Stochastic models of charge carrier dynamics in semiconducting nanosystems

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Abstract
We discuss recent experiments on photoexcited charge carrier relaxation
dynamics in semiconducting nanotubes and nanoparticles within the framework
of the stochastic model. We conclude that the elementary excitations in these
nanosystems are excitons. Since the average number of excitons per nanosystem
is typically small and comparable to a fluctuation, the quantized character of the
number of excitons in nanosystems turns out to be essential, with no sufficient
evidence to reduce the stochastic model to a bulk description.

1. Introduction

Reactions in nanosystems exhibit interesting dynamics quite different from those in the bulk.
Besides the cage effect, occupancy statistics becomes important. Since the average number of
reactants per nanosystem is typically small and comparable to a fluctuation, a bulk description
of the kinetics in terms of average densities is generally inappropriate and one has to deal
with the evolution of a discrete distribution of reactants. A general stochastic formulation
for microheterogeneous kinetics was developed in the 1960s [1]. Since then, it has proven
itself successful at describing the reaction kinetics in a variety of systems, such as micellar
assemblies [2], semiconducting nanotubes [3–5] and nanoparticles [6, 7], and conjugated
polymers [8, 9]. In this paper, we focus on the stochastic modelling of charge carrier dynamics
in isolated single-walled carbon nanotubes as well as in semiconductor nanoparticles. We
discuss different models of the elementary excitations and show how the stochastic approach
can provide additional evidence to distinguish between them.

Since the recent discovery of band-gap fluorescence from individual semiconducting
single-walled nanotubes (SWNTs) [10], there has been considerable interest in understand-
ing the optical spectra, ultrafast excitation dynamics, and related photophysical mecha-
nisms [3, 5, 11–19] due to their fundamental importance and relevance to many of the potential
applications. Two theoretical approaches have been used, in accord with the two possibilities
for the nature of the elementary excitations. In the first approach, the electrons and holes are

treated as independent, uncorrelated quasiparticles [11, 14]. The alternative approach assumes that the Coulombically bound electron and hole form a stable neutral exciton [3, 5, 13, 15–19]. Increasing theoretical [20–22] and experimental evidence [3, 5, 15–19] has been gathered recently in favour of the excitonic formulation. In particular, the exciton binding energy in SWNTs has been measured [16, 19] to be $\sim$0.4 eV, which is also in agreement with theoretical estimations [20, 22]. The obtained exciton binding energy constitutes a substantial fraction of the gap energy ($\sim$1.3 eV) and exceeds the thermal energy at room temperature. This large binding energy is largely due to spatial confinement. In contrast, bulk exciton binding energies typically lie in the range of several millielectronvolts, and thus excitonic effects in bulk materials can usually be neglected.

Time-resolved fluorescence and pump–probe absorption studies have shown [3, 5, 11–19] that after photoexcitation of the second van Hove singularity, the primary excitonic relaxation to the fundamental band edge occurs within 0.1 ps. The fluorescence decay from this band takes place on a timescale of $\sim$10 ps, mainly due to a non-radiative relaxation, identified as trapping at defects. The radiative lifetime is much longer, $\sim$100 ns [15]. A rapid decay component on a timescale of $\sim$1 ps emerges at high excitation intensities as a result of exciton–exciton annihilation via the Auger mechanism [3]. Analysis of the decay kinetics in SWNTs on the basis of the conventional bimolecular reaction theory led Ma *et al* to rule out one-dimensional diffusion of excitons as a limiting step of their annihilation [17]. Instead, they have demonstrated [5, 17–19] that both the fluorescence and the optical bleaching signal decays measured at different excitation intensities can be satisfactorily described by a simple rate equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{n}(t) = -\gamma\bar{n}(t) - \frac{1}{2}\gamma_{\mathrm{A}}\bar{n}^2(t),\tag{1}$$

formally corresponding to bulk exciton annihilation in the absence of any geometric restriction. Here $\bar{n}(t)$ is the average number density of excitons, and γ and γ_{A} are the rate constants for linear relaxation (trapping) and annihilation, respectively. Note that the large Bohr radius of excitons in comparison to the nanotube diameter makes SWNTs strictly one-dimensional structures in terms of exciton migration. If the reaction were limited by exciton diffusion in one dimension, the rate constant for nonlinear relaxation would be time dependent (proportional to $t^{-1/2}$), which is not observed experimentally [5, 17]. A possible explanation is the coherent character of the exciton states in SWNTs [5].

Wang *et al* noticed [3] that even at the highest experimental pump fluences only a few electron–hole (e–h) pairs per nanotube are actually excited and, therefore, a bulk description of a nanotube ensemble in terms of an average carrier density may be inappropriate. Instead, the quantized character of the number of excitations in a given nanotube must be taken into account. This approach leads to a master equation for the time-dependent probability distribution function which can be solved analytically [4]. The stochastic model (discussed in detail below) found good quantitative agreement with the experimentally observed fluorescence decay kinetics [3]. Now, how does this finding correlate with equation (1)? Valkunas *et al* [5] have recently discussed the physical background of the stochastic model, and they came to the conclusion that the exciton states in semiconducting nanotubes are coherent, similar to the situation in molecular chromophore complexes [23]. The multiexciton manifolds are resonantly coupled with other excited states, which decay by subsequent linear relaxation due to electron–phonon coupling. It was shown [5] that equation (1) can be derived from the stochastic model under the assumption of Poissonian distribution of excitons at all times. One of our goals is to test the validity of this assumption.

Exciton–exciton annihilation is also important in the excitation kinetics of other nanoscale semiconducting systems, such as quantum rods and wires [24]. However, further reduction

of dimensionality in quantum dots is argued to lead to a change in the physical nature of the elementary excitations [6, 7]. The arguments are as follows. In sub-10 nm quantum dots, the confinement energies are significantly greater than the excitonic interactions and, therefore, electrons and holes can be treated as uncorrelated particles. In this case, Auger recombination may be described in terms of a three-particle process [25], as was done for CdSe nanocrystals [6]. The analysis was based on a comparison of the discrete relaxation times characteristic of the multiple e–h pair states, extracted from the transient absorption data. As we will see below, this identification is not at all straightforward. By comparing a stochastic model corresponding to uncorrelated carriers versus the exciton model we come to the conclusion that experimental data actually support the excitonic mechanism.

2. Stochastic model of exciton relaxation in nanotubes

The excited e–h population in an isolated nanotube decays along two main channels [3]: linearly, by trapping at defects with the rate constant γ, and nonlinearly, by Auger recombination with the rate constant γ_A. Here both γ and γ_A are first-order rate constants. Their typical experimental values are 10^{11} and 10^{12} s^{-1}, respectively [3]. The contribution of the radiative decay is negligible. The nonlinear channel results from the interaction of multiple excitons, producing annihilation via resonant population of the coupled manifold of electronic excitations in the system [5]. Since the relaxation from all higher excited states to the energetically lowest excitonic state is very fast (<0.1 ps) [17–19], the kinetics can be formulated schematically in terms of the probabilities $\rho_n(t)$ that the system contains n excitons. Assuming instantaneous generation, one can write the following master equation for $\rho_n(t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_n(t) = -(\gamma + \tfrac{1}{2}(n-1)\gamma_A)n\rho_n(t) + (\gamma + \tfrac{1}{2}n\gamma_A)(n+1)\rho_{n+1}(t). \qquad (2)$$

The master equation (2) contains no spatial dependence of the probability density. As in standard stochastic models of reaction kinetics in finite systems [1, 2], the effect of spatial motion, if any, is factored into the corresponding first-order rate constant γ_A.

Experimental observables are proportional to the average number of excitons per nanotube,

$$\bar{n}(t) = \sum_{n=1}^{\infty} n\rho_n(t). \qquad (3)$$

By substituting equation (3) into (2) we obtain [5]

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{n}(t) = -\gamma\bar{n}(t) - \frac{1}{2}\gamma_A\overline{n(n-1)}. \qquad (4)$$

Equation (4) reduces to equation (1) only if $\overline{n(n-1)} = \bar{n}^2$, which holds for the Poisson distribution. When multiple excitons are generated by high-intensity pump pulses via the traditional process of absorption of multiple photons, initial exciton populations in SWNTs (right after the pulse) indeed exhibit a Poisson distribution [7],

$$\rho_n(0) = \frac{\bar{n}_0^n}{n!}\exp(-\bar{n}_0), \qquad (5)$$

where the initial average occupancy number is given by the product of the nanotube absorption cross section at the pump wavelength and the number of photons per unit area in the pulse, $\bar{n}_0 \equiv \bar{n}(0) = \sigma\phi$. However, Poissonian statistics is violated in time. This is particularly true at long times, when the nonlinear relaxation stage is over. All nanotubes with initially at least one exciton will contain exactly one exciton, while the fraction of initially empty nanotubes will

remain basically unchanged (assuming timescale separation of linear and nonlinear relaxation which holds for SWNTs). This is not a Poisson distribution. As a result, the exciton decay predicted by the stochastic model of equation (2) becomes functionally different from that predicted by the 'bulk' equation (1). Indeed, we obtain from equation (2), at long times,

$$\bar{n}(t) \simeq \bar{n}_\infty \exp(-\gamma t), \tag{6}$$

where $\bar{n}_\infty \simeq 1 - \exp(-\bar{n}_0)$ is approximately the fraction of nanotubes initially containing at least one exciton. On the other hand, equation (1) leads to

$$\bar{n}(t) \simeq \bar{n}_0 \exp(-\gamma t) \left[1 + \tfrac{1}{2}\gamma_A \bar{n}_0 t\right]^{-1}, \tag{7}$$

i.e., an inverse linear decay modulated by a slow exponential[1]. We may conclude from this simple analysis that the 'bulk' formulation makes sense only at short times.

Rigorous analysis requires solution of the master equation. This can be done by introducing the moment generating function [1]

$$F(s, t) = \sum_{n=0}^{\infty} s^n \rho_n(t), \tag{8}$$

and thus reducing the system of equations (2) to a partial differential equation

$$\frac{\partial}{\partial t} F(s, t) = \tfrac{1}{2}\gamma_A s(1 - s) \frac{\partial^2}{\partial s^2} F(s, t) + \gamma(1 - s) \frac{\partial}{\partial s} F(s, t), \tag{9}$$

with a general solution

$$F(s, t) = \sum_{i=0}^{\infty} \frac{A_i}{r + i - 1} P_i^{(-1, r-1)}(2s - 1) \, e^{-\lambda_i t}, \tag{10}$$

where

$$\lambda_i = i\gamma + \tfrac{1}{2}i(i - 1)\gamma_A, \tag{11}$$

$r = 2\gamma/\gamma_A$, and $P_i^{(\alpha, \beta)}(x)$ are the Jacobi polynomials orthogonal on $x \in [-1, 1]$. The coefficients A_i are determined from the initial condition. We obtain [4] for the Poisson distribution (5),

$$A_i = \bar{n}_0^i \, e^{-\bar{n}_0} \, (r + 2i - 1) \sum_{j=0}^{\infty} \frac{\bar{n}_0^j}{j!} \frac{\Gamma(r + i + j)}{\Gamma(r + 2i + j)}. \tag{12}$$

Knowing the generating function, one can recover the whole time-dependent exciton distribution $\rho_n(t)$ in a standard way [1]. Experimental observables are related to the average,

$$\bar{n}(t) = \left.\frac{\partial}{\partial s} F(s, t)\right|_{s=1} = \sum_{i=1}^{\infty} A_i \, e^{-\lambda_i t}. \tag{13}$$

In order to test the validity of the arguments leading to equation (1) we also need

$$\overline{n(n - 1)} = \left.\frac{\partial^2}{\partial s^2} F(s, t)\right|_{s=1} = \sum_{i=1}^{\infty} A_i \, (i - 1)(r + i) \, e^{-\lambda_i t}. \tag{14}$$

We can see that the slowest relaxation rate for $\bar{n}(t)$ is $\lambda_1 = \gamma$, while for $\overline{n(n - 1)}$ it is $\lambda_2 \simeq \gamma_A \gg \gamma$, and hence one cannot expect the condition $\overline{n(n - 1)} = \bar{n}^2$ to hold at all times, even approximately. Figure 1 shows the plot of $\overline{n(n - 1)}/\bar{n}^2$ as a function of time. This

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[1] Equation (7) assumes timescale separation, i.e., $\gamma \ll \gamma_A$, typically observed in experiment (e.g., $\gamma/\gamma_A \simeq 0.1$ was obtained by Wang *et al* [3]). The exact solution to equation (1) is given by $\bar{n}(t) = \bar{n}_0 \exp(-\gamma t)\{1 + \tfrac{1}{2}\frac{\gamma_A}{\gamma}\bar{n}_0[1 - \exp(-\gamma t)]\}^{-1}$.
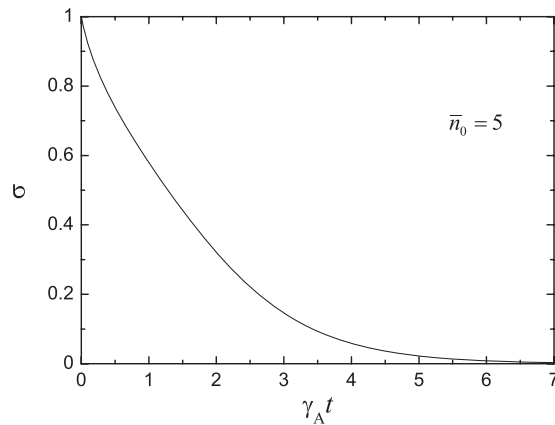
Figure 1. Time dependence of $\sigma = \overline{n(n-1)}/\bar{n}^2$ for the Poissonian initial condition with $\bar{n}_0 = 5$ and $\gamma/\gamma_A = 0.05$, based on the stochastic model of equations (11)–(14).
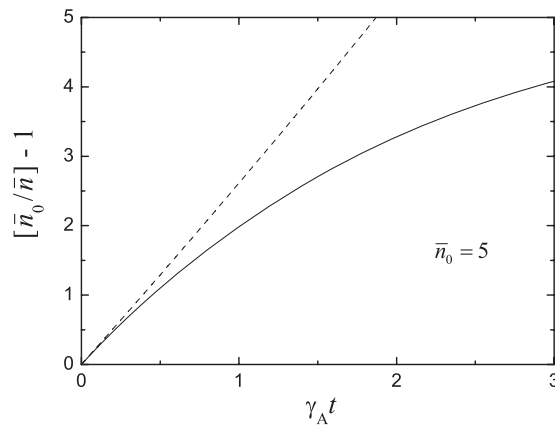

Figure 2. Plot of the inverse average exciton population as a function of time for the Poissonian initial condition with $\bar{n}_0 = 5$ and $\gamma/\gamma_A = 0.05$, based on the stochastic model (equations (11)–(13), solid) and the bulk model (equation (7), dashed).

ratio has to be unity for equation (1) to be a valid approximation of the discrete stochastic formulation. Further, in figure 2, we compare the kinetics predicted by the stochastic model, equation (13), versus the 'bulk' kinetics based on the average number density, equation (7). The linear time dependence of the inverse average number of excitons is supported by the stochastic model only at very short times, $\gamma_A t \ll 1$, for a typical initial value of $\bar{n}_0 = 5$. Thus for SWNTs, where even at the highest experimental excitation intensities only a few excitons per nanotube are formed, the bulk treatment of the relaxation kinetics is acceptable with a great reserve only at short times. Note that if we carefully inspect the experimental data of Ma *et al* [5, 17–19], we will observe a considerable downward curvature in the time dependence of the inverse average exciton population at long times, consistent with expectations of the discrete stochastic model. Characteristic features of the stochastic model solution have been discussed in detail elsewhere [4]. They include multimode relaxation and saturation of the long-time decay amplitude at elevated excitation densities, all observed in experiment [3].

3. Excitonic versus free carrier relaxation in nanoparticles

Intuitively, as long as one-dimensional diffusion in SWNTs plays no significant role, no principal variation in the carrier relaxation dynamics is to be expected upon change from nanotubes to quantum dots (QDs). However, the analysis by Klimov *et al* of their experimental data on charge carrier relaxation dynamics in QDs seems to be confused. As shown below, they mixed a bulk approach with a stochastic approach. The decay kinetics of e–h pairs was first analysed within a bulk semiconductor approach by introducing an effective carrier concentration in the dot ($c_{eh} = n/V_0$, where n is the number of e–h pairs per QD and V_0 is the QD volume) [6]. The decay rate was assumed to be proportional to the cubic concentration [25],

$$\frac{\mathrm{d}}{\mathrm{d}t}c_{eh}(t) = -k_A c_{eh}^3(t), \tag{15}$$

where k_A is the Auger constant. The number of e–h pairs per QD is actually distributed. In the above equation c_{eh} actually stands for the average carrier concentration. If the system is very large, like a bulk semiconductor, the number of e–h pairs is very large and fluctuations in the number of e–h pairs are much smaller compared with the average number. In this situation, one can use the bulk approach, equation (15), which describes the decay kinetics of e–h pairs in terms of the average carrier concentration. In QDs, however, the number of e–h pairs per dot is very small and fluctuations in the number of e–h pairs are comparable with the average number. In this situation, the decay kinetics cannot be described by the bulk approach. Instead, one has to use a stochastic approach which properly takes into account the distribution of e–h pairs in a QD. In addition, as shown below, the physical model underlying equation (15) is not consistent with the experimental results, even if an appropriate stochastic approach is used instead of the bulk approach.

If we denote the rate constant for the transition from n e–h pairs to $n-1$ pairs by $1/\tau_n$, in a generalized stochastic model the decay kinetics of e–h pairs is described by

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_n(t) = -\frac{\rho_n(t)}{\tau_n} + \frac{\rho_{n+1}(t)}{\tau_{n+1}}, \tag{16}$$

where $\rho_n(t)$ is a fraction of QDs which contain n e–h pairs at time t. Klimov *et al* [6] analysed the decay kinetics of e–h pairs in 2.3 nm cadmium selenide (CdSe) colloidal QDs and obtained the following values for τ_n:

$$\tau_1 = 510 \text{ ps}, \qquad \tau_2 = 45 \text{ ps}, \qquad \tau_3 = 21 \text{ ps}, \qquad \tau_4 = 10 \text{ ps}. \tag{17}$$

In the case of $n = 1$ there is only one e–h pair in the dot, and Auger recombination does not occur. So τ_1 should correspond not to Auger recombination but to linear relaxation. The linear relaxation should be operative not only in the single e–h pair case but also in multiple e–h pair cases. Therefore, the rate constant $1/\tau_n$ should be given by the sum of the rate constants k_n^A for the Auger recombination and k_n' for the linear relaxation,

$$\frac{1}{\tau_n} = k_n^A + k_n' \qquad (n > 1). \tag{18}$$

The latter is given by

$$k_n' = n k_1' = n/\tau_1, \tag{19}$$

where $k_1' = 1/\tau_1$ is the first-order rate constant for non-radiative linear relaxation in a quantum dot which contains one e–h pair. We have from equations (17)–(19),

$$k_2^A : k_3^A : k_4^A = 1:2.3:5.1. \tag{20}$$

Two models are conceivable for the dependence of k_n^A on n. In the first model we assume that in QDs an electron and a hole are paired as an exciton and the Auger recombination occurs between two excitons, as in SWNTs. In this case, k_n^A is proportional to the number of ways of choosing two excitons from n excitons,

$$k_n^A = \frac{1}{2}n(n-1)k_{ex}^A, \tag{21}$$

where k_{ex}^A is the first-order rate constant for Auger recombination in a QD which contains two excitons. The subscript 'ex' refers to the excitonic mechanism. The k_n^A calculated from equation (21) have the following ratios:

$$k_2^A : k_3^A : k_4^A = 1 : 3 : 6. \tag{22}$$

In the second model we assume that in QDs an electron and a hole are not paired and Auger recombination occurs between two electrons and one hole (or one electron and two holes) which are mutually independent. In this case, k_n^A is proportional to the number of ways of choosing two electrons from n electrons and one hole from n holes,

$$k_n^A = \frac{1}{2}n^2(n-1)k_{eh}^A, \tag{23}$$

where k_{eh}^A is the first-order rate constant for Auger recombination in a QD which contains two pairs of mutually independent electrons and holes. The subscript 'eh' refers to uncorrelated e–h pairs. The k_n^A calculated from equation (23) have the following ratios:

$$k_2^A : k_3^A : k_4^A = 1 : 4.5 : 12. \tag{24}$$

Comparison of equation (20) with equations (22) and (24) shows that the exciton model explains the experimental results much better than the free carrier model. Equations (20) and (22) coincide within the reported experimental accuracy of 20%.

It is interesting to compare the analysis of Klimov *et al* with the present one. In their analysis, the ratios of $1/\tau_n$ are compared with those of n^2 which they claim is derived from equation (15). On the other hand, in the present analysis the ratios of the experimentally derived k_n^A, equation (20), are compared with those of $n(n-1)$ or $n^2(n-1)$ which come from equations (21) or (23). First, in their analysis the effect of linear relaxation was not taken into account. Second, the experimentally derived k_n^A is the rate constant in the stochastic approach and it cannot be compared with equation (15) which is based on the bulk approach. c_{eh} in equation (15) refers not to an individual but to an average number of e–h pairs, and equation (15) is valid only for very large average numbers. On the other hand, the average number of e–h pairs in a QD is actually very small (only a few).

Now we discuss the dependence of k_{ex}^A on the dot volume V_0. Klimov *et al* found that k_{ex}^A is inversely proportional to V_0. On the other hand, simple calculations based on classical mechanics show [26] that the first-order recombination rate constant for two particles confined in the volume V_0 is inversely proportional to V_0. The experimental results seem to be explained by these simple calculations, although this may be fortuitous. Quantum mechanical calculations of the Auger recombination rate constant for two excitons in a QD as a function of the dot volume are highly needed.

When the rate constants k_n^A for the Auger recombination and k_n' for the linear relaxation are given by equations (21) and (19), respectively, equation (16) can be solved analytically by using the generating function technique, as discussed in the preceding section. The experimentally important average number of excitons per QD is given by the following equation:

$$\bar{n}(t) = \sum_{i=1}^{\infty} A_i \exp\left[-i\left(\frac{1}{\tau_1} + \frac{1}{2}(i-1)k_{ex}^A\right)t\right], \tag{25}$$

where the initial distribution of excitons in the QD is assumed to be Poissonian with the average $\bar{n}_0$ and thus the coefficients A_i are given by equation (12). Equation (25) can be used to analyse the carrier relaxation dynamics in QDs instead of the method used by Klimov *et al*.

Finally, we discuss the relation between the bulk approach and the stochastic approach for free charge carriers. The physical model which is described by equation (15) in the bulk approach corresponds to the following master equation in the stochastic approach:

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_n(t) = -\frac{1}{2}n^2(n-1)k_{\mathrm{eh}}^{\mathrm{A}}\rho_n(t) + \frac{1}{2}(n+1)^2 n k_{\mathrm{eh}}^{\mathrm{A}}\rho_{n+1}(t). \tag{26}$$

This model is equivalent to equation (16) with k_n^{A} given by equation (23) and $k_n' = 0$ irrespective of n. When the average number of e–h pairs is very large, we can derive equation (15) by substituting equation (3) into (26),

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{n}(t) = -\frac{1}{2}k_{\mathrm{eh}}^{\mathrm{A}}\langle n^2(n-1)\rangle \approx -\frac{1}{2}k_{\mathrm{eh}}^{\mathrm{A}}\bar{n}^3, \tag{27}$$

and identifying c_{eh} with $\bar{n}$ and

$$k_{\mathrm{A}} = \tfrac{1}{2}k_{\mathrm{eh}}^{\mathrm{A}}. \tag{28}$$

Note that the approximate equality in equation (27) is valid only in the limit of $\bar{n} \gg 1$; that is, for bulk systems.

We have already pointed out that equation (26), which corresponds to the free carrier model, does not explain the experimental results for QDs satisfactorily. Therefore, equation (15) is not appropriate for the description of the Auger recombination in QDs in two ways. First, equation (15) is based on the bulk approach while the stochastic approach should be used for QDs, since the average number of e–h pairs per QD is very small. Second, equation (15) assumes the free carrier model while the exciton model explains the experimental results better. In other words, the stochastic exciton model and its exact solution should apply equally well to carrier relaxation dynamics in SWNTs and QDs.

4. Conclusions

We have discussed implications of the stochastic model of excitation dynamics in nanosystems, which has been under recent active debate in the context of charge carrier relaxation in isolated single-walled carbon nanotubes and semiconductor nanocrystals. Analysis of available experimental data leads us to conclude that the elementary excitations in all these systems are excitons. The quantized character of the number of excitons in nanosystems is essential. A bulk description of the relaxation kinetics in terms of the average exciton density is inappropriate and not at all necessary because the discrete stochastic model itself admits a simple analytical solution.

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