn–type distribution function drawn for three values of a dipole moment are presented by full lines. The observed tendency looks similar to theoretical curves shown in Fig. 4. We can see a satisfactory agreement between simulations and experimental results which validates the usefulness of the model.

4. Summary

In summary, the Druyvesteyn–type distribution function has been used to calculate the generalized Einstein relation for disordered organic semiconductors with a Gaussian density of states. The Druyvesteyn function is used in a solid state when the acoustic phonons–charge carriers scattering plays a key role. It has been experimentally demonstrated that such a distribution function can describe a behavior of hot electrons in the electroluminescent inorganic rare–earth–doped zinc chalcogenides. Thus, we expect that in a part of organic materials used in OLEDs, it is also possible to find the Druyvesteyn distribution of charge carriers under external electric fields. The theoretical analysis has shown that the diffusivity–mobility ratio reaches values lower than 1 (in kT/q units) for lower concentrations of charge carriers. The temperature dependencies of the factor D/μ are similar to theoretical results obtained with the equilibrium Fermi–Dirac distribution function. Furthermore, a comparison between calculations and experimental data for the donor–doped polymer confirms a validity of the theoretical approach based on the Druyvesteyn–type distribution function.

Declaration of competing interest

The author declare that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.commatsci.2023.112131.

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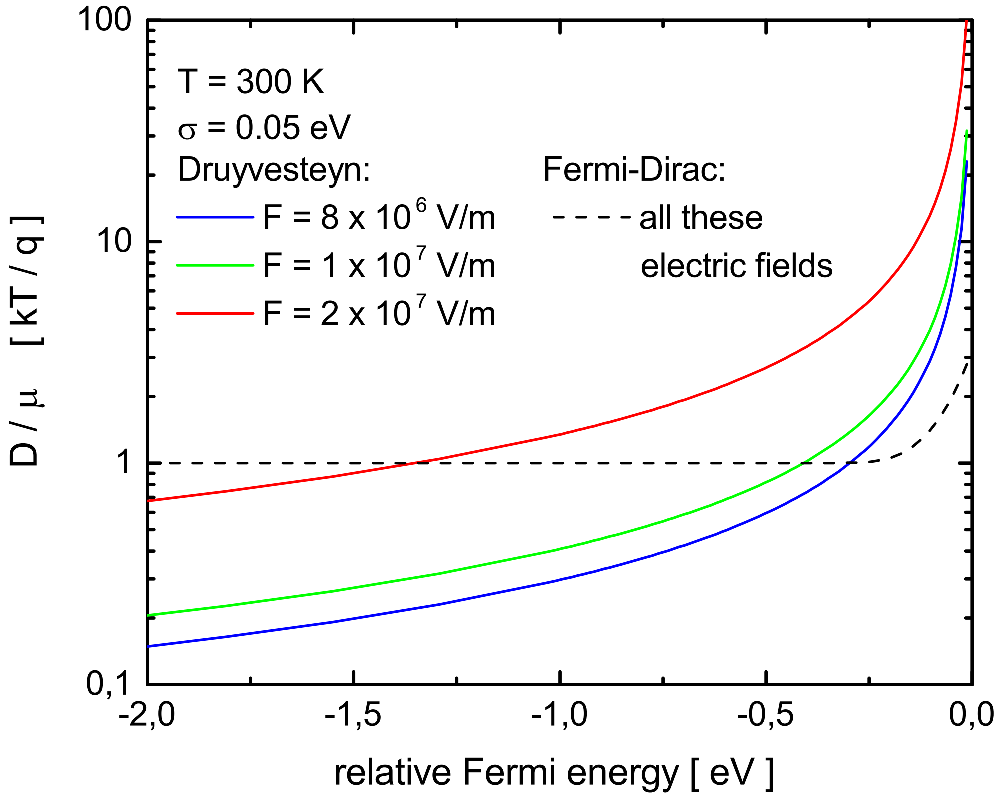

Figure 1: The ratio D/μ calculated with the Druyvesteyn–type distribution function versus a relative Fermi energy drawn for three electric fields F (solid lines). The dashed line shows D/μ obtained with the Fermi–Dirac function. Parameters used for calculations: T = 300 K, σ = 0.05 eV, N_0 = 10^{26} m^{-3}, E_0 = -2.8 eV, x = 10 nm, u = 2000 m/s, l = 0.8 nm and m^* = $1.5m_e$.

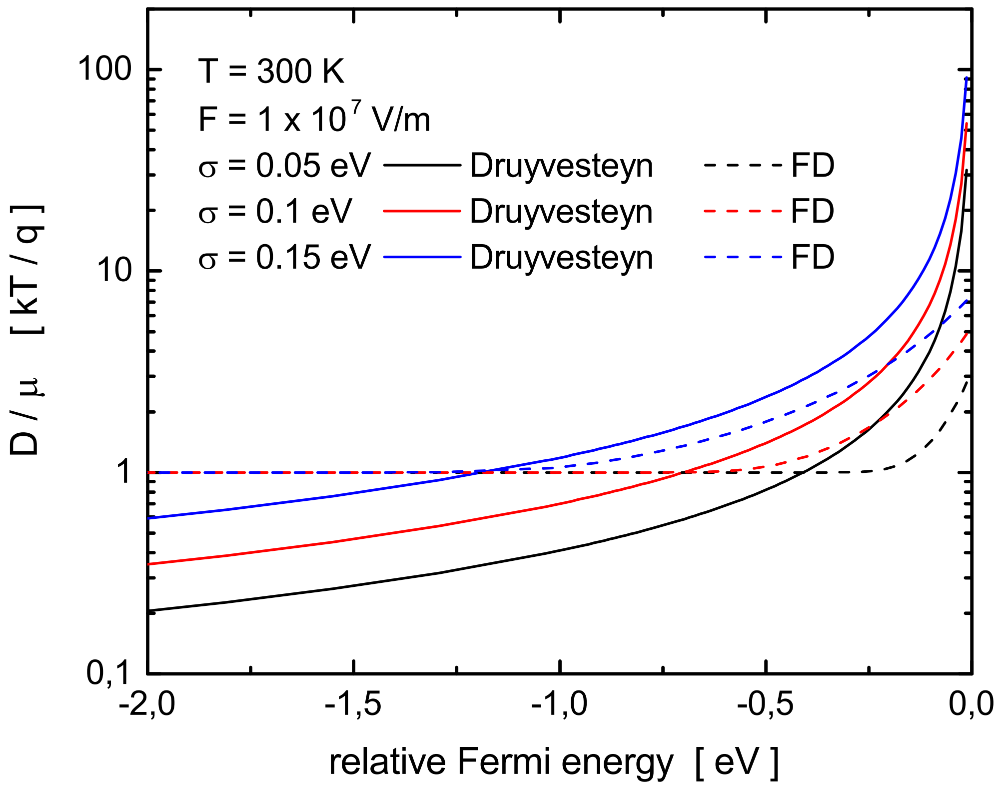

Figure 2: The ratio D/μ versus a relative Fermi energy drawn for three σ obtained with the Druyvesteyn–type function (solid lines) and with the Fermi–Dirac (FD) function (dashed lines). Parameters used for calculations: T = 300 K, $N_0 = 10^{26}$ m^{-3}, E_0 = -2.8 eV, F = 1 x 10^7 V/m, x = 10 nm, u = 2000 m/s, l = 0.8 nm and $m^* = 1.5m_e$.

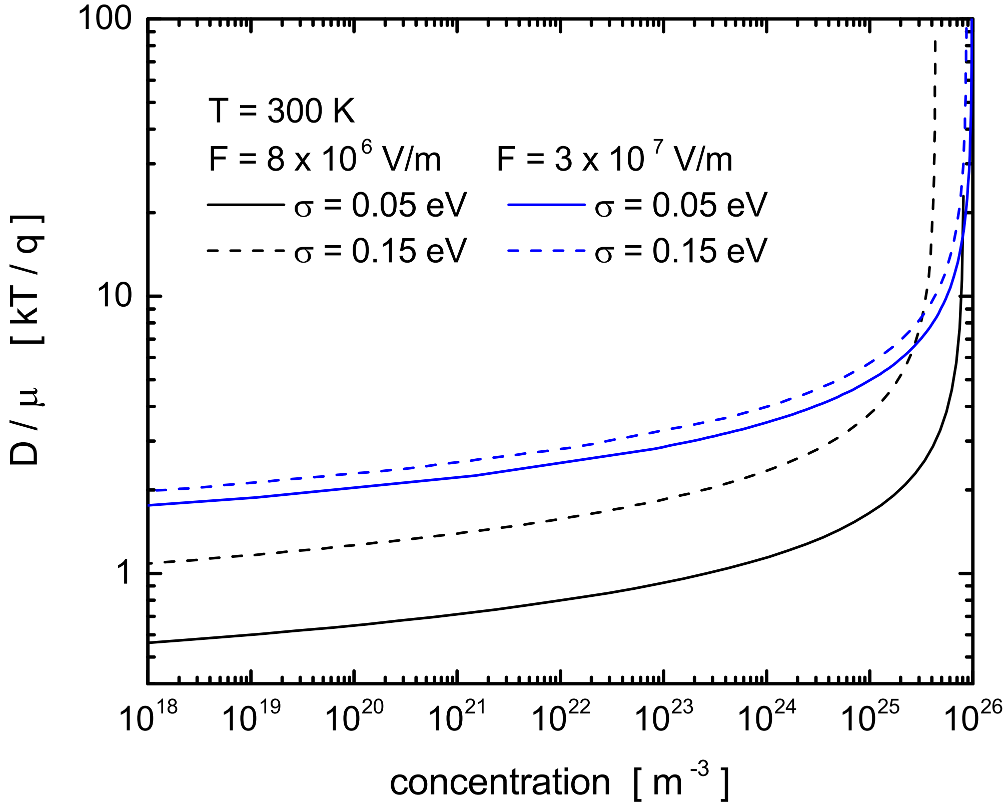

Figure 3: The ratio D/μ calculated with the Druyvesteyn–type distribution function versus a concentration of charge carriers drawn for two electric fields. Solid and dashed lines represent results for σ = 0.05 eV and σ = 0.15 eV, respectively. Parameters used for calculations: T = 300 K, N_0 = 10^{26} m^{-3}, E_0 = -2.8 eV, x = 10 nm, u = 2000 m/s, l = 0.8 nm and m^* = $1.5m_e$.

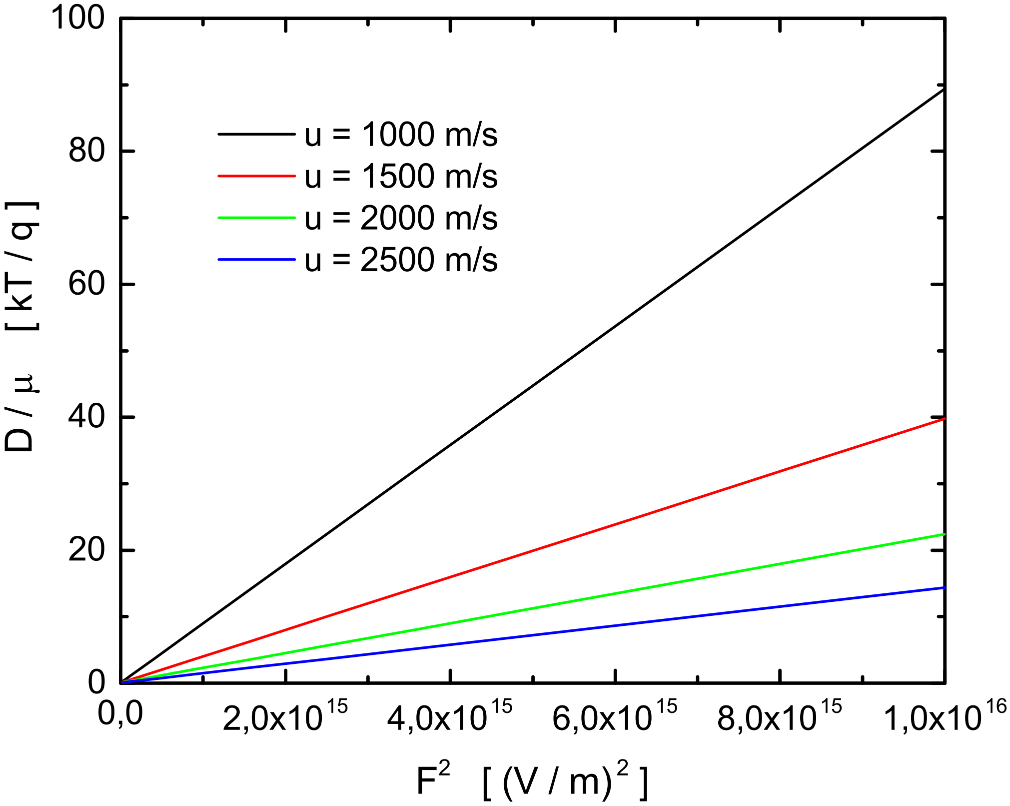

Figure 4: The ratio D/μ obtained with the Druyvesteyn–type distribution function versus a square of the electric field drawn for four sound velocities. Parameters used for calculations: T = 300 K, σ = 0.05 eV, $N_0 = 10^{26}$ m^{-3}, E_0 = -2.8 eV, E_F = -4.2 eV, x = 10 nm, l = 0.8 nm and $m^* = 1.5m_e$.

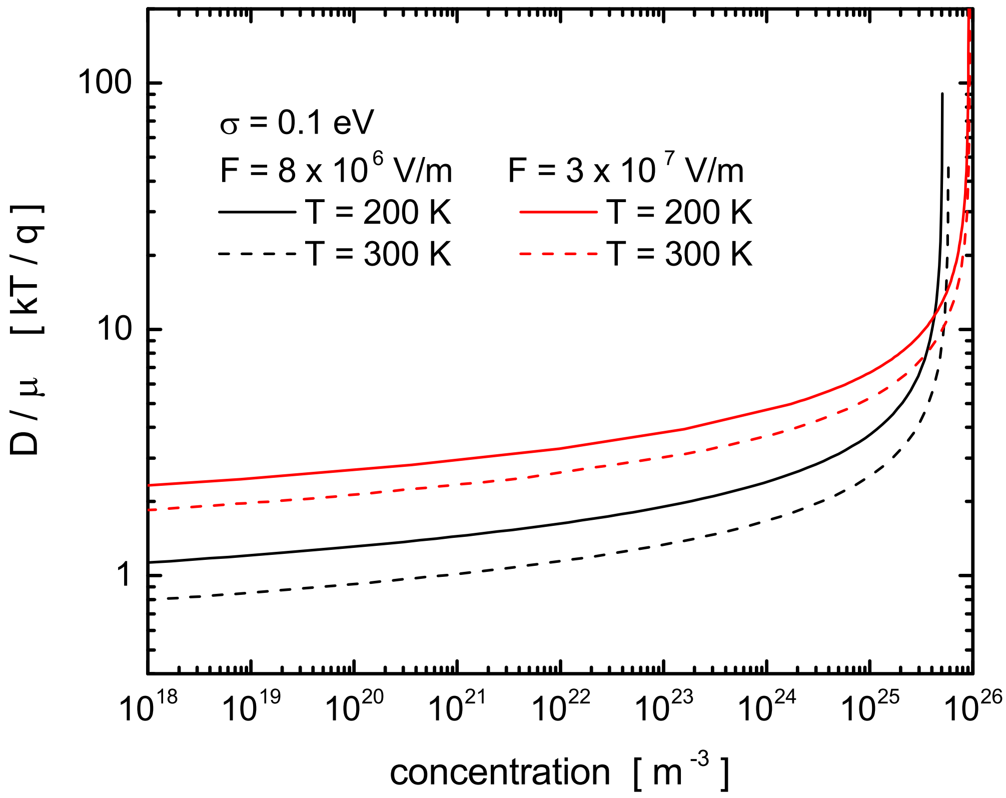

Figure 5: The ratio D/μ calculated with the Druyvesteyn–type distribution function versus a concentration of charge carriers drawn for two temperatures and two electric fields. Solid and dashed lines represent results for T = 200 K and T = 300 K, respectively. Parameters used for calculations: σ = 0.1 eV, $N_0 = 10^{26}$ m^{-3}, E_0 = -2.8 eV, x = 10 nm, u = 2000 m/s, l = 0.8 nm and $m^* = 1.5m_e$.

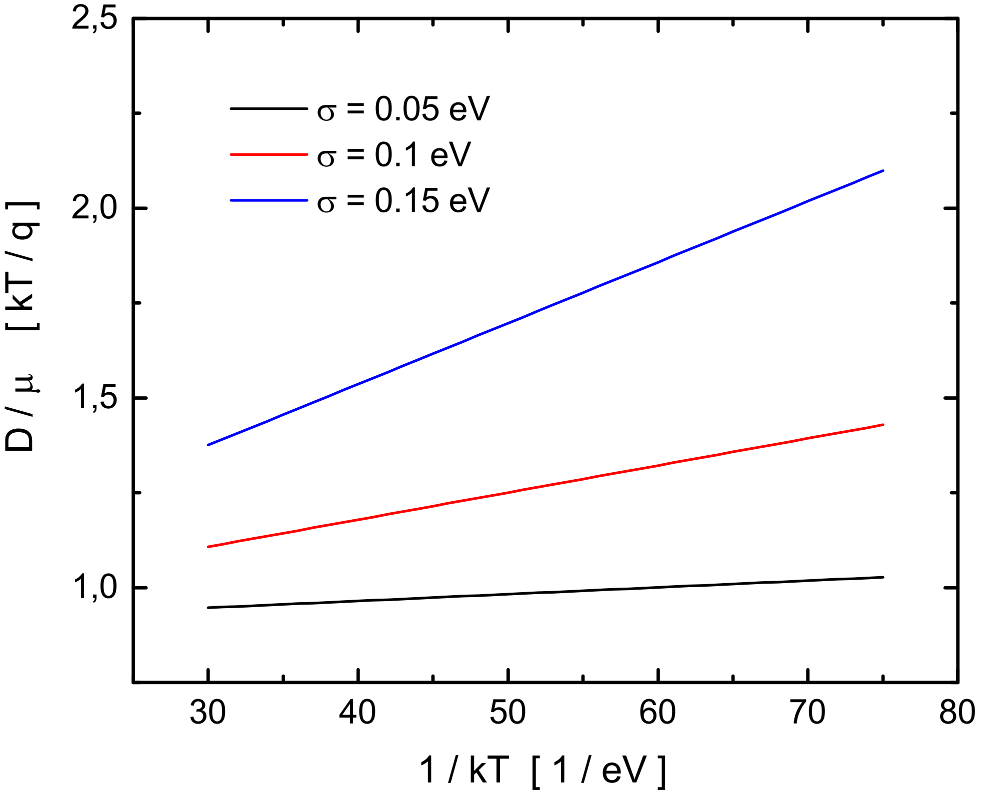

Figure 6: The ratio D/μ obtained with the Druyvesteyn–type distribution function versus the reciprocal of kT drawn for three values of a distribution width σ. Parameters used for calculations: $N_0 = 10^{26}$ m^{-3}, E_0 = -2.8 eV, E_F = -4.2 eV, F = 2 x 10^7 V/m, x = 10 nm, u = 2000 m/s, l = 0.8 nm and $m^* = 1.5m_e$.

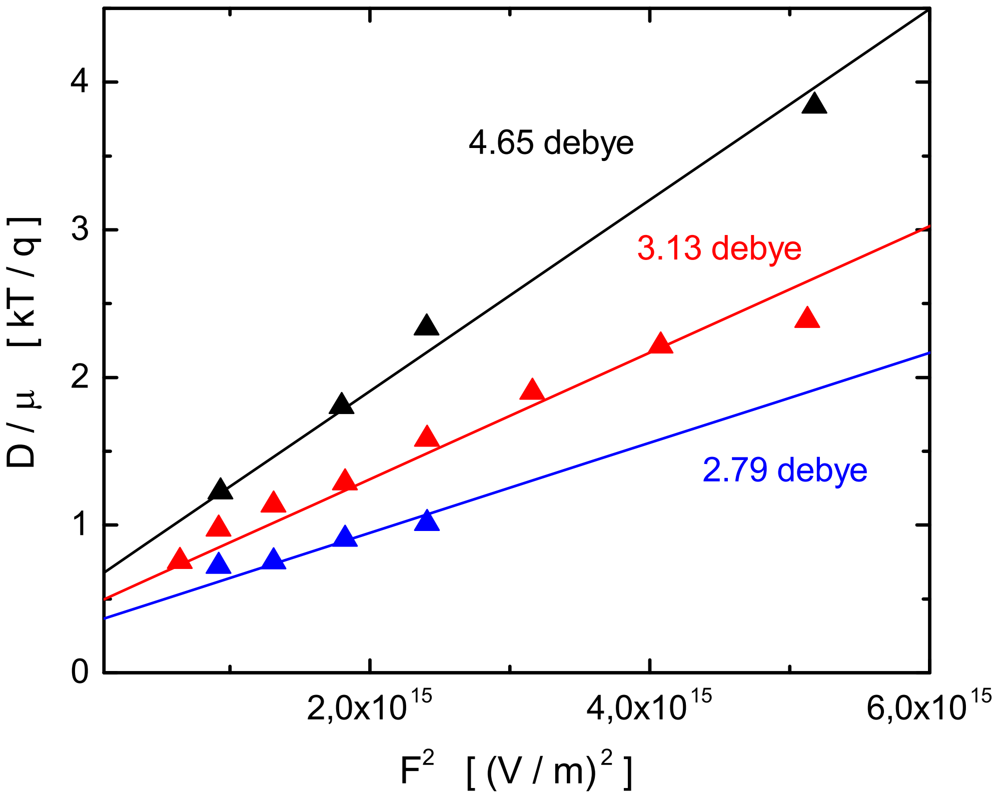

Figure 7: The ratio D/μ versus a square of the electric field drawn for three values of the donor dipole moment. The triangle symbols represent experimental data taken from [57]. The lines were calculated from equation (8). The physical quantities T = 293 K, $N_0 = 10^{26}$ m^{-3}, E_0 = -0.625 eV, x = 3.5 μm, l = 0.5 nm and $m^* = 2.5m_e$ are the same for all samples. Other values of parameters used for calculations are: E_F = -1.85 eV, u = 2800 m/s and σ = 0.102 eV (for 2.79 debye); E_F = -1.55 eV, u = 2720 m/s and σ = 0.103 eV (for 3.13 debye); E_F = -1.35 eV, u = 2500 m/s and σ = 0.106 eV (for 4.65 debye).