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ORIGINAL PAPER

Stochastic model for the fluctuation-limited reaction–diffusion kinetics in inhomogeneous media based on the nonlinear Smoluchowski equations

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Abstract To describe the annihilation of spatially separate electrons and holes in a disordered semiconductor, we suggest the use of a model based on the spatially inhomogeneous, nonlinear Smoluchowski equations with random initial distribution density. Furthermore, we present a Monte Carlo algorithm for solving this equation. Our approach provides a general method for the computation of the electron-hole kinetics in inhomogeneous media, taking into account both their radiative and nonradiative recombination by tunneling as well as their diffusion. To validate the simulation algorithm, we compare our model with a more general approach based on a statistical description and the Kirkwood closure of the Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy equations. A comparison with recent experimental results is also discussed.

Keywords Fluctuation-limited reactions · Reaction–diffusion kinetics · Electron-hole kinetics · Photoluminescence · Nonradiative recombination · Smoluchowski equation

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1 Introduction

The fluctuation-limited kinetics of diffusion-controlled reactions plays a crucial role in many physical, chemical and biological processes (see, e.g., Ref. [12,30]). However, the diffusion equations are often treated macroscopically, ignoring density fluctuations. In the absence of nonlinear interactions such as chemical reactions, the macroscopic diffusion equations govern uniform concentration distributions. Thermal fluctuations, initial density inhomogeneities, and the randomness of reaction events lead to non-uniform concentration fields, thus drastically changing the time dependence of the density for asymptotically long times.

For instance, let us consider a reaction of two types of particles, A and B, $A+B \to P$. The simplest kinetic approach to this reaction first considered by Smoluchowski [29] is based on the rate equations

$$dn_A/dt = -g\, n_A(t) n_B(t), \quad dn_B/dt = -g\, n_A(t) n_B(t), \quad n_A(0) = a_0, n_B(0) = b_0$$

where g is the reaction rate. For diffusion-controlled reactions, Smoluchowski obtained $g = 4\pi D r_0$, where r_0 is the particle radius and D is the relative diffusion coefficient. This equation can be solved explicitly: $n_A(t) = a_0/(1 + a_0 g t)$ for $a_0 = b_0$, and $n_A(t) = a_0 f_0/[b_0 \exp(f_0 g t) - a_0]$ for $a_0 < b_0$, where $f_0 = b_0 - a_0$.

This description of chemical reactions implies conditions such that the rate at which the reactants approach each other (the diffusion rate) is much larger than the rate at which they react chemically with each other (the reaction rate). Hence, the basic assumption underlying this reaction is a homogeneous spatial distribution of particles during the reaction at any time instant, i.e., the components A and B should be always perfectly mixed. Independent of the dimension d, this assumption results in solutions with a long-time asymptotics $\sim \exp(-f_0 g t)$ if $a_0 \neq b_0$, and $\sim 1/gt$ if $a_0 = b_0$.

Fluctuations lead to drastically different solutions. In particular, spatial correlations of the particles cause segregation, i.e., the formation of spatially separated clusters composed entirely of particles of either type A or B. The formation of these clusters slows down the reaction dramatically, because only particles near the boundary of the clusters are likely to react, while particles inside the cluster have to diffuse to the boundary before they have a chance to react with a particle of the other type. In other words, fluctuations induce the formation of a mosaic of continuously growing domains which contain only one of the two components, A or B. It was first shown by Ovchinnikov and Zeldovich [21] that in this case, the long-time asymptotics is $\sim t^{-3/4}$ if $a_0 = b_0$. Generally, for $a_0 = b_0$, the asymptotics $\sim t^{-d/4}$ is valid for any dimensionality $d \leq 4$, while for $d \geq 4$, $\sim t^{-1}$. This law was obtained by several authors using different arguments (see, e.g., Refs. [2,16,21]).

This asymptotics follows from a more general quantity, namely, the correlation function $B_n(\mathbf{r}_1 - \mathbf{r}_2; t) = \langle n(\mathbf{r}_1, t) n(\mathbf{r}_2, t)\rangle$. The concentration $n(\mathbf{r}, t)$ is assumed to satisfy the diffusion equation $\partial n(\mathbf{r}, t)/\partial t = D\Delta n(\mathbf{r}, t)$ with the random initial condition $n(\mathbf{r}, 0) = n_0(\mathbf{r})$ where $n_0(\mathbf{r})$ is a Gaussian random field with the correlation $\langle n_0(\mathbf{r}_1, t) n_0(\mathbf{r}_2, t)\rangle = \delta(\mathbf{r}_1 - \mathbf{r}_2)$. Using the representation

$$n(\mathbf{r},t)=\int\limits_{\mathbf{R}^d} G(\mathbf{r},\mathbf{r}';t)n_0(\mathbf{r}')d\mathbf{r}'$$

with Green's function $G(\mathbf{r},\mathbf{r}';t)=(\sqrt{4Dt\pi})^{-d/2}\exp\{-\frac{|\mathbf{r}-\mathbf{r}'|^2}{4Dt}\}$, we obtain

$$\begin{aligned}B_n(\mathbf{r}_1-\mathbf{r}_2;t)&=\langle n(\mathbf{r}_1,t)n(\mathbf{r}_2,t)\rangle\\&=\int\limits_{\mathbf{R}^d}\int\limits_{\mathbf{R}^d} G(\mathbf{r}_1,\mathbf{r}';t)G(\mathbf{r}_2,\mathbf{r}'';t)\langle n_0(\mathbf{r}')n_0(\mathbf{r}'')\rangle d\mathbf{r}'d\mathbf{r}''.\end{aligned}$$

Since $\langle n_0(\mathbf{r}_1)n_0(\mathbf{r}_2)\rangle=\delta(\mathbf{r}_1-\mathbf{r}_2)$, it follows that

$$\begin{aligned}\langle n(\mathbf{r}_1,t)n(\mathbf{r}_2,t)\rangle&=\int\limits_{\mathbf{R}^d}\int\limits_{\mathbf{R}^d} G(\mathbf{r}_1,\mathbf{r}';t)G(\mathbf{r}_2,\mathbf{r}';t)d\mathbf{r}'\\&=C(Dt)^{-d/2}\exp\left\{-\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{8Dt}\right\}\end{aligned}$$

with $C=(4\pi)^{-d/2}$. This result implies that $\langle n^2\rangle=B_n(0;t)=C(Dt)^{-d/2}$, hence, $\langle n\rangle\sim(\langle n^2\rangle)^{1/2}\sim t^{-d/4}$.

If the densities of the components are not equal, the asymptotics is modified. For instance, if $a_0<b_0$, $n_A\sim a_0\exp(-\sqrt{t})$ for $d=1$, $n_A\sim a_0\exp\{-t/\log(t)\}$ for $d=2$, while for $d\geq 3$, the asymptotic law again coincides with the homogeneous case: $n_A\sim a_0\exp(-t)$ [2].

In all previous considerations, both types of particles, A and B, are assumed to be able of diffusion. If, e.g., the particles of type B are immobile, and $a_0<b_0$, the asymptotics has the form $n_A\sim\exp(-Ct^{d/d+2})$ (see Ref. [2]). For $a_0=b_0$, $n\sim t^{-1/2}$ for $d=3$. For $d=2$, the exact asymptotics is unknown, but we will show numerically that it is most likely close to the one obtained in three dimensions.

Note that this difference between the homogeneous and fluctuation-limited kinetics holds regardless of the type of reaction between the particles. In particular, it applies to the Smoluchowski coagulation equation. Coagulation, or coalescence, is a process by which two particles collide and adhere, or coagulate. There are many different mechanisms that bring two particles to each other: molecular diffusion, gravitational sedimentation, free molecule collisions, turbulent motion of the host gas, acoustic waves, density, concentration and temperature gradients, electric charges, etc. (see, e.g., Refs. [14,33]). Assuming a number density n_i of particles A_i consisting of i monomers of the same type, the coalescence reaction $A_i+A_j\to A_{i+j}$ is governed by the nonlinear Smoluchowski equation in its most simple homogeneous form:

$$\frac{\partial n_l}{\partial t}=\frac{1}{2}\sum_{i+j=l}R_{ij}n_in_j-n_l\sum_{i=1}^{\infty}R_{li}n_i \tag{1}$$

where $R_{ij}=R_{ji}$ is a coagulation coefficient describing the frequency of collisions between the particles A_i and A_j. Note that the equation governs the aggregation of a set of clusters in the bulk, and the solution does not depend on the spatial coordinates.

Taking into account the generation of particles A_l with the external rate F_l, and allowing for the diffusion of the particles in between their collisions with the diffusion coefficient D_l, the coagulation equation reads

$$\frac{\partial n_l}{\partial t} = D_l \Delta n_l(\mathbf{r}, t) + \frac{1}{2} \sum_{i+j=l} R_{ij} n_i n_j - n_l \sum_{i=1}^{\infty} R_{li} n_i + F_l. \tag{2}$$

The numerical solution of this equation is a difficult problem: for realistic systems of coagulating particles, many thousands of equations have to be solved, and the functions $n_l(\mathbf{r}, t)$ depend both on the spatial and temporal coordinates $\mathbf{r}$ and t. To accurately keep track of rapid changes of $n_l(\mathbf{r}, t)$ in time, the step size Δt has to be chosen so small that algorithms based on finite-difference or finite-element methods would need enormous computational resources. For the solution of Eq. (2), Monte Carlo algorithms are thus the methods of choice.

Note that Eq. (2) describes the coagulation of particles of one type: the particle clusters differ only in their size. More generally, one can consider particles characterized by size, mass, or chemical composition. Assuming, for example, the mass m of a cluster to be a continuously varying quantity, the spatially homogeneous coagulation equation governing the particle dynamics can be written in the form

$$\frac{\partial n(m,t)}{\partial t} = \frac{1}{2} \int_0^{m_1} \dots \int_0^{m_s} R(u, m-u) n(m-u, t) n(u, t) du - n(m,t) \int_0^{\infty} \dots \int_0^{\infty} R(u, m) n(u, t) du. \tag{3}$$

Here, m_i is the mass of the i-th component in a particle, and m is a vector of compositions $(m_1, \dots, m_s)$, where s is the total number of components; $n(m, t)dm$ is the number of particles having mass of component i in the range $[m_i, m_i + dm_i]$ at time t, and $R(u, m) = R(m, u)$ is the binary coagulation coefficient.

The numerical solution of the Smoluchowski-type equations discussed above is a highly challenging problem even for only a few particle types in the spatially homogeneous case. We will deal in this paper with only three particle types (electrons, holes, and nonradiative recombination centers), and neglect the implicit formation of excitons, trions, biexcitons, or other excitonic complexes. The first and major difficulty of this apparently simple problem arises from the fact that it is inhomogeneous in space. The second difficulty of our problem is caused by the low particle densities. Third, we are interested in the particle kinetics for very long times. Finally, we deal with stochastic initial conditions, so we have to take an average over the ensemble of initial distributions. Conventional numerical methods are not suitable for handling problems of this kind, and we will therefore extend the Monte Carlo methods we have developed previously in Refs. [15,24–26] to the case we deal with in this paper.

The main idea of Monte Carlo methods for solving the spatially homogeneous Smoluchowski equation lies in the probabilistic interpretation of the evolution of the interacting particles as a Markov chain (see, e.g., Ref. [15]). In Refs. [14] and [26], we

have applied the Monte Carlo technique to the inhomogeneous Smoluchowski equation without diffusion term. In this paper, we will consider the general inhomogeneous case with diffusion. Note that the direct Monte Carlo simulation of the particle interactions and diffusion jumps on a grid is computationally expensive, because one has to consider a huge number of jumps per one particle interaction. We suggest a new Monte Carlo method for this case, introducing "long diffusion jumps" which accelerate the simulation process significantly.

The Smoluchowski equation for homogeneous particle densities is a mean-field approach, where the evolution of the mean number of particles is governed by the collision frequency on average. These mean-field equations do not involve fluctuations, and we cannot extract information on the particle correlations and other statistical properties of the particle dynamics. Fluctuations can be introduced in the inhomogeneous Smoluchowski equations by, for example, taking the initial solution as a random distribution. Alternatively, the diffusion coefficient may be taken to be random, the interaction kernel R may depend on a random parameter, the external source F may involve random fluctuations, and even the boundary conditions may produce random perturbations. We can derive the mean-field Smoluchowski equations from these random equations by an averaging and closure procedure. To compare the mean-field approach and the approach based on the random equations and closure, we will derive equations for the mean particle concentrations and their correlations.

In this paper we deal with the recombination of electrons and holes in an inhomogeneous semiconductor (see, e.g., [7,11,28]). This topic has attracted considerable experimental and theoretical interest during the past five decades since the optoelectronic properties of technologically important materials have been found to be controlled by the electron-hole recombination dynamics. Recently, it has been discovered that (In,Ga)N/GaN quantum wells, used in light-emitting diodes for solid-state lighting, exhibit properties analogous to amorphous semiconductors due to the spatial localization of charge carriers and their recombination as spatially separate electron-hole pairs [3,5,8].

We consider that both electrons and holes are able to diffuse, and will recombine with each other either radiatively (i.e., giving rise to the generation of a photon) or nonradiatively via immobile recombination centers. Since electrons and holes are, in general, spatially separated, these recombination processes are considered to be induced by tunneling from one localization site to the other, and to be assisted by diffusion, allowing electrons and holes to meet each other in the same spatial location. What governs the recombination dynamics are both the fluctuations of the initial spatial distributions of electrons and holes and the fluctuations in their diffusivity resulting from the random depth of the localization sites. Hence, spatial correlations are crucial for the evaluation of the mean concentrations. We will see that ignoring even a part of these correlations leads to considerable deviations from the exact results.

2 The mean field equations

We consider electrons, holes and nonradiative recombination centers distributed in a domain G with densities $n(\mathbf{r};t)$, $p(\mathbf{r};t)$, and $N(\mathbf{r})$, respectively. A part of these

recombination centers with a density $N^+(\mathbf{r};t)$ are in the state waiting for capturing an electron, while the remaining centers $N(\mathbf{r}) - N^+(\mathbf{r};t)$ are waiting for a hole.

The radiative recombination of spatially separate electron-hole pairs is due to tunneling with the rate $B(r) = B_0 \exp(-r/a)$, where r is the distance between electron and hole. The decrease of the electron density at the location $\mathbf{r}$ due to the recombination with holes in the vicinity is $-n(\mathbf{r};t)\int B(|\mathbf{x}|)p(\mathbf{r}+\mathbf{x};t)d\mathbf{x}$. The decrease of the electron density due to an interaction with a nonradiative recombination center is described analogously: $-n(\mathbf{r};t)\int b_n(|\mathbf{x}|)N^+(\mathbf{r}+\mathbf{x};t)d\mathbf{x}$. Here $b_n(r) = b_{n0}\exp(-r/a_n)$, and the same kernel is defined for the hole-recombination center interaction: $b_p(r) = b_{p0}\exp(-r/a_p)$.

The electron can also diffuse spatially with a diffusion coefficient $D_n(\mathbf{r})$ that may vary randomly with the spatial position $\mathbf{r}$. Altogether, the electron density thus follows the equation

$$\frac{\partial n(\mathbf{r};t)}{\partial t} = D_n(\mathbf{r})\Delta n(\mathbf{r};t) - n(\mathbf{r};t)\int B(|\mathbf{x}|)p(\mathbf{r}+\mathbf{x};t)d\mathbf{x} - n(\mathbf{r};t)\int b_n(|\mathbf{x}|)N^+(\mathbf{r}+\mathbf{x};t)d\mathbf{x}. \quad (4)$$

Analogously, the holes are described by the equation

$$\frac{\partial p(\mathbf{r};t)}{\partial t} = D_p(\mathbf{r})\Delta p(\mathbf{r};t) - p(\mathbf{r};t)\int B(|\mathbf{x}|)n(\mathbf{r}+\mathbf{x};t)d\mathbf{x} - p(\mathbf{r};t)\int b_p(|\mathbf{x}|)[N(\mathbf{r}+\mathbf{x}) - N^+(\mathbf{r}+\mathbf{x};t)]\,d\mathbf{x}. \quad (5)$$

The number of recombination centers waiting for an electron is reduced when the electron is captured, and increased when the hole is captured:

$$\frac{\partial N^+(\mathbf{r};t)}{\partial t} = -n(\mathbf{r};t)\int b_n(|\mathbf{x}|)N^+(\mathbf{r}+\mathbf{x};t)d\mathbf{x} + p(\mathbf{r};t)\int b_p(|\mathbf{x}|)[N(\mathbf{r}+\mathbf{x}) - N^+(\mathbf{r}+\mathbf{x};t)]\,d\mathbf{x}. \quad (6)$$

Without loss of generality, we assume that the initial numbers of electrons and holes are equal (say, to n_0). At the initial time $t = 0$, the electrons, holes, and recombination centers are randomly distributed:

$$n(\mathbf{r};0) = \sum_{i=1}^{n_0}\delta(\mathbf{r}-\mathbf{r}_i), \quad p(\mathbf{r};0) = \sum_{j=1}^{n_0}\delta(\mathbf{r}-\mathbf{r}_j), \quad N(\mathbf{r};0) = \sum_{k=1}^{N^{(0)}}\delta(\mathbf{r}-\mathbf{r}_k). \quad (7)$$

Here $\mathbf{r}_i$, $\mathbf{r}_j$, and $\mathbf{r}_k$ are independent uniformly distributed random positions, and $N^{(0)}$ is the total number of recombination centers. At $t = 0$, we can assume that all recombination centers are waiting for an electron, i.e., $N^+(\mathbf{r};0) = N(\mathbf{r};0)$ if the background doping density n_s is zero. Finally, the experimentally observed radiative

intensity $I(t)$ is proportional to the photon flux $\phi(t)$ due to the generation of photons by the radiative recombination of electrons and holes:

$$\phi(t) = \left\langle \int \frac{1}{|G|} d\mathbf{r} \int B(|\mathbf{x}|) n(\mathbf{r}; t) p(\mathbf{r}+\mathbf{x}; t) d\mathbf{x} \right\rangle \tag{8}$$

where the angle brackets stand for the mathematical expectation with respect to the initial random distribution of electrons, holes and recombination centers, and $|G|$ is the volume of the domain G. Since $I(t) = \hbar\omega\phi(t)$, where $\hbar\omega$ is the photon energy, we use the terms photon flux and intensity interchangeably.

The random fields n and p are statistically homogeneous and isotropic, implying that the correlation functions of n and p, and the cross-correlation function $L_{np}(\mathbf{x}, t) = \langle n(\mathbf{r}, t) p(\mathbf{r}+\mathbf{x}, t) \rangle$ depend only on $|\mathbf{x}|$, the distance between $\mathbf{r}$ and $\mathbf{r}+\mathbf{x}$. We denote by $K_{np}(\mathbf{x}, t)$ the normalized cross-correlation coefficient: $K_{np}(\mathbf{x}, t) = L_{np}(\mathbf{x}, t)/n(t)p(t)$. Here $n(t) = \langle n(\mathbf{r}, t) \rangle$ and $p(t) = \langle p(\mathbf{r}, t) \rangle$, since the random fields n and p are homogeneous. In this terms, the photon flux reads:

$$\phi(t) = n(t) p(t) \int B(|\mathbf{x}|) K_{np}(\mathbf{x}, t) d\mathbf{x}. \tag{9}$$

At low temperatures, it may be a sensible approximation to neglect the first and third terms in Eqs. (4) and (5), i.e., those related to diffusion and the nonradiative recombination centers. The model would then reduce to two partial integro-differential equations for electrons and holes which contain only the radiative term:

$$\begin{aligned} \frac{\partial n(\mathbf{r}; t)}{\partial t} &= -n(\mathbf{r}; t) \int B(|\mathbf{x}|) p(\mathbf{r}+\mathbf{x}; t) d\mathbf{x}, \\ \frac{\partial p(\mathbf{r}; t)}{\partial t} &= -p(\mathbf{r}; t) \int B(|\mathbf{x}|) n(\mathbf{r}+\mathbf{x}; t) d\mathbf{x}. \end{aligned} \tag{10}$$

In this case, we have obviously $\phi(t) = -\frac{\partial n(t)}{\partial t} = -\frac{\partial p(t)}{\partial t}$, provided the initial mean concentrations n_0 and p_0 are equal.

Let us consider this last case in more details. In the next section we treat this pure radiative recombination process of immobile electrons and holes from a statistical viewpoint.

3 Correlation analysis

When new Monte Carlo methods are constructed and applied to simulate complicated processes, it is imperative to validate them by solving simplified benchmark problems. Let us thus consider the case of pure radiative recombination i.e., there is no diffusion, no nonradiative recombination centers, and the process is governed by Eq. (10).

Taking the average over the initial distribution of electrons and holes and assuming that this distribution is homogeneous and isotropic in space, we can rewrite Eq. (9) as

$$\frac{\partial n(t)}{\partial t} = -n(t)p(t)\int B(|\mathbf{x}|)K_{np}(\mathbf{x};t)d\mathbf{x}. \tag{11}$$

Due to the initial conditions, the number of electrons is equal to the number of holes, which also applies to their mean values $n(t) = p(t)$, and Eq. (11) thus reads

$$\frac{\partial n(t)}{\partial t} = -n^2(t)\int B(|\mathbf{x}|)K_{np}(\mathbf{x};t)d\mathbf{x}. \tag{12}$$

We are going to find the cross-correlation $K_{np}(\mathbf{x};t)$ from a closed system of equations. To this end we also need to introduce the correlation functions L_n, L_p and the relevant correlation coefficients K_n and K_p:

$$\begin{aligned} L_n(\mathbf{x},t) &= \langle n(\mathbf{r},t)n(\mathbf{r}+\mathbf{x},t)\rangle = n^2(t)K_n(\mathbf{x},t),\\ L_p(\mathbf{x},t) &= \langle p(\mathbf{r},t)p(\mathbf{r}+\mathbf{x},t)\rangle = p^2(t)K_p(\mathbf{x},t). \end{aligned} \tag{13}$$

Since $n(t) = p(t)$, the statistics of n and p are equal, and we thus use the notation $K(\mathbf{x},t) = K_p = K_n$.

Generally, when calculating the many-particle correlations $G_{m,k}$ of n at points $r_1,\ldots,r_m$ and p at points $\tilde{\mathbf{r}}_1,\ldots,\tilde{\mathbf{r}}_k$, for Markovian random processes,

$$G_{m,k}(\mathbf{r}_1,\ldots,\mathbf{r}_m;\tilde{\mathbf{r}}_1,\ldots,\tilde{\mathbf{r}}_k) = \left\langle \prod_{i=1}^{m} n(\mathbf{r}_i,t)\prod_{j=1}^{k} p(\tilde{\mathbf{r}}_j,t)\right\rangle,$$

and the following kinetic equations can be derived from the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy of equations (see, e.g., Eq. 2.15 in Ref. [1], and the corresponding equations in Refs. [16,18]):

$$\begin{aligned} \frac{\partial G_{m,k}}{\partial t} = &-\sum_{i=1}^{m}\sum_{j=1}^{k} B(\mathbf{r}_i-\tilde{\mathbf{r}}_j)G_{m,k} - \sum_{i=1}^{m}\int B(\mathbf{r}_i-\tilde{\mathbf{r}}_{k+1})G_{m,k+1}\,d\tilde{\mathbf{r}}_{k+1}\\ &-\sum_{j=1}^{k}\int B(\tilde{\mathbf{r}}_j-\mathbf{r}_{m+1})G_{m+1,k}\,d\mathbf{r}_{m+1}. \end{aligned} \tag{14}$$

For $G_{11} = L_{np}$, we obtain:

$$\frac{\partial G_{11}}{\partial t} = -B(\mathbf{r}_1-\tilde{\mathbf{r}}_1)G_{11} - \int B(\mathbf{r}_1-\tilde{\mathbf{r}}_2)G_{1,2}\,d\tilde{\mathbf{r}}_2 - \int B(\tilde{\mathbf{r}}_1-\mathbf{r}_2)G_{2,1}\,d\mathbf{r}_2 \tag{15}$$

with

$$G_{1,2} = \langle n(\mathbf{r}_1,t)p(\tilde{\mathbf{r}}_1,t)p(\tilde{\mathbf{r}}_2,t)\rangle \equiv L_{npp}$$

and

$$G_{2,1} = \langle n(\mathbf{r}_1, t) n(\mathbf{r}_2, t) p(\tilde{\mathbf{r}}_1, t) \rangle \equiv L_{nnp}.$$

We thus arrive at

$$\frac{\partial L_{np}}{\partial t} = -B(\mathbf{r}_1 - \tilde{\mathbf{r}}_1) L_{np} - \int B(\mathbf{r}_1 - \tilde{\mathbf{r}}_2) L_{npp}\, d\tilde{\mathbf{r}}_2 - \int B(\tilde{\mathbf{r}}_1 - \mathbf{r}_2) L_{nnp}\, d\mathbf{r}_2. \tag{16}$$

We next employ the Kirkwood [13] approximation:

$$\begin{aligned} L_{npp} &\approx \langle n(\mathbf{r}_1, t) p(\tilde{\mathbf{r}}_1, t) \rangle \langle n(\mathbf{r}_1, t) p(\tilde{\mathbf{r}}_2, t) \rangle \langle p(\tilde{\mathbf{r}}_2, t) p(\tilde{\mathbf{r}}_1, t) \rangle \\ &= n^3 K_{np}(\mathbf{r}_1 - \tilde{\mathbf{r}}_1, t) K_{np}(\mathbf{r}_1 - \tilde{\mathbf{r}}_2, t) K(\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2, t) \end{aligned} \tag{17}$$

and

$$\begin{aligned} L_{nnp} &\approx \langle n(\mathbf{r}_1, t) n(\mathbf{r}_2, t) \rangle \langle n(\mathbf{r}_2, t) p(\tilde{\mathbf{r}}_1, t) \rangle \langle p(\tilde{\mathbf{r}}_1, t) n(\mathbf{r}_1, t) \rangle \\ &= n^3 K(\mathbf{r}_1 - \mathbf{r}_2, t) K_{np}(\mathbf{r}_1 - \tilde{\mathbf{r}}_1, t) K_{np}(\mathbf{r}_2 - \tilde{\mathbf{r}}_1, t). \end{aligned} \tag{18}$$

Using Eq. (17), we obtain from Eq. (16)

$$\frac{\partial L_{np}}{\partial t} = -B(\mathbf{r}) n^2(t) K_{np}(\mathbf{r}, t) - 2n^3(t) K_{np}(\mathbf{r}, t) \int B(\tilde{\mathbf{r}}) K(\tilde{\mathbf{r}} - \mathbf{r}, t) K_{np}(\tilde{\mathbf{r}}, t)\, d\tilde{\mathbf{r}} \tag{19}$$

with $\mathbf{r} = \mathbf{r}_1 - \tilde{\mathbf{r}}_1$ where $\tilde{\mathbf{r}} = \mathbf{r}_1 - \tilde{\mathbf{r}}_2$ (or $\tilde{\mathbf{r}} = \tilde{\mathbf{r}}_1 - \mathbf{r}_2$). By differentiating $L_{np} = n(t) p(t) K_{np}$ we also obtain:

$$\begin{aligned} \frac{\partial L_{np}}{\partial t} &= n^2(t) \frac{\partial K_{np}}{\partial t} + 2n(t) K_{np} \frac{\partial n(t)}{\partial t} \\ &= n^2(t) \frac{\partial K_{np}}{\partial t} - 2n^3(t) K_{np}(\mathbf{r}, t) \int B(\tilde{\mathbf{r}}) K_{np}(\tilde{\mathbf{r}}, t)\, d\tilde{\mathbf{r}}. \end{aligned}$$

Combining this result with Eq. (19) we arrive at the desired equation:

$$\begin{aligned} \frac{\partial K_{np}(\mathbf{r}, t)}{\partial t} &= -B(\mathbf{r}) K_{np}(\mathbf{r}, t) - 2n(t) K_{np}(\mathbf{r}, t) \\ &\quad \int B(\tilde{\mathbf{r}}) K_{np}(\tilde{\mathbf{r}}, t) [K(\mathbf{r} - \tilde{\mathbf{r}}, t) - 1]\, d\tilde{\mathbf{r}}. \end{aligned} \tag{20}$$

We proceed analogously for the correlation K. Differentiating L_n in Eq. (13), and combining the result with the equation for $G_{2,0} = L_n$ [employing the approximation in Eq. (18)] yields:

$$\frac{\partial K}{\partial t} = -2n(t) K(\mathbf{r}, t) \int B(\tilde{\mathbf{r}}) K_{np}(\tilde{\mathbf{r}}, t) [K_{np}(\mathbf{r} - \tilde{\mathbf{r}}, t) - 1]\, d\tilde{\mathbf{r}}. \tag{21}$$

These two equations are closed with the expression

$$\frac{\partial n(t)}{\partial t} = -n^2(t) \int B(\tilde{\mathbf{r}}) K_{np}(\tilde{\mathbf{r}}, t)\, d\tilde{\mathbf{r}}. \tag{22}$$

From the system of Eqs. (20)–(22), we can calculate the functions n, K, and K_{np}.

An interesting special case is obtained when assuming $K = 1$, i.e., when ignoring the hole-hole and electron-electron correlations, and taking into account only the electron-hole correlations. From Eq. (20), it follows that

$$\frac{\partial K_{np}}{\partial t} = -B(\mathbf{r}) K_{np}(\mathbf{r}, t). \tag{23}$$

with the solution

$$K_{np}(\mathbf{r}, t) = \exp\{-B(\mathbf{r})t\}. \tag{24}$$

We can derive an expression for the photon flux in any dimension d. Indeed, substituting Eqs. (24) in (22) yields

$$\frac{\partial}{\partial t}\left\{\frac{1}{n(t)}\right\} = \Omega_d \int_0^\infty B_0 \exp(-r/a) \exp\{-t\, B_0 \exp(-r/a)\} r^{d-1} dr, \tag{25}$$

where Ω_d is the surface area of a unit d-dimensional sphere. This equation can be used to calculate the mean concentration $n(t)$ and the photon flux $\phi(t)$. Generally, in d dimensions, the long-time asymptotics in the case of purely radiative recombination is $n(t) \sim [\log(t)]^{-d}$ if only the electron–hole correlations are taken into account (see also Ref. [16]), i.e., for two dimensions

$$\phi(t) \sim t^{-1} (\log t)^{-3}. \tag{26}$$

If the electron-electron and hole-hole correlations are taken into account in addition, the system of Eqs. (20)–(22) leads to an asymptotics $n(t) \sim [\log(t)]^{-d/2}$. For the photon flux, this result implies $\phi(t) \sim t^{-1} [\log(t)]^{-(d/2+1)}$, i.e.,

$$\phi(t) \sim t^{-1} (\log t)^{-2} \tag{27}$$

for the two-dimensional case considered here.

At the first glance, Eq. (25) is similar to expressions derived in previous studies of the radiative recombination of electrons and holes in disordered media. For example, in Ref. [9], the authors used the linear Smoluchowski equation [29] for the probability density function $p(r, t)$ of the electron-hole pair separation r with the recombination coefficient proportional to $B_0 \exp(-r/a)$. Taking into account electron-hole correlations, but ignoring the electron-electron and hole-hole correlations, these authors derived an expression for the photoluminescence intensity (proportional to the photon flux) which is similar to Eq. (25) but not equivalent. A different approach was

used in Ref. [10], where the author assumed that an electron will tunnel to the nearest recombination center only. The resulting expression looks again similar, but leads to a different long-time behavior of the intensity transient. In Ref. [31], the authors treated the set of spatially separated electrons and holes as Poissonian point distributions in three dimensions, and derived explicit expressions in an integral form which is again similar to Eq. (25). The same approach has been used in Ref. [19] for the two-dimensional case. Many of these existing models basically predict a power law decay with $I(t) \sim t^{\nu}$ with ν varying between -1 and -2 to within a logarithmic factor. For comparison, we recall that our approach yields $I(t) \sim t^{-1}(\log t)^{-2}$.

When both radiative recombination and diffusion are taken into account, and the case of equal mean concentrations $\langle n_0 \rangle = \langle p_0 \rangle$ is considered, we are dealing with the equations

$$\begin{aligned} \frac{\partial n(\mathbf{r};t)}{\partial t} &= D_n \Delta n(\mathbf{r};t) - n(\mathbf{r};t) \int B(|\mathbf{x}|) p(\mathbf{r}+\mathbf{x};t) d\mathbf{x}, \\ \frac{\partial p(\mathbf{r};t)}{\partial t} &= D_p \Delta p(\mathbf{r};t) - p(\mathbf{r};t) \int B(|\mathbf{x}|) n(\mathbf{r}+\mathbf{x};t) d\mathbf{x} \end{aligned} \tag{28}$$

with the initial concentrations taken as Gaussian white noise. These equations can be solved for $D_n = D_p = D$ by introducing new functions: $m = n - p$ and $s = n + p$. Then,

$$\begin{aligned} \frac{\partial m(\mathbf{r};t)}{\partial t} &= D\Delta m - \int B(|\mathbf{x}|)[n(\mathbf{r},t)p(\mathbf{r}+\mathbf{x},t) - n(\mathbf{r}+\mathbf{x},t)p(\mathbf{r},t)]\, d\mathbf{x} \\ \frac{\partial s(\mathbf{r};t)}{\partial t} &= D\Delta s - \int B(|\mathbf{x}|)[n(\mathbf{r},t)p(\mathbf{r}+\mathbf{x},t) + n(\mathbf{r}+\mathbf{x},t)p(\mathbf{r},t)]\, d\mathbf{x}. \end{aligned} \tag{29}$$

It can be shown that the solution of the first equation is close to the solution of the diffusion equation $\partial n(\mathbf{r},t)/\partial t = Dn_0(\mathbf{r},t)$ and has the same long-time asymptotics, namely, $(\langle m^2 \rangle)^{1/2} \sim t^{-d/4}$. From this result we conclude $\langle n \rangle = \langle s \rangle/2 \sim \langle |m| \rangle/2 \sim (\langle m^2 \rangle)^{1/2} \sim t^{-d/4}$. Thus $n(t) \sim t^{-d/4}$, and

$$\phi(t) \sim t^{-(d/4+1)} \tag{30}$$

remains true when both diffusion and radiative recombination are in the game as we will show by our simulations.

4 Monte Carlo algorithms

As mentioned in the introduction, the system of Eqs. (4)–(6) has exactly the same structure as the inhomogeneous Smoluchowski coagulation equations (see, e.g., Ref. [14]) for three distinct species. The Smoluchowski equations may be interpreted probabilistically as an equation generated by Markov chains describing the pair interactions. In Ref. [14]), we developed a Monte Carlo algorithm which we adapt here to solve Eqs. (4–6) for the two-dimensional case with $d = 2$.

4.1 Radiative recombination only

For simplicity, let us first present the algorithm for the case without diffusion. The direct simulation assumes that the process of interactions (in our case, the radiative decay or the capture by recombination centers) is pairwise and Markovian, i.e., having made a time step, the next time step is simulated independently. The interacting pair is sampled according to the kernel of the equation $B = B_0 \exp(-|\mathbf{x}|/a)$.

The algorithm can be described as follows (for details see Refs. [14,15,24]). We do not use any mesh, so our phase space is continuous. The process is simulated in a square box with size $L \times L$ and periodic boundary conditions. Let's assume that we know a constant $B_{\max}$ such that $B \leq B_{\max}$; in our case, we may take $B_{\max} = B_0$.

0. Put $t = 0$.
1. Sample $n = n_0$ electrons at random, independently and uniformly distributed in the box. Do the same for holes and recombination centers. Here n_0 is the initial number of electrons (equal to the number of holes). We denote the current number of electrons by n, and the current number of holes by p.
2. Choose an electron-hole pair to interact. These pairs are sampled uniformly and independently, i.e., the electron is sampled from all existing electrons, and the hole is sampled from all existing holes.
3. Obtain the random time dt between interactions as

$$dt = -\log(rand)/\lambda, \quad \lambda = n\, p\, B_{\max}/(2n_0).$$

   The current time increases as $t := t + dt$.
4. Simulate the interaction itself. For the interacting pair sampled, we calculate the probability that the interaction takes place as $Pr = B/B_{\max}$: we generate *rand*, a random number uniformly distributed on [0, 1], and if $rand \leq Pr$, then the interaction takes place (e.g., in the case of electron-hole annihilation, we set $n := n - 1$, $p := p - 1$). Otherwise nothing happens. Then, we go back to step 2.

Note that in our case the constant $B_{\max} = B_0$ would be too crude, much better is $B_{\max} = B_0 \exp(-r_{\min})$ where $r_{\min}$ is the minimal distance between any two particles. The problem is that unlike the constant B_0, the majorant $B_{\max} = B_0 \exp(-r_{\min})$ is changing with time. However, we have to recalculate this majorant only after annihilations (if there are no recombination centers). This technique accelerates the algorithm significantly.

4.2 Radiative and nonradiative recombination in the absence of diffusion

Let us now turn to the case where also nonradiative recombination centers are present with a finite concentration. In the first step, we have to choose one of the possible events: (*i*) radiative recombination, i.e., direct annihilation of an electron-hole pair, (*ii*) an electron is captured by one of the empty recombination centers N^+, (*iii*) a hole is captured by one of the $N - N^+$ filled recombination centers (if there are any). The latter processes are described by the probabilities $b_n \exp(-|\mathbf{x}|/a_n)$, or $b_p \exp(-|\mathbf{x}|/a_p)$.

To unify the notation, we write $B_{ij} = B_0 \exp(-|\mathbf{r}_{ij}|/a)$ where $|\mathbf{r}_{ij}|$ is the distance between the reacting particles. The next steps are the same as described above. Thus, the simulation algorithm in the absence of diffusion can be described as follows.

1. Put $t = 0$, and sample $n = n_0$ electrons and $p = n_0$ holes at random, independently and uniformly distributed in the box. Independently, N recombination centers are also sampled uniformly and mutually independently distributed in the box. Without loss of generality, assume that $N = N^+$.
2. Sample one of the three possible events: (*i*) direct (radiative) electron-hole annihilation, (*ii*) electron capture by an empty center, (*iii*) hole capture by a filled center. To do this, first calculate the majorant frequencies for the three events:

$$\lambda_1 = npB_0 \exp\left\{-\frac{r_{np,min}}{a}\right\}, \tag{31}$$

$$\lambda_2 = nN_+ b_n \exp\left\{-\frac{r_{nN_+,min}}{a_n}\right\}, \tag{32}$$

$$\lambda_3 = p(N - N_+) b_p \exp\left\{-\frac{r_{p(N-N_+),min}}{a_p}\right\}, \tag{33}$$

   where $r_{np,\min}$ is the minimal of all possible distances between n electrons and p holes in the box, $r_{nN^+,\min}$ the same for the distances between n electrons and N^+ centers, and $r_{p(N-N^+),\min}$ for the distances between p holes and $N - N^+$ centers.

   From these frequencies, calculate the probabilities p_1, p_2, p_3 of the events (*i*), (*ii*), and (*iii*), respectively: $p_1 = \lambda_1/\lambda$, $p_2 = \lambda_2/\lambda$, and $p_3 = 1 - p_1 - p_2$, where $\lambda = \lambda_1 + \lambda_2 + \lambda_3$.
3. From the probabilities p_1, p_2, p_3, sample the event $k = i, ii, iii$, calculate the time increment as $\Delta t = -\log(rand))/\lambda_k$, and calculate $t := t + \Delta t$.
4. For the sampled event $k(= i, ii, iii)$, choose uniformly the relevant interacting pair, and check if the interaction takes place. For instance, if $k = i$, i.e., the sampled event happens to be radiative recombination of an electron-hole pair, calculate $\bar{P}_{np} = \exp\{\frac{-r+r_{np,min}}{a}\}$. If $rand < \bar{P}_{np}$, then the event occurs. Hence, recalculate $n := n - 1$ and $p := p - 1$, and go back to step 2. Otherwise, nothing happens, the probabilities p_1, p_2, p_3 remain the same, and so return to step 3. Here r is the distance between the sampled interacting pair. For the case $k = ii$, when an electron is captured by the recombination center, put $n := n - 1$, $N^+ := N^+ - 1$, but when a hole is captured by the recombination center, you have $p := p - 1$, $N^+ = N^+ + 1$.

   If the concentrations n and p are calculated at some prescribed time instances t_m, $m = 1, \ldots M$, just score the values $n(t_m)$, $p(t_m)$, $m = 1, \ldots M$. To calculate the photon flux $\phi(t)$, say, at a time t from the interval $t \in [t_1, t_2]$, count M, the number of electron-hole annihilations which have occurred during this time interval, and take the approximation $I(t) \approx M/(t_2 - t_1)$.
5. To carry out the average, run the steps 1–4 independently, say, ν times, with ν being a sufficiently large number, and take the arithmetic mean.

Note that there is no need to recalculate the value $r_{\min}$ after each annihilation or capture in the recombination center: this should be done only if the pair with $r_{\min}$ reacts.

4.3 Radiative and nonradiative recombination in the presence of diffusion

In the general case when the electrons and holes not only recombine, but also diffuse, the algorithm becomes more sophisticated. In our case, a realistic assumption is that the holes are immobile because of their large mass in group III-nitrides [32], so we take $D_p = 0$, and $D_n = D$. Usually, we would consider diffusion to occur by microscopic random jumps according to the law $dl = \omega\sqrt{D\,dt}$, where dl is the length of the random jump, ω is a random (isotropic) direction, and D is the diffusion coefficient. However, since the time between individual annihilation events may be very large compared to dt, a huge number of diffusion jumps would be required to simulate the electron-hole dynamics.

To accelerate this algorithm, we employ the random walk on spheres (see, e.g., Ref. [23]). The idea behind this method is simple. Around each electron, we construct a disk of maximal radius which does not contain any hole or recombination center. We then simulate the random exit times τ_k of electrons from these disks. We chose the electron which has a minimal exit time, and let this electron jump out of the disk, so that the new random position of the electron is uniformly distributed on the boundary of this disk. The distribution of the exit time is known, and we are thus able to simulate the random time dt according to this distribution, giving us the time $t := t + dt$. Note that this approach, in a slightly different formulation, is used in many physical applications (see, e.g., Refs. [6,17,20]).

For a unit disk, the exit time distribution of the standard Wiener process has the series representation [22]

$$H(t) = \sum_{k=1}^{\infty} \frac{2}{j_k J_1(j_k)} \exp\{-j_k^2 t/2\} \tag{34}$$

where J_1 is the Bessel function, and j_k are the positive zeros of the Bessel function J_0. It is sufficient to simulate the exit times from a unit disk, since for the Wiener process, the exit time τ_r from a disk of radius r has the property $\tau_r = r^2\tau_1$. The standard Wiener process corresponds to $D = 1/2$, so in our case the random exit time is simulated as $\tau_r = r^2\tau_1/2D$.

To simulate the exit times according the Eq. (34), we tabulated this distribution, and used Walker's algorithm (we have presented an efficient implementation of this method in Ref. [27]) which uses only one sample of *rand* to generate one sample of τ_1.

Note that in the diffusion-controlled case, our model described by Eqs. (4)–(6) should be modified to account for the recombination of an electron and hole at distance $x = 0$ (which is physically equivalent to the formation and radiative decay of an exciton). Since the radiative decay of an exciton is orders of magnitude faster than any other process in the problem, we consider this process to be instantaneous. The same applies for the case when an electron and a hole are in the same location as a recombination center. In terms of Eqs. (4)–(6), the kernels B, b_n and b_p should include

a singular part, such that the modified kernel B' has the form $B' = \beta\delta(|\mathbf{x}|) + B(|\mathbf{x}|)$ where δ is the Dirac delta-function and $\beta \propto D_n$ is a constant characterizing the recombination rate for a vanishing distance $|\mathbf{x}|$.

The general code described in Sect. 4.2 above remains the same. We have only to sample, in addition, the forth event that an electron makes a jump with the random time τ_k. Let τ_{min} be the minimal time among all $\tau_k, k = 1, 2, \ldots$ Then, introducing $\lambda_4 = 1/\tau_{\min}$, $\lambda = \sum_{i=1}^{4} \lambda_i$, the probabilities are calculated as $p_i = \lambda_i/\lambda$.

5 Simulation results and comparison

In this section, we present the results of our simulations and compare the different approximations and methods described above. Our simulations are adapted to take place on a spatial and temporal scale comparable to the experiment. Hence, we use nm and ns as natural units. Specifically, the characteristic tunneling distance a is given in nm, the recombination rate B_0 in ns^{-1}, the diffusion coefficient in $\mathrm{nm}^2\,\mathrm{ns}^{-1}$, and the photon flux transients are calculated for times up to 10^{12} ns.

Initial conditions are set by assuming that the concentrations $n_0 = p_0$ as well as N are all randomly, independently and uniformly distributed in a two-dimensional box of size $L \times L = 2000 \times 2000\,\mathrm{nm}^2$. For the Monte Carlo simulations, the results detailed below was obtained by averaging over ν runs which corresponds to ν independent initial configurations with ν varying between 400 and 2,000. Except otherwise mentioned, the calculations were done assuming $a = 2\,\mathrm{nm}$, $B_0 = 0.04\,\mathrm{ns}^{-1}$, and $n_0 = 2.5 \times 10^{-3}\,\mathrm{nm}^{-2}$.

Figure 1 compares a Monte Carlo simulation of the transient photon flux produced by the purely radiative recombination of electrons and holes with the solutions obtained

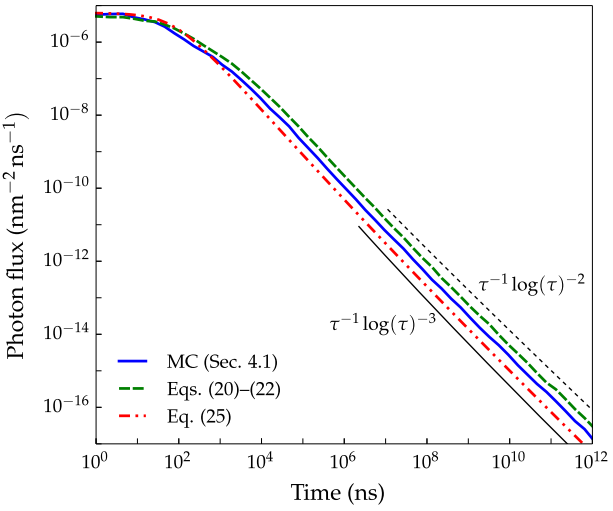

Fig. 1 (online colour) Comparison of photon flux transients for purely radiative recombination of spatially separated and immobile electrons and holes calculated by means of the two different mean-field equations derived in Sect. 3 and the Monte Carlo approach outlined in Sect. 4.1. The recombination-controlled asymptotics are indicated by the *thin black lines* with the dimensionless parameter $\tau = B_0 t$.

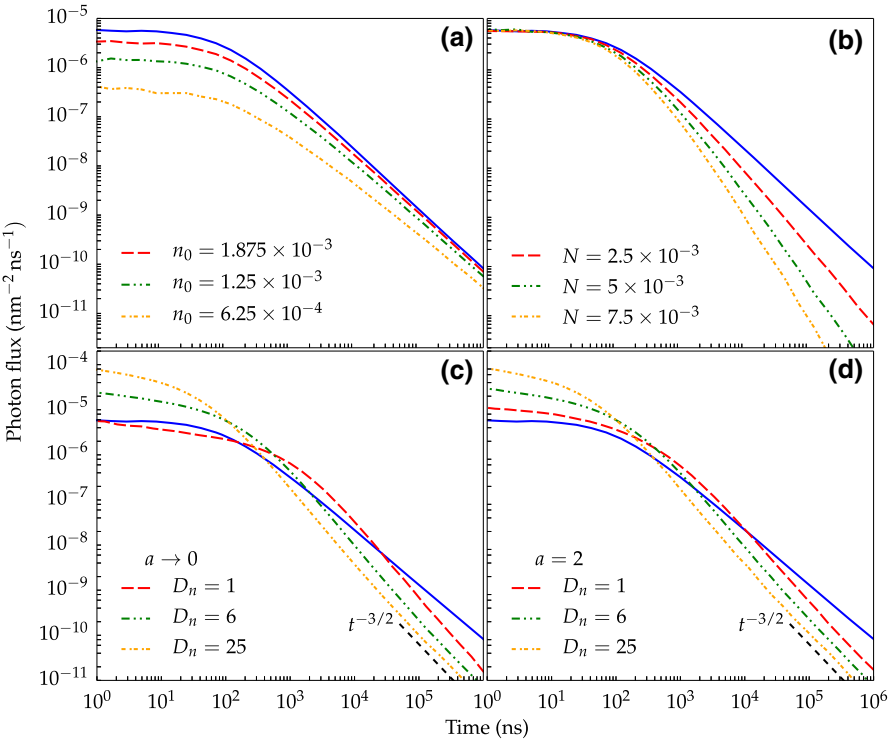

Fig. 2 (online colour) Photon flux transients obtained by Monte Carlo simulations of the recombination-diffusion kinetics of spatially separated electrons and holes. The *solid blue curve* is the same in all figures and has been obtained with $B_0 = 0.04\,\mathrm{ns}^{-1}$, $a = 2\,\mathrm{nm}$, $n_0 = 2.5 \times 10^{-3}\,\mathrm{nm}^{-2}$, $N = 0$, and $D_n = D_p = 0$. The parameters changed for each of the other transients are indicated in the respective figures. **a** Transients for purely radiative recombination calculated for different initial electron-hole densities n_0 in nm^{-2}. **b** Transients for simultaneous radiative and nonradiative recombination with different densities N of nonradiative centers in nm^{-2}. **c** and **d** Transients for the radiative recombination of electrons and holes with different electron diffusivities D_n in $\mathrm{nm}^2\,\mathrm{ns}^{-1}$. The diffusion-controlled asymptotics is indicated by the *black dashed line*. In (**c**), recombination of electrons and holes is assumed to occur instantaneously when they meet at $|\mathbf{x}| = 0$ (i.e., the contribution of tunneling is set to zero). In (**d**), electrons and holes may also recombine via tunneling with $B_0 = 0.04\,\mathrm{ns}^{-1}$

by the equations derived in Sect. 3 [Eqs. (25), (20)–(22)]. To ensure that we enter the asymptotic behavior of these solutions, the transients were calculated for a time up to 10^{12} ns. The Monte Carlo simulation is seen to be close to the transient obtained by Eqs. (20)–(22). The relevant two asymptotics are in perfect agreement with the numerical results as shown in the figure.

Figures 2a–d show Monte Carlo simulations illustrating the impact of various parameters entering our model. Figure 2a shows transients obtained for four different values of the initial electron and hole density n_0. The transients are affected primarily at short times, while they converge at long times approaching the recombination-controlled asymptotics. In Fig. 2b, we vary the density of nonradiative recombination centers. Here, the decay at short times remain unaffected but nonradiative recombination accelerates the decay at times between 1 μs and 1 ms.

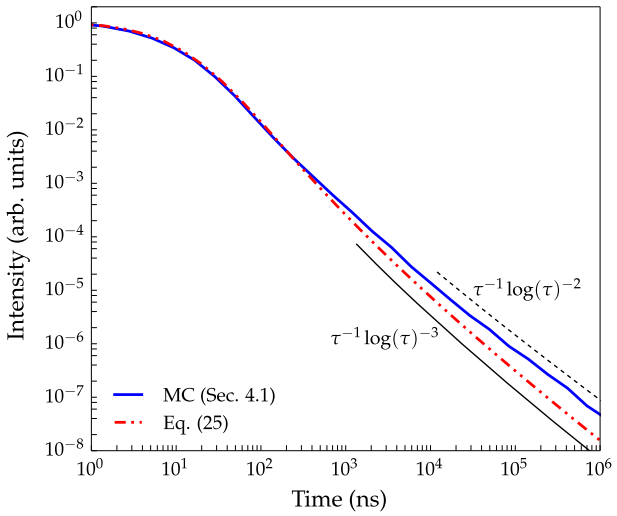

Fig. 3 (online colour) Photoluminescence transients for purely radiative recombination of spatially separated electrons and holes calculated by means of Eq. (25) and the Monte Carlo approach outlined in Sect. 4.1. The recombination-controlled asymptotics are indicated by the *thin black lines*. The transient obtained by the Monte Carlo approach closely approximates the experimentally observed behavior for (In,Ga)N/GaN quantum wells in Ref. [4]

Figures 2c, d address the impact of the diffusion of electrons. In both cases, diffusion speeds up the initial decay significantly, and ends up in a diffusion-controlled asymptotics $\sim t^{-3/2}$ already for very small diffusion coefficients. The inclusion of radiative recombination by tunneling in Fig. 2d results only in subtle changes of the overall dynamics. For diffusion coefficients larger than $1\,\mathrm{nm}^2\,\mathrm{ns}^{-1}$, the transients are basically identical. In these cases, electrons and holes will meet each other by diffusion and decay as an exciton faster than they are able to recombine radiatively via the inefficient tunneling process.

Finally, Fig. 3 shows transients for parameters chosen such as to approximate experimental results. For $a = 4\,\mathrm{nm}$, $B_0 = 0.04\,\mathrm{ns}^{-1}$, and $n_0 = 0.025\,\mathrm{nm}^{-2}$, we obtain a transient close to that shown in Ref. [4]. In particular, note the characteristic acceleration of the transient at intermediate times, followed by the slowdown at times longer than 300 ns. This behavior is not as pronounced in the solution of the approximate model represented by Eq. (25). To distinguish these two models experimentally, however, requires measurements with a high signal-to-noise ratio over at least five orders of magnitude of intensity, such as indeed presented in Ref. [4]. For unambiguously determining the functional form of the asymptotics, even this measurement range may not suffice.

6 Summary and conclusion

We have developed an efficient Monte Carlo algorithm for the simulation of the electron-hole recombination and diffusion dynamics in the presence of nonradiative recombination centers in disordered media. To do so, we have described the concen-

trations of electrons, holes and recombination centers by a system of nonlinear Smoluchowski equations, and we have used a probabilistic interpretation of these equations to construct a suitable Monte Carlo algorithm. To avoid the time-consuming simulation of microscopic diffusion jumps, we have developed a variant of the "Random Walk on Spheres" technique which accelerates the algorithm significantly. To validate this algorithm, we have performed a statistical analysis based on the derivation of equations for the electron-electron, hole-hole, and electron-hole correlation functions. This analysis has also allowed us to derive the long-time asymptotics of the solution. We have performed simulations reproducing the experimental data available for (In,Ga)N/GaN quantum wells, the materials system used for solid-state lighting. We have shown that our model can reproduce these data, and we have presented simulations predicting the electron-hole dynamics for various different conditions which are experimentally accessible.

Acknowledgments KKS suggested the mathematical model, developed stochastic algorithms and codes for the efficient computation of the nonlinear Smoluchowski equations, and performed the correlation analysis with different levels of approximations. He kindly acknowledges support of the Russian Science Foundation under Grant 14-11-00083. OB and VMK formulated the physical problem, provided the relevant parameters and analyzed the physical consequences of the solutions. They acknowledge the support of the European Commission (FP7-NMP-2013- SMALL-7) under grant agreement no. 604416 (DEEPEN). We are indebted to Pierre Corfdir (PDI) for a critical reading of the manuscript. Special thanks are due to Felix Feix (PDI) for revising the code and suggestions resulting in a consistent treatment of electron diffusion.

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