Excitons diffusion and singlet–triplet occupation at high Bose–Einstein chemical potential

Juan Bisquert *

Departament de Física, Universitat Jaume I, 12071 Castelló, Spain

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ABSTRACT

The paper investigates the bosonic aspects of exciton statistics in non-equilibrium situations. A kinetic model is formulated treating the excitons in different states as chemical species, using a master equation consistent with Bose–Einstein statistics. The model reveals that in two-state model for singlet–triplet generation–recombination, the chemical potential of the lower state becomes pinned at high concentration. Analysis of exciton diffusion shows that the chemical diffusion coefficient is independent of the concentration, while the single particle (tracer) diffusion coefficient increases strongly due to the attractive statistical force.

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1. Introduction

In semiconductors with low dielectric constant, photogenerated or injected electrons and holes form excitons bound by the Coulomb attraction, with energies $\ll 1$ eV, and with a Bohr radius a_{Bohr} of the order of nm. Exciton dynamics is governed by the kinetics of transformation between the different excitonic states, i.e. orthoexcitons (angular momentum triplet) and paraexcitons (angular momentum singlet), and by the recombination lifetimes of such states. Dynamical properties of the excitons are interesting in many applications of inorganic semiconductors, such as room temperature lasing in wide bandgap semiconductors like ZnO, either in bulk [1] or nanoscale systems [2], and the observation of Bose–Einstein condensates in Cu$_2$O [3–6], as well as for many experimental results on exciton–polariton dynamics [7,8]. In organic materials, exciton diffusion and annihilation is a limiting step in the functioning of organic solar cells [9] and photosynthesis [10], and the ratio of singlets to triplets is critical to the efficiency of organic light emitting devices (OLEDs) [11].

An important tool for the analysis of solar cells is monitoring the quasi-Fermi levels of photogenerated electrons and holes, since their separation amounts to the photovoltage [12]. Photogenerated excitons have a chemical potential too, μ, and the aim of this paper is to provide a picture of singlet–triplet occupation and exciton diffusion coefficient as a function of the chemical potential. Our results have especial relevance for the recent studies of exciton migration in self-organized molecular solids and nanocrystal superlattices [13,14].

If the density of excitons n is such that $n^{-1/3} > a_{Bohr}$, the screening of the electron–hole interaction can be neglected and the exci-

tons can be treated as pointlike particles that behave as bosons [15,16]. The occupancy of a state of energy E relates to μ as

$$f(E, \mu) = \frac{1}{e^{(E-\mu)/k_B T} - 1} \tag{1}$$

where k_B is Boltzmann's constant and T is the absolute temperature. At $\mu \ll E$, Eq. (1) is characterized by a classical Boltzmann tail $f = e^{-(E-\mu)/k_B T}$. In addition, when $\mu \approx E$ the Bose–Einstein condensation occurs in the ground state above a critical concentration n_c (lower than the Mott density) and below a critical temperature $T_c = 2\pi \zeta^{-2/3}(3/2)(\hbar^2/m)n_c^{2/3}$ [3–5].

Here, we discuss the circumstance in which the excitons densities depart from Boltzmann statistics as μ approaches E. Peculiar effects of the Bose–Einstein distribution occur, in comparison with the more familiar Fermi–Dirac statistical features of electrons in semiconductors, when we consider the occupation of different energy states (e.g. singlet–triplet), even without entering the quantum condensation value n_c.

2. Chemical kinetic models for excitons

As a motivating example, the thermalized occupation of an exponential distribution in the bandgap, that forms the basis of the analysis of amorphous semiconductors, is shown in Fig. 1. Well above the energy of the (electro-)chemical potential, both fermions and bosons occupy the available states in a Boltzmann tail. The striking differences occur at and below the energy of the chemical potential. Electrons fill completely the states at $E < E_F$, while excitons cannot exist in states of energy $< \mu$. Furthermore, the exciton occupation at $E = \mu$ is larger than 1, so that excitons agglomerate at the lowest energy state. In addition, in the thermalized situation the chemical potential of excitons cannot rise higher than the lowest energy state. Therefore *the lowest energy state imposes an upper bound* on μ.

* Fax: +34 964 728 066.
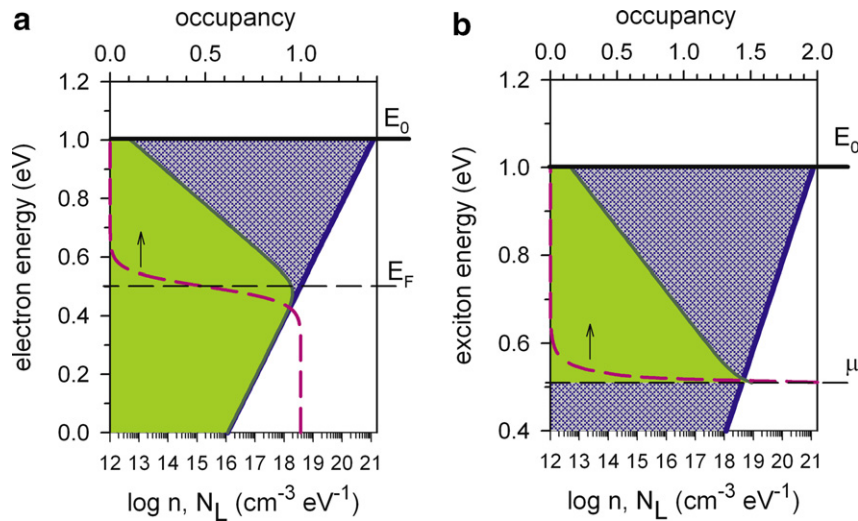 E-mail address: bisquert@fca.uji.es

Fig. 1. Energy diagrams showing the thermal occupation at temperature $T = 300$ K of an exponential DOS (tail parameter $T_0 = 800$ K, total density $N_t = 10^{20}$ cm^{-3}). E_F is the Fermi level of electrons, μ is chemical potential of excitons and E_0 is the conduction band energy. The clear (green) shaded region indicates the bandgap states that are occupied, and the dark (blue) shaded region indicates empty levels, as determined by (a) the Fermi–Dirac distribution and (b) the Bose–Einstein distribution functions (dashed line).

Fig. 1b, though illustrative, is not particularly realistic, since repulsion of the excitons in localized states makes them follow the Fermi–Dirac statistics usually used in amorphous semiconductors [17]. However, excitons in semiconductors such as Cu$_2$O exist in different quantum states according to the angular momentum, and the distribution of excitons and their chemical potentials in the separate states is extracted by fitting the phonon-assisted recombination lines to Bose–Einstein distributions [3–5]. It makes sense, therefore, to consider the occupations of excitons in a model of two states S and T separated by the energy $\varepsilon = E_T - E_s$.

Chemical equilibrium between a species in different states is determined by a general equation that formulates the loss–gain for the probabilities f of the separate states A and B, and is usually denoted a master equation [18]:

$$\frac{df_A}{dt} = -f_A \Gamma_{AB} h(f_B) + f_B \Gamma_{BA} h(f_A) \tag{2}$$

Eq. (2) describes the rate of loss from state A proportional to: the occupation f_A, the transition rate Γ_{AB}, and another (so far undetermined) function h of the occupancy f_B of the receptor state, plus a symmetrical term for the gain of A species. The form of the transition rates Γ_{AB} depends on microscopic details of the process, but in any case the transition rates must obey the detailed balance condition, that imposes the constraint that the distribution of probabilities governed by the master equation must reduce to the equilibrium distribution in an unbiased steady state. This condition requires that the rates of forward and backward transitions between a pair of states *balance in detail*, i.e. they should be equal in equilibrium

$$\frac{f_A}{h(f_A)} = \frac{\Gamma_{BA}}{\Gamma_{AB}} \frac{f_B}{h(f_B)} \tag{3}$$

The equilibrium statistics Eq. (1) at a common chemical potential [19] for states S and T requires $\mu_S = \mu_T$, where

$$\mu_i = E_i + k_B T \ln \frac{f_i}{1 + f_i} \quad (i = S, T) \tag{4}$$

The *simplest* way that Eq. (3) becomes consistent with (4) requires that

$$h(f) = 1 + f \tag{5}$$

Similarly, for *electrons* hopping between localized states, one uses the $h(f) = 1 - f$ term in Eq. (2) [20,21], that becomes relevant at high occupation, since this term forbids further hops to the localized state as $f \approx 1$. In strong contrast to this, we appreciate

in Eq. (5) that for bosons, a large occupation of the receptor state strongly increases the rate of transitions into that state. Therefore, the well-known fermionic repulsion at large occupation becomes an attraction 'force' in the case of bosons.

In addition, Eq. (3) requires that the ratio of rates for a transition and its time reverse, Γ_{BA}/Γ_{AB}, is given by the Boltzmann factor of the energy cost [22]. The individual transition rates usually take the form $\Gamma_{AB} = \nu_0 \phi(E_A, E_B)$, where ν_0 is a constant frequency that indicates the timescale of the transitions, and φ is a function of the energies that states the probability of transitions in each direction and satisfies

$$\phi(E_A, E_B) = e^{-(E_B - E_A)/k_B T} \phi(E_B, E_A) \tag{6}$$

in order to obey detailed balance.

There is a fundamental assumption that allows one to formulate the required equation for non-equilibrium transitions from the detailed balance prescription: it is commonly assumed that *the same rates* should be used for the dynamics of local transitions in non-equilibrium situations.

Many papers in the literature of excitons dynamics [3,23,24] use a master equation of the type

$$\begin{aligned}\frac{df_S}{dt} &= -k_{ST} f_S + \alpha k_{TS} f_T - \gamma_S f_S + G_S \\ \frac{df_T}{dt} &= \alpha^{-1} k_{ST} f_S - k_{TS} f_T - \gamma_T f_T + G_T\end{aligned} \tag{7}$$

where k_{ST} and k_{TS} are the kinetic constants for exciton exchange between S and T states, γ_S and γ_T are the reciprocal recombination lifetimes of the separate states, α is the number of T-sites per S-site (e.g., $\alpha = 3$ for singlet–triplet) and G_S (G_T) is the rate of photogeneration per S (T) site. Eq. (7) is correct at $f \ll 1$ but is not well suited to describe the bosonic aspects of excitons, since it clearly fails to satisfy the criterion of Eqs. (3) and (4).

The simplest master equation that satisfies such requirement is based on Eq. (5) and takes the form

$$\begin{aligned}\frac{df_S}{dt} &= -k_{ST} f_S (1 + f_T) + \alpha k_{TS} f_T (1 + f_S) - \gamma_S f_S + G_S \\ \frac{df_T}{dt} &= \alpha^{-1} k_{ST} f_S (1 + f_T) - k_{TS} f_T (1 + f_S) - \gamma_T f_T + G_T\end{aligned} \tag{8}$$

while detailed balance further requires that

$$\frac{k_{TS} \alpha}{k_{ST}} = \exp(\varepsilon/k_B T) \tag{9}$$

For simplicity we have not included Auger recombination terms in Eq. (8) pertinent to inorganic semiconductors [25], but we remark that Eq. (8) contains non-linear terms of statistical origin. It should be also recognized that in more complex approaches to the transition rates, than those used in our model, the non-linear terms in Eq. (8) will remain, since they are imposed by the fundamental requirement of detailed balance. Additionally, it may be required to include in the model the rate of exciton formation from precursor polaron pairs in luminescent polymers [11], or the kinetics (governed by the exciton-binding energy) that relates the excitons with the separated electrons and holes in crystalline semiconductors. For simplicity, here we assume that generation creates relatively fast the excitons with unity efficiency.

3. Non-equilibrium excitons statistics

In the following we explore the occupation of the two states at steady generation following this model.

If we denote the total generation rate as $G = G_S + \alpha G_T$, we have

$$G = \gamma_S f_S + \alpha \gamma_T f_T \tag{10}$$

To solve Eq. (8) in steady state, we define

$$
\begin{aligned}
k_1 &= k_{ST} + \gamma_S \\
k_2 &= \alpha k_{TS} - k_{ST} \\
B &= k_1 \gamma_T + \gamma_S k_{TS} - \gamma^{-1} k_2 G \\
C &= \gamma_T G_S + k_{TS} G
\end{aligned}
\tag{11}
$$

and we obtain

$$f_S = \frac{-B + (B^2 + 4\alpha^{-1} k_2 \gamma_S C)^{1/2}}{2\alpha^{-1} k_2 \gamma_S} \tag{12}$$

From Eqs. (10) and (12) we can plot the occupancies of the two excitonic states as a function of generation rates and the respective non-equilibrium quasi-chemical potentials, defined in Eq. (4). This is shown in Fig. 2, for generation in the high energy state, and in Fig. 3 for the opposite case. Representative cases are shown according to the relative values of the kinetic constants for exchange and recombination.

In all the cases we find a linear regime at low generation rate, $f_S \propto f_T \propto G$. The relative occupancies of the two states in this regime can be derived from Eq. (7)

$$\frac{f_T}{f_S} = \frac{(k_{ST} + \gamma_S) G_T + \alpha^{-1} k_{ST} G_S}{\alpha k_{TS} G_T + (k_{TS} + \gamma_T) G_S} \tag{13}$$

The results for generation in either upper or lower state when $f \ll 1$ are given in Table 1. For generation in the high energy state, the occupancies maintain the equilibrium ratio $f_T/f_S = e^{-\varepsilon/k_B T}$, unless $\gamma_S \gg k_{ST}$. This last case is shown in Fig. 2d, where it is observed that the upper state exceeds the population of the lower state, at low concentration. For generation in either state, if k_{ST} is much larger than recombination rates the chemical potentials remain equilibrated, Figs. 2b and 3b, but the chemical potentials split if recombination is faster than exchange, Fig. 2c and d, and Fig. 3c and d. It should be noted in Figs. 2 and 3 and Table 1 that when the chemical potentials separate, due to strong recombination, the chemical potential remains higher in the state where generation occurs. It is also observed in Fig. 3 and Table 1 that for generation in the lower energy state, we always have $f_T < f_S$, and the crossover of the occupations as that in Fig. 2d is therefore not possible.

In all cases in Fig. 2, the bosonic aspects come into play at high occupation: the concentration in the low energy state grows unlimited (eventually entering the quantum degeneracy), while the concentration in the upper state remains stable by the pinning of the chemical potential below E_T. In Fig. 3d, at increasing G_S, there is an abrupt rise of the concentration, characterized by supralinear
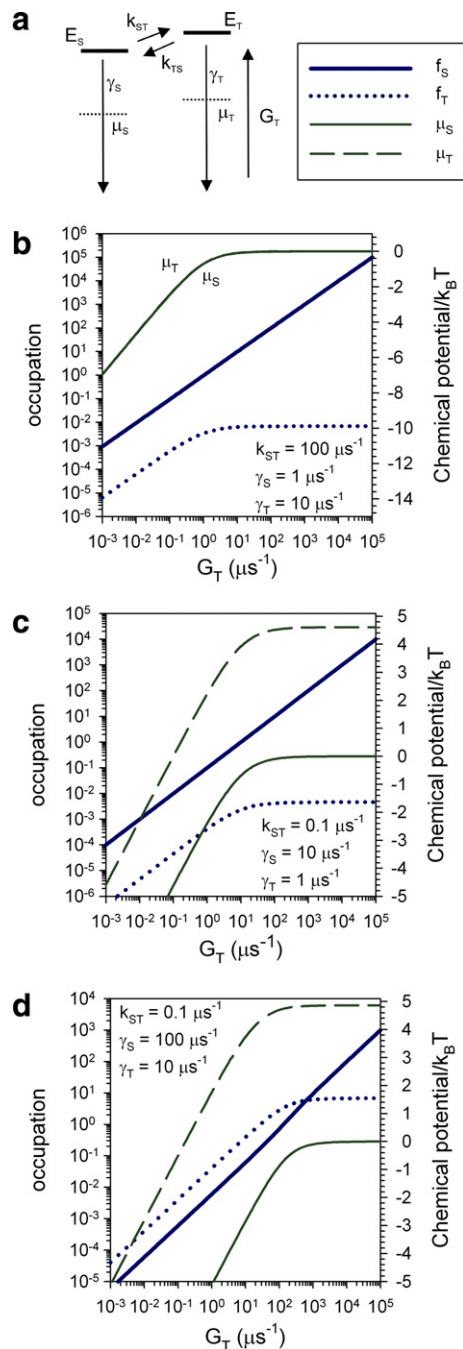

Fig. 2. Occupation (f) and chemical potential (μ) of two excitonic states S and T ($\alpha = 1$), as a function of generation rate per T-site, G_T. Parameters used in the calculation: $E_S = 0$, $E_T = 5k_B T$, $T = 70$ K.

dependence on G_S. We find that in all circumstances μ_S comes closer to E_S than μ_T does to E_T, even for T-generation and very strong recombination in S, Fig. 2c and d, where we observe that f_T achieves a stationary value. Therefore, one should expect that in two-state systems *only the lower energy state* crosses the $T_c(n_c)$ critical line towards quantum degeneracy, and this has been reported for ortho-excitons in Cu_2O, which lie lower than paraexcitons by 12 meV [6].

4. Chemical diffusion coefficient of excitons

We now consider how the diffusion of excitons may be affected by the deviation from Boltzmann statistics. Therefore, we wish to
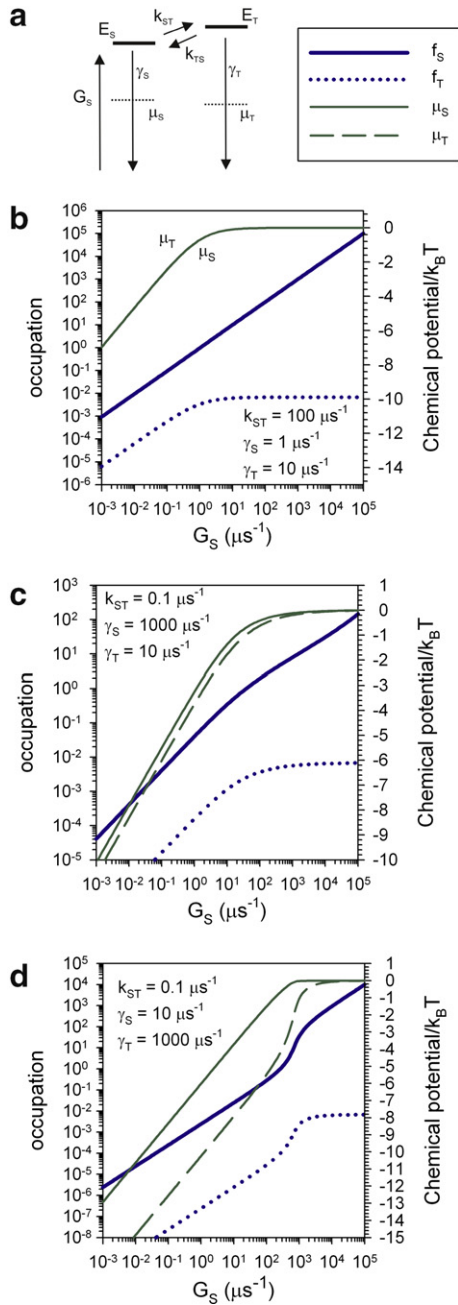
Fig. 3. Occupation (f) and chemical potential (μ) of two excitonic states S and T, as a function of S-generation rate per S-site, G_S. Parameters used in the calculation: $E_S = 0$, $E_T = 5k_BT$, $T = 70$ K.

Table 1
Relative occupancies with respect to equilibrium and separation of quasi-chemical potentials in two-state model, at low concentration

	$\dfrac{f_T}{f_S}e^{\varepsilon/k_BT}$	$\dfrac{\mu_T - \mu_S}{k_BT}$
$G_S = 0$	$1 + \dfrac{\gamma_S}{\alpha k_{ST}}$	$\ln(1 + \dfrac{\gamma_S}{\alpha k_{ST}})$
$G_T = 0$	$(1 + \dfrac{\gamma_T}{\alpha k_{TS}})^{-1}$	$-\ln(1 + \dfrac{\gamma_T}{\alpha k_{TS}})$

parameterize the main transport coefficients in terms of the chemical potential. First, we must determine the diffusion coefficient that relates the flux of excitons to the gradient of their concentration (Fick's law)

$$J_n = -D_n \frac{\partial n}{\partial x} \tag{14}$$

D_n is usually termed the *chemical diffusion coefficient* [26,27]. Another quantity of interest is the *jump (or tracer) diffusion coefficient*, D_J, that describes single particle random walk. Both are related by the expression [28]

$$D_n = \chi_n D_J \tag{15}$$

where χ_n is called the thermodynamic factor and is defined as follows

$$\chi_n = \frac{n}{k_BT} \frac{\partial \mu}{\partial n} \tag{16}$$

For the Boltzmann statistics $\chi_n = 1$, and there is no difference between jump and chemical diffusion coefficient, but when the statistics departs from ideality, χ_n can substantially differ from 1. We should remark that for electrically charged particles, the mobility is proportional to D_J according to the generalized Einstein relation [28,29]. Calculation of the thermodynamic factor gives

$$\chi_n = \frac{1}{1+f} \tag{17}$$

In order to find D_n, we start from a master equation of the type of Eq. (8) describing transitions between neighbor exciton sites 1 and 2 of the same energy, separated by a distance a, and we follow the method previously explained in Ref. [30] for electrons. The flux of excitons moving from site 1 to site 2 is $J_1 = v_0 f_1(1 + f_2)$, where v_0 is the rate constant for exciton hopping, and the flux in the opposite direction is $J_2 = v_0 f_2(1 + f_1)$. Therefore, the net flux is

$$J_n = J_1 - J_2 = -v_0(f_2 - f_1) = -v_0 a^2 \frac{(n_2 - n_1)}{a} \tag{18}$$

In the last equality of Eq. (18) we have expressed the occupations in terms of concentrations in the respective sites. By comparison with Eq. (14), it follows from Eq. (18) that the chemical diffusion coefficient of excitons is a constant $D_n = v_0 a^2$. This is because the non-Boltzmann terms in the separate fluxes of forward and backward jumps between two neighbor sites compensate. Ex-
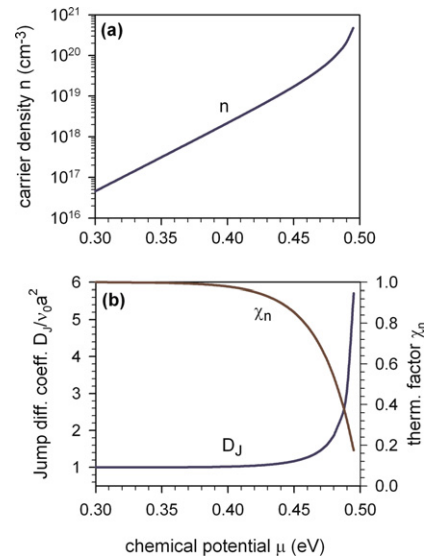

Fig. 4. Representation of several quantities for accumulation and diffusion of excitons of energy $E_0 = 0.5$ eV, as a function of chemical potential. (a) Exciton density. (b) Jump diffusion coefficient and thermodynamic factor. The following parameters were used in the calculation: $T = 300$ K, $N_0 = 1.0 \times 10^{20}$ cm^{-3}, $v_0 = 10^{12}$ s^{-1}, $a = N_0^{-1/3}$.

actly the same result is found for electrons in single occupancy sites [28,30]. For the jump diffusion coefficient of excitons, we obtain from Eq. (15)

$$D_J = (1 + f) v_0 a^2 \qquad (19)$$

The calculated quantities are shown in Fig. 4 as a function of μ. The remarkable result is that since the thermodynamic factor decreases when $f \approx 1$, the jump diffusion coefficient increases with respect to the value at dilution, see Fig. 4b. A recent survey of electron transport in disordered materials [28] shows that at high occupation the *exclusion* effect always causes a repulsive force that decreases the mobility (i.e. $\chi_n > 1$ in all cases). In contrast to this, the favoured increasing occupation of exciton sites at high chemical potential causes an attractive force that accelerates the single particle transport.

5. Conclusion

A simple chemical–physical model of excitons dynamics, based on the master equation consistent with Bose–Einstein statistics at high concentration, shows (a) the limitation to the rise of chemical potential of lower energy state in two-state models; (b) a boost of the single-particle diffusion coefficient.

Acknowledgments

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