Kinetics of geminate recombination of subdiffusing particles in the presence of interparticle interaction

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The kinetics of geminate subdiffusion-assisted reactions (SDARs) of interacting particles is analyzed in detail with the use of the non-Markovian fractional Smoluchowski equation (FSE). It is suggested that the interparticle interaction potential is of the shape of potential well and reactivity is located within the well. The reaction kinetics is studied in the limit of deep well, in which the FSE can be solved analytically. This solution enables one to obtain the kinetics in a simple analytical form. The analytical expression shows that the SDAR kinetics fairly substantially depends on the mechanism of reactivity within the well. Specific features of the kinetics are thoroughly analyzed in two models of reactivity: the subdiffusion assisted activated rate model and the first order reaction model. The theory developed is applied to the interpretation of experimental kinetics of photoluminescence decay in amorphous $\alpha$-Si:H semiconductors governed by geminate recombination of electrons and holes which are recently found to undergo subdiffusive relative motion. Analysis of results demonstrates that the subdiffusion assisted activated rate mechanism of reaction is closer to reality as applied to amorphous $\alpha$-Si:H semiconductors. Comparison of experimental and theoretical kinetics allowed for obtaining some kinetic parameters of the systems under study: the rate of escaping from the well and the parameter characterizing the deviation of the subdiffusive motion from the conventional one.

I. INTRODUCTION

Diffusion assisted reactions (DARs) is the important stage of a large number of chemical and physical condensed phase processes. In many of these processes the DARs are known to be strongly affected by interaction between reacting particles. The effect of the interaction on the DAR kinetics is actively studied both experimentally and theoretically for a long time.

In the case of conventional diffusion the problem of the analysis of DAR kinetics reduces to solving the Smoluchowski equation for the pair distribution function (PDF) of reacting particles. This equation is fairly complicated and can, in general, be solved only numerically. As for analytical study, usually it is made with the use of steady state analytical solutions. The general time dependent analytical solutions can be found only for very few interreaction potentials, for example, in the case Coulomb interaction. This solutions, however, are very cumbersome and complicated for applications.

Some years ago much more simple and rigorous method of analytical solution of the Smoluchowski equation was proposed, which is applicable in the practically interesting limit of deep well of attractive interaction (reactivity assumed to be localized in the well). The solution shows that the interaction strongly manifests itself in the reaction kinetics resulting in the long life time of particles within the well (i.e. caging). The time evolution of the PDF of pairs captured and reacting in the well appears to be non-exponential. This specific feature of the PDF time evolution shows itself, for example, in non-exponential kinetics of geminate DARs with the long time tail of inverse power type.

In this work we will consider the kinetics of geminate reaction of interacting particles undergoing subdiffusive motion. Recall that subdiffusion is a certain type of anomalous diffusion, which is characterized by the anomalously slow time dependence of the mean square of displacement $\langle r^2(t) \rangle \sim t^\alpha$ with $\alpha < 1$. Recently, the specific features of the kinetics of subdiffusion assisted reactions (SDARs) is a subject of active discussions. The anomaly of diffusion is shown to affect fairly strongly the reaction kinetics leading to the effective slowing down of the reaction at long times, to the strong fluctuations of concentrations of reacting particles at long times, etc.

In the absence of interparticle interaction (i.e. in the case of free subdiffusion) the time evolution of the PDF of subdiffusing particles is usually described by the analog of diffusion equation $\frac{\partial \rho}{\partial t} = \frac{1}{\Gamma(\alpha)} \nabla \cdot (\nabla \rho + \rho \nabla \mathbf{U})$ which is called fractional diffusion equation and in which the effect of diffusion anomaly shows itself in anomalously long time memory. The predictions of the theory based on fractional diffusion equation are analyzed in a large number of papers (see, for example, reviews [8] and [9]).

As for the SDARs of interacting particles, these processes are not studied theoretically yet. The kinetics of them is also determined by the corresponding PDF, but the PDF evolution is described by the fractional Smoluchowski equation. Similarly to the case of conventional diffusion, the factional equation is much more complicated for numerical and analytical analysis than that for free diffusion. In this work we propose the analytical solution of the fractional Smoluchowski equation in the limit of deep well, assuming the reactivity to be localized within the well. With the use of the obtained solution...
the PDF evolution and the kinetics of geminate SDARs are analyzed in detail in this limit.

The analysis shows that, unlike the case of conventional DAR, the SDAR kinetics strongly depends on the mechanism of reaction. In particular, the kinetics appears to be essentially different for two models of reactivity: the subdiffusion assisted activated rate model [or, more generally, the kinetically (i.e. mobility) controlled reaction model] and the first order reaction model. This strong difference enables one to select the realistic reaction model and the first order reaction model. This more generally, the kinetically (i.e. mobility) controlled reaction mechanism of reaction. In particular, the kinetics appears to be essentially different for two models of reaction.

The obtained results are applied to the interpretation of the experimental kinetics of photoluminescence decay in amorphous semiconductors $\alpha$-Si:H resulting from geminate recombination of photoexcited electrons ($e$) and holes ($h$). Electrons in these semiconductors are known to be highly mobile, undergoing subdiffusive (dispersive) migration, while holes are nearly immobile. Recently, fairly detailed experimental investigation of the kinetics of geminate $e-h$ recombination at different temperatures has been carried out and experimental results have been semiquantitatively described within the free subdiffusion model. It is worth noting, however, that the kinetics of the process under study is, clearly, significantly affected by the Coulomb $e-h$ interaction which is quite strong in the investigated semiconductors: for dielectric constant $\varepsilon \approx 10$ characteristic for these semiconductors and temperatures $T < 300 K$ the Onsager radius (distance, at which the Coulomb interaction is equal to the thermal energy) is estimated as $l_c > 50 \text{Å}$.

Analysis of theoretical kinetic dependences, obtained in this work, shows that the activated rate model describes the experimental results better than the first order reaction one. This analysis allowed us to obtain the characteristic model parameters of the system: the parameter $\alpha$ characterizing the diffusion anomaly, the rate of escaping from the $e-h$ interaction well, etc., which result in the best fitting, and estimated their dependence on temperature. The proposed interpretation is compared with another one applied in ref. [24] to treat some earlier experimental results on the same process.

II. DIFFUSION ASSISTED REACTIONS

We start our analysis with the discussion of geminate reactions of interacting particles assisted by conventional diffusion. The reacting particles are assumed to be spherically symmetric. We also assume that the interparticle interaction potential is spherically symmetric: $u(r) = u(r) = U(r)/(k_B T)$, where $r = |r|$ is the interparticle distance, and is of the type of potential well with the reaction barrier at short (contact) distance $r = d$, the bottom at $r = r_b$ (see Fig. 1). It is suggested, in addition, that the well is deep enough so that the activation energies of escaping from the well and reaction are large: $u_a = -u(r_b) \gg 1$ and $u(d) - u(r_b) \gg 1$. In this limit the characteristic time of reaction in the well is much larger than the time of equilibration in the well and the long distance (Coulomb) part of the potential can be characterized by the effective Onsager radius

$$l_c = \left[ \int_{r_b}^{\infty} dr r^{-2} e^{u(r)} \right]^{-1}. \quad (2.1)$$

nearly independent of $r_b$ [this radius satisfies the relation $u(l_c) \approx 1$]. Noteworthy is that in the deep well limit the explicit shape of the well of $u(r)$ at short distance turns out to be not important for the kinetics: it can be, for example, of parabolic shape with $r_b > d$ or edge type one with $r_b \approx d$ (see Fig. 1).

In the Markovian approach implied by the conventional diffusion approximations the DAR kinetics is described by the PDF $\rho(r, t)$ of reactive pairs, satisfying the kinetic equation

$$\dot{\rho}(r, t) = -\hat{L}\rho(r, t), \quad (2.2)$$

where $\hat{L}$ is the operator which determines space/time evolution of the system under study. The form of this operator depends on the process considered (see Sec. III).

In this work the observable under study is the geminate DAR kinetics, i.e. the time dependent probability $Y_r(t)$
of geminate reaction, which we will call the DAR yield. In our further analysis, however, it will be more convenient to analyze the DAR flux

\[ J_r(t) = \dot{Y}_r(t). \]  

To obtain the expression for DAR yield and DAR flux one needs to specify the model of reactivity. In our work we assume that the reactivity is localized within the well and consider two most well known models of reactivity: the diffusion assisted activated rate and first order reaction models. They correspond to two different reaction mechanisms: kinetically controlled (controlled by relative migration) and first order reaction controlled reactivity, respectively. Possible examples of these reaction models are discussed below as applied to analysis of experimental results (see Sec. IV). Here we will restrict ourselves to discussion of the mathematical details of the models.

1) **Activated rate model.** This model treats the DAR as a diffusive flux over a barrier located at the reaction surface [in the studied model of spherically symmetric particles this is the barrier at \( r = d \) (see Fig. 1)]. Some well known formulas for the reaction yield obtained in this model are presented below (in Sec. IIIB). The activated rate model is, actually, a particular example of the general class of kinetically controlled reaction models, which predict the reaction rate proportional to the diffusion coefficient, or more generally speaking, to the mobility of particles (Sec. IV).

2) **First order reaction model.** In this model the DAR flux \( J_r(t) \) is determined by the fluctuating rate \( k_r[r(t)] \) of first order reaction and is expressed in terms of the functional:

\[ J_r(t) = \left\langle k_r[r(t)] \right\rangle \exp \left(-\int_0^t \! \! \left[ k_r[r(\tau)] \right] \, d\tau \right) \bigg|_{r(t)} , \]

in which the average is made over the stochastic fluctuations of \( r(t) \) governed by process (2.2).

In the considered approach the DAR flux can be written in a universal form in terms of the the Green’s function \( \rho(r, r_i|t) \) of the stochastic Liouville equation

\[ \dot{\rho} = -[\mathcal{L} + k_r(r)]\rho + \delta(t)\delta(r - r_i) : \]

\[ J_r(t) = -\int_{r > d} \! \! \! dr \int_{r_d} \! \! \! dr_i \rho_i(r_i) \rho(r_i|t), \]

where \( \rho_i(r) \) is the initial spatial distribution of particles [naturally, in the activated rate model \( k_r(r) = 0 \)].

A. **Mechanisms of stochastic motion**

Here we will briefly discuss some useful models for description of relative jump-like stochastic motion of reacting particles and analyze the validity of the diffusion approximation for description of the process under study.

One of the most general models of spatial jump-like evolution of the system is based on the Kolmogorov-Feller approach in which

\[ \mathcal{L} = -w(1 - \mathcal{P}), \]

where \( w \) is the jump rate, for simplicity assumed to be independent of the coordinate, and \( \mathcal{P} \) is the matrix of transition probabilities satisfying the detail balance relation and the normalization condition which in the coordinate representation \( \mathcal{P}(r, r_i) \) for \( \mathcal{P} \) is written as

\[ \int dr \mathcal{P}(r, r_i) = 1. \]

In general, there is a large variety of jump models for \( \mathcal{P} \) satisfying above relations. Here we will discuss a class of models especially convenient for theoretical analysis. These models are based on the representation of the matrix \( \mathcal{P} \) in terms of the differential Smoluchowski-like diffusion operator

\[ \mathcal{L}\rho = -D \nabla r(\nabla_r \rho + \rho \nabla_r w), \]

in which \( \nabla_r \) is the gradient operator in \( \{r\} \)-space and \( D \) is the diffusion coefficient.

\[ \mathcal{P} = \tilde{\mathcal{P}}(\mathcal{L}) = \int_0^\infty \! \! \! d\tau e^{-\mathcal{L}\tau} P(\tau). \]

In the representation (2.10) the function \( P(\tau) \) is properly normalized: \( \int_0^\infty \! \! \! d\tau P(\tau) = 1 \), so that \( \mathcal{P} \) can be considered as the operator of diffusive evolution averaged over some distribution function \( P(\tau) \) of evolution times. Evidently, the operator \( \mathcal{P} \) (2.10), which has the form of the Laplace transform of \( P(\tau) \), satisfies the normalization relation (2.8).

The model (2.10) is very useful for the analysis of applicability of the diffusion (Smoluchowski) approximation which appears to be valid in a wide region of parameters of the model and times. The validity criterion can easily be obtained with the use of eq. (2.2) written for the Laplace transform in time \( \tilde{P}(r, \epsilon) = \int_0^\infty \! \! \! d\tau e^{-\mathcal{L}\tau} P(\tau) : \)

\[ \epsilon \tilde{P} = -w(1 - \tilde{\mathcal{P}}) \tilde{P}. \]

According to eq. (2.11) for small \( \epsilon/w \ll 1 \), when the left hand side of this equation is small, the operator \( 1 - \tilde{\mathcal{P}} \) in the right hand side can be expanded in \( \mathcal{L} \tau: 1 - \tilde{\mathcal{P}} \approx -\mathcal{L} \tau, \)

\[ \bar{\mathcal{L}} = \int_0^\infty \! \! \! dt t P(t) \]

is the average time of diffusion-like evolution resulting in the jump operator \( \mathcal{P} \). The effect of next orders of expansion of \( \mathcal{P} \) in \( \mathcal{L} \tau \) is evidently of higher orders in \( \epsilon/w \ll 1 \) and therefore is negligibly small. The correctness of this statement can also be demonstrated by expanding the solution of eq. (2.11) in the (complete) basis of eigenfunctions of the operator \( \mathcal{L} \).
The presented analysis shows that at relatively long times \( t > 1/w \) the kinetics of processes, governed by jump-like operator (2.10), is quite accurately described by the corresponding Smoluchowski equation.

In what follows we will restrict ourselves to this long time limit of the reaction kinetics and correspondingly to the Smoluchowski approximation. In addition, for simplicity, we will consider the spherically symmetric geminate processes which are described by distribution functions depending only on distance \( r = |r| \).

B. Equations of diffusion approximation and two-state model

In the considered case of spherically symmetric geminate reactions the PDF \( \rho(r,t) \), depending on the inter-particle distance \( r = |r| \), satisfies the Smoluchowski kinetic equation, which for

\[
\sigma(r,t) = r \rho(r,t)
\]

is written as

\[
\dot{\sigma} = D \nabla_r (\nabla_r \sigma + \sigma \nabla_r u) - k_r \sigma,
\]

where \( \nabla_r = \partial/\partial r \) and \( D \) is the diffusion coefficient.

The function \( \sigma(r,t) \) obeys the boundary conditions \( \sigma(r \to \infty, t) \to 0 \) and \( \sigma(r \to 0, t) \to 0 \), and the isotropic initial condition

\[
\sigma_i(r) = \sigma(r,0) = \delta(r-r_i)/(4\pi r_i)
\]

with \( r_i \sim r_b \) corresponding to the creation of particles within the well. This equation can also be represented in terms of the Laplace transform \( \tilde{\sigma}(r,\epsilon) = \int_0^\infty \sigma(r,\tau) e^{-\epsilon \tau} \):\n
\[
\epsilon \tilde{\sigma} - \sigma_i = D \nabla_r (\nabla_r \tilde{\sigma} + \tilde{\sigma} \nabla_r u) - k_r \tilde{\sigma}.
\]

This representation appears to be more convenient for our further analysis.

In general, eqs. (2.14) and (2.16) cannot be solved analytically. In the limit of deep well, however, the solution can be obtained in a simple form by expansion in a small parameter \( \tau_r/\tau_e \ll 1 \), where \( \tau_r \sim l_c^2/D \) is the time of equilibration within the well and \( \tau_e \sim r_e^{-u_a} \) is the time of escaping from the well.\n
Analysis of this solution shows that in the lowest order in the parameter \( \tau_r/\tau_e \) the Smoluchowski approximation (2.14) and (2.16) is equivalent to the model of two kinetically coupled states. This two-state model treats the process under study as transitions between the state within the well \((d < r < l_e)\), whose population is

\[
n(t) = 4\pi \int_d^{l_e} dr \sigma_r(r,t),
\]

and the state of free diffusion outside the well \((r > l)\) described by the distribution function \( C(r,t) = r^{-1} c(r,t) \).

The functions \( n(t) \) and \( c(r,t) \) satisfy simple kinetic equations \( \tilde{n}(\epsilon) \) which can be written in the most compact form in terms of Laplace transforms \( \tilde{n}(\epsilon) \) and \( \tilde{c}(r,\epsilon) \):

\[
\tilde{c} = 1 + [S_l^{-1} K_+ \tilde{c}(l_e,\epsilon) - (K_- + w_r) \tilde{n}] \quad (2.18a)
\]

\[
\tilde{c} = [D \nabla_r^2 \tilde{c} + (S_l K_- \tilde{n} - K_+ \tilde{c}) \delta(r - l_e)], \quad (2.18b)
\]

where \( S_l = (4\pi l_c)^{-1} \). The terms proportional to \( K_\pm \) describe the above-mentioned kinetic coupling (transitions) between the state within the well, located at \( r = l_e \), and the free diffusion state outside the well. In the considered limit \( \tau_r/\tau_e \ll 1 \) the transition rates \( K_\pm \) satisfy the relations:

\[
K_+ \to \infty \quad \text{and} \quad K_+/K_- = K_c = Z_w, \quad (2.19)
\]

where

\[
Z_w = \int_{d<r<l_e} dr r^2 e^{-u(r)}
\]

is the partition function for the well. Equations (2.18) are written for the initial condition

\[
n(0) = 1 \quad \text{and} \quad c(r,0) = 0.
\]

corresponding to the initial population of the well implied by eq. (2.15). As to the boundary conditions for \( c(r,t) \), they are given by \( l_e \nabla_r c(r,t) - c(r,t) |_{r=l_e} = 0 \) and \( c(r \to \infty) = 0 \).

The term \( w_r \tilde{n} \) in eq. (2.18a) describes the effect of the first order reaction in the well. In the considered (Markovian) diffusion approximation the two above-mentioned models of reactivity in the well result in the similar kinetic equations of the form (2.18). The only difference consists in the analytical expression for \( w_r \):

a. Activated reaction model \((k_r = 0)\). In the diffusion assisted activated reaction model, implying activated diffusive passing over the barrier at \( r \sim d \), one gets\n
\[
w_r = w_{ra} = \frac{D}{Z_w} \left( \int_{r \sim d} dr r^{-2} e^{u(r)} \right)^{-1}.
\]

As we have already mentioned above this model is an example of a large class of kinetically controlled reaction models, in which the reaction rate is determined by the mobility of particles: \( w_r \sim D \). Some examples of such models are discussed in Sec. IV.

b. First order reaction model \((k_r \neq 0)\). In the model describing the reaction as a first order process with rate \( k_r(r) \) the expression for \( w_r \), for example, in quite realistic case of relatively small values of \( k_r \) within the well, is

\[
w_r = w_{r_0} = \left< k_r \right> = \frac{1}{Z_w} \int w_k k_r(r) r^2 e^{-u(r)}. \quad (2.23)
\]

In this equation the parameter \( w \), used as a limit of integration, denotes integration over the region near the bottom of the well \((d < r < l_e)\).
In both models the Markovian DAR kinetics, expressed in terms of the Laplace transform \( \tilde{J}_r(\epsilon) \) of the DAR flux \(^{(2.3)}\) is proportional to the Laplace transform \( \tilde{n}(\epsilon) \) of the well population:

\[
\tilde{J}_r(\epsilon) = w_r \tilde{n}(\epsilon),
\]

(2.24)
i.e to analyze the reaction kinetics one should find the time dependent well population \( n(t) \).

For our further discussion it is convenient to represent equations \(^{(2.18)}\) in a matrix form:

\[
e\tilde{R} = -(\hat{\Lambda} + \tilde{W}_r)\tilde{R} + \tilde{R}_t, \quad \text{where} \quad \tilde{R} = (\tilde{n}, \tilde{c})^T,
\]

(2.25)

\[
\tilde{R}_t = (1, 0)^T \quad \text{is the vector representation of the initial condition \(^{(2.21)}\)},
\]

(2.25)

\[
\hat{\Lambda} = \begin{bmatrix}
K_- & -S_l^{-1}K_+ \int dr \delta(r - l_c) \\
-S_l K_- \delta(r - l_c) & -D \nabla_r^2 + K_+ \delta(r - l_c)
\end{bmatrix},
\]

(2.26)

and

\[
\tilde{W}_r = \begin{bmatrix}
w_r & 0 \\
0 & 0
\end{bmatrix}.
\]

(2.27)

This representation shows that equations \(^{(2.18)}\) can be considered as a two-state analog of the SLE \(^{(2.5)}\), corresponding to the two-state model of \( k_r \)-fluctuations in the functional \(^{(2.3)}\). Naturally, in this SLE the effect of reactivity is represented by \((2 \times 2)\)-matrix of the form \(^{(2.27)}\).

It is also worth emphasizing that the two-state model \(^{(2.18)}\) is actually based on the approximate replacement of the Smoluchowski operator \( \tilde{L}_r = D \nabla_r (\nabla_r + \nabla_u) \) by the simpler one \( \hat{\Lambda} + \tilde{W}_r \), operating on the reduced PDF \( \tilde{R} \). The approximation is valid in the limit of deep well, when all eigenvalues of \( \tilde{L}_r \) representing population relaxation within the well are much larger than the lowest one, which describes quasistationary escaping from the well and reaction. In the deep well limit the effect of high eigenvalues is negligibly small and the kinetics of the process is quite accurately treated within the approximation taking into account the coupling of the lowest state in the well with the continuum of states outside the well (which is just equivalent to the proposed two-state model\(^{(2)}\)). This main idea of the proposed method is important point in our further analysis of SDARs.

It is also important to note that in the deep well limit the two-state model is valid independently of the shape of the well near the bottom of the well (see Fig. 1).

The shape manifests itself only in the value of partition function \( Z_w \) defined in eq. \(^{(2.20)}\).

### C. Reaction kinetics

In accordance with the relation \(^{(2.21)}\) the DAR kinetics [i.e. the reaction flux \( J_r(t) \)] is determined by that of the well population \( n(t) \) which can be obtained by solution of eqs. \(^{(2.18)}\) and subsequent inverse Laplace transformation\(^{6,7}\):

\[
n(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \exp(\epsilon t) \, d\epsilon \quad \frac{\exp(\epsilon w_r + \frac{2}{\lambda} K_r V(\epsilon))}{\epsilon + w_r + \frac{2}{\lambda} K_r V(\epsilon)}.
\]

(2.28)

The function \( V(\epsilon) \) is directly related to the Green’s function of the operator which controls diffusion outside the well [with the reflective boundary condition \( (l_r \nabla g - g)|_{r=l_e} = 0 \)]

\[
g(r, r_i | \epsilon) := \langle r | (\epsilon + D \nabla_r^2)^{-1} | r_i \rangle : \quad V(\epsilon) := 1/g(l_r, l_e | \epsilon) = D[l_e^{-1} + (\epsilon/D)^{1/2}].
\]

(2.29)

(2.30)

Substitution of the expression \(^{(2.30)}\) into eq. \(^{(2.28)}\) leads to the following formula for the well population \( n(t) \):

\[
n(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \frac{\exp(\epsilon w_{e,0})}{1 + \epsilon + \gamma \epsilon^{1/2}} \exp\frac{\epsilon}{\epsilon \pm \sqrt{\epsilon}} \, d\epsilon,
\]

(2.31)

where \( \gamma = \sqrt{(w_{e,0}/w_{e,0})(t^2_{e,0} w_{e,0} / D)} \), \( \epsilon_{\pm} = \frac{1}{2} \gamma \pm i \sqrt{1 - \frac{1}{4}\gamma^2} \) are the roots of equation \( z^2 - \gamma z + 1 = 0 \), and

\[
\Phi_{\pm}^2(z) = [1 - \text{erf}(\epsilon \pm \sqrt{\epsilon})] \exp(\epsilon^{2/\gamma} z).
\]

(2.32)

The rate

\[
w_{e,0} = w_e + w_r
\]

(2.33)

is a sum of the rate of escaping from the well

\[
w_e = \frac{D}{Z_w} \left( \int_{r_0}^{r_e} dr r^{-2} e^{u(r)} \right)^{-1} = D l_e / Z_w
\]

(2.34)

and the rate of reaction in the well \( w_r \) [see eqs. \(^{(2.22)}\) and \(^{(2.23)}\)].

Specific features of the well population \( n(t) \) are analyzed in detail in refs. 6 and 7. In general, this function is non-exponential and the analytical properties are essentially determined by the parameter \( \gamma \) introduced in eq. \(^{(2.31)}\). The physical meaning of this parameter is clear from the relation \( \gamma = \sqrt{(w_{e,0}/w_{e,0})(t^2_{e,0} w_{e,0} / D)} \sim l_e / l_D \), in which \( l_D = \sqrt{D/w_0} \) is the average distance of diffusive motion during the life time \( \tau_0 = w_0^{-1} \) of the particle in the well. This relation shows that if the well is deep enough, \( l_D \gg l_e \) and therefore \( \gamma \ll 1 \). The parameter \( \gamma \) controls the qualitative change of the analytical behavior of the kinetics:

\[
n(t) = \exp(-w_{e,0} t) \quad \text{at} \quad \tau \lesssim \ln(1/\gamma),
\]

(2.35)

\[
n(t) \sim 1/t^{3/2} \quad \text{at} \quad \tau \gg \ln(1/\gamma).
\]

(2.36)
In the limit of small \( \gamma \ll 1 \) more detailed analysis of the dependence \( n(t) \) is possible, however, here we will restrict ourselves to these simple relations only.

In addition to the kinetic time dependences the steady state characteristics of type of the total DAR yield \( Y_r^{\infty} = \gamma_r(t \to \infty) \) are also of certain interest for further applications. They can easily be obtained with the use of expressions derived. For example,

\[
Y_r^{\infty} = \int_0^{\infty} dt J_r(t) = w_r \tilde{n}(0) = \frac{u_r}{w_r + u_r}.
\]

III. SUBDIFFUSION ASSISTED REACTIONS

A. Equations in subdiffusion approximation

In the case of subdiffusive motion the evolution of \( \rho(r, t) \) is described the subdiffusion (fractional) variant of the Smoluchowski equation. This equation can be derived within the continuous time random walk approach for jump-like motion of particles assuming long time tailed behavior of the probability density function of waiting times for jumps and using formula (2.10) for the distribution of jumps \( \mathcal{P}(r, \tau) \). Similar to the case of the conventional diffusion considered (Sec. II A) the fractional Smoluchowski equation is obtained in the limit of relatively weak deviation of \( \rho(r, t) \) from the equilibrium PDF, when \( (\tau L) \rho \ll \rho \) and therefore one can expand \( \tilde{\mathcal{P}} = \tilde{L} \) in powers of \( \tilde{L} \):

\[
\tilde{\sigma} = D_s t^{-\alpha} \nabla_r \sigma + \sigma \nabla_r u),
\]

where \( \nabla_r = \partial/\partial r \), \( D_s \) is the subdiffusion coefficient, and

\[
\alpha = \frac{1}{\Gamma(1 - \alpha)} \int_0^t \frac{dt'}{(t - t')^{1 - \alpha}} \sigma(r, t')
\]

is the Riemann-Liouville fractional derivative with \( \alpha < 1 \). The function \( \sigma(r, t) \) satisfies the boundary and initial conditions similar to those used for the case of conventional diffusion [see Sec. IIB].

The corresponding equations for the Laplace transform \( \tilde{\sigma}(r, \epsilon) \) is written as

\[
\tilde{\sigma} - \sigma = D_s \epsilon^{1 - \alpha} \nabla_r (\sigma \nabla_r u).
\]

It is seen that from mathematical point of view in the absence of reaction the difference of the subdiffusion variant of the Smoluchowski equation for Laplace transform \( \tilde{\sigma} \) from the conventional Markovian equation reduces to the replacement of \( D \) with \( D_s \epsilon^{1 - \alpha} \). The problem becomes more complicated, however, when one is going to analyze the effect of reactivity. Below we will obtain the kinetic equations describing the SDAR processes in the two models of reactivity proposed above: the activated rate model and the model of first order reaction.

Since the coordinate part of the subdiffusion differential equations (3.1) and (3.3) coincides with that of the Smoluchowski equation (2.14) and (2.16) the two state model is still applicable though with some modification of the form of time dependences or, as applied to equations for Laplace transforms, the dependences on the parameter \( \epsilon \) [i.e. the functions \( \tilde{n}(\epsilon) \) and \( \tilde{c}(r, \epsilon) \)].

B. Activated rate reaction in the well

In the model of subdiffusion assisted activated rate reaction in the well the corresponding fractional analog of the kinetic equation for \( \tilde{R} = (\tilde{\eta}, \tilde{c})^T \) can be written by taking into account that the fractional Smoluchowski equations (3.2) and (3.3) differ from the conventional ones only in operators which determine the time dependence of the PDF. As for the coordinate operators, they are similar in both equations differing only in diffusion coefficients: \( L_{rs} = D_s \nabla_r (\nabla_r + \nabla_r u) \sim L_r = D \nabla_r (\nabla_r + \nabla_r u) \). This fact is important because the two-state model actually reduces to the special two-state representation of the coordinate operator. Correspondingly, if in the deep well limit this model is valid in the case of conventional diffusion it is also valid as applied to the subdiffusion processes since the validity conditions (emphasized in the end of Sec. IIB) appeal only to the characteristic properties of the coordinate operator (eigenvalues, describing population relaxation in the well, should be much larger than the lowest eigenvalue representing the escape rate). The similarity of coordinate operators: \( \tilde{L}_{rs} = (D_s/D) L_{rs} \), enables us to easily obtain the corresponding subdiffusion variant of the two-state representation of \( L_{rs} \):

\[
\Lambda_s + \tilde{W}_r = (D_s/D)(\Lambda_s + \tilde{W}_r),
\]

in which we set \( \tilde{W}_r = [(D_s/D) \tilde{W}_r]^{1/\alpha} \) to reveal the anomalous dimensionality of \( D_s \). Thus, finally, we arrive at equation

\[
[\epsilon + \epsilon^{1 - \alpha}(\Lambda_s + \tilde{W}_r)] \tilde{R} = \tilde{R}_i, \text{ where } \tilde{R} = (\tilde{\eta}, \tilde{c})^T
\]

\[
\tilde{R}_i = (1, 0)^T
\]

is the initial condition [see eq. (2.20)],

\[
\Lambda_s = -S_i K^{1/\alpha} \int d\delta(r - l_c) - S_i K^{1/\alpha} \int d\delta(r - l_c),
\]

and

\[
\tilde{W}_r = \begin{bmatrix} u_r & 0 \\ 0 & 0 \end{bmatrix}
\]

is the matrix of SDAR rates in the well.

The parameters in these equations are similar to those in eqs. (2.18) [see eqs. (2.19) and (2.20)], except the effective rate \( \tilde{w}_r \), (of anomalous) reaction in the well modeled by subdiffusive passing over the barrier at \( r \sim d \):

\[
\tilde{w}_r = \frac{D_s}{Z_w} \left( \int_{r = d} dr r^{-2e^{\nu(r)}} \right)^{-1/\alpha}.
\]

Recall that in our calculation we take the limit (2.19), i.e. \( K^{1/\alpha} \to \infty \) with \( K_c = K^{1/\alpha} / K^{1/\alpha} = Z_w \).
Solution of eqs. (5.4) and inverse Laplace transformation give for the well population
\[
n(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\exp(\varepsilon t)}{\varepsilon + \varepsilon^{-\alpha} \left[ w_{\alpha_+} \varepsilon_+^2 + l_2^2 K_\varepsilon V(\varepsilon) \right]} \, d\varepsilon. \tag{3.8}
\]

As in the case of conventional diffusion the function \( V(\varepsilon) \) is determined by the Green’s function of the operator describing subdiffusive relative motion of particles outside the well [with the reflective boundary condition \( (l_\varepsilon \nabla g - g)_{|t=t_0} = 0 \)]
\[
g(r, r_0|\varepsilon) = |r| \left( \varepsilon^2 + D_0 \nabla^2 \right)^{-1} |r_0| \tag{3.9}
\]

\( V(\varepsilon) = 1/g(l_\varepsilon, l_\varepsilon|\varepsilon) = D_0 l_\varepsilon^{-1} + (\varepsilon^2 / D_0)^{1/2} \tag{3.10} \)

Formulas (3.3) - (3.11) reduce the problem of calculating \( n(t) \) to the evaluation of the Green’s function (3.9) and subsequent inverse Laplace transformation (3.8).
\[
n(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\exp[\varepsilon(w_\alpha t)]}{\varepsilon^{\alpha-1} + \varepsilon^{\alpha} + \gamma_a \varepsilon^{\alpha/2}} \varepsilon_a \Phi_a(w_\alpha t) - \varepsilon_a \Phi_a(w_\alpha t) \varepsilon_a^+ - \varepsilon_a^-, \tag{3.11}
\]

where
\[
\gamma_a = (l_\varepsilon^2 w_{\varepsilon_+}^{\alpha} / D_\varepsilon)^{1/2} (w_{\varepsilon_-} / w_\alpha)^{\alpha/2}, \tag{3.12}
\]

the parameters \( \varepsilon_a^{\pm} = \frac{1}{2} \gamma_a \pm i \sqrt{1 - \frac{1}{4} \gamma_a^2} \) are similar to those introduced earlier [see eq. (2.31)], and \( \Phi_a^{\pm}(\tau) \) are expressed in terms of the Mittag-Leffler function \( L_{\alpha/2}(-x)^{\pm} \).
\[
\Phi_a^{\pm}(t) = L_{\alpha/2}[\varepsilon_a^{\pm} (w_\alpha t)^{\alpha}] = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\exp[\varepsilon(w_\alpha t)]}{\varepsilon^{\alpha} + \varepsilon_a^{\pm} \varepsilon^{1-\alpha/2}} \tag{3.13}
\]

It is easily seen that for \( \alpha = 1 \) \( \Phi_a^{\pm}(t) \) coincide with functions defined in eq. (2.32). Similarly to formulas for conventional diffusion in eq. (3.11) we have introduced the rate
\[
w_{\alpha_+} = (w_{\varepsilon_+}^{\alpha} + w_{\alpha_+}^{\alpha})^{1/\alpha} \tag{3.14}
\]
in which
\[
w_{\varepsilon_+} = (D_\varepsilon l_\varepsilon / Z_{\varepsilon_+})^{1/\alpha} \tag{3.15}
\]
is the rate of subdiffusive escaping from the well and \( w_{\alpha_+} \) is the anomalous SDAR rate in the well [see eqs. (3.7)].

Unlike the conventional diffusive well depopulation kinetics (2.31), the subdiffusive kinetics (3.11) is non-exponential at all times. Moreover, in the most interesting case of small \( \gamma \ll 1 \) with high accuracy one can neglect the last term in denominator of the integrand in eq. (3.11) and get the expression
\[
n(t) \approx L_{\alpha_a}[-(w_\alpha t)^{\alpha}], \tag{3.16}
\]

which predicts the behavior \( n(t) \sim (w_\alpha t)^{-\alpha} \) at \( w_\alpha t \gg 1 \).

With the use of relation (2.24), which in the subdiffusion case is written as
\[
\tilde{J}_r(\varepsilon) = \varepsilon^{1-\alpha} w_{\alpha_r} \tilde{\eta}(\varepsilon), \tag{3.17}
\]

formula similar to eq. (3.8) can also be obtained for the SDAR flux \( J_r(t) \)
\[
J_r(t) = \frac{w_{\alpha_+}}{2\pi i} \frac{w_{\alpha_-}}{w_0} \int_{-\infty}^{\infty} \left[ \frac{\exp[\varepsilon(w_\alpha t)]}{1 + \varepsilon^{\alpha} + \gamma_a \varepsilon^{\alpha/2}} \right. \varepsilon^{\alpha_+} \varepsilon_a^{\pm} \Phi_a(w_\alpha t) - \varepsilon_a^{\pm} \Phi_a^{\pm}(w_\alpha t) \left. \varepsilon_a^+ - \varepsilon_a^-, \right] \tag{3.18}
\]

This expression shows the important peculiarity of the activated variant of the SDAR kinetics: the time dependence of the SDAR flux \( J_r(t) \) is essentially different from that of the well population \( n(t) \). Unlike relations obtained above for the conventional diffusion and prediction of the expression (3.11), in the considered limit \( \gamma \ll 1 \) at relatively short times \( t \lesssim 1/\gamma^{1/\alpha} \) the flux \( J_r(t) \sim \tilde{L}_{\alpha_a}[-(w_\alpha t)^{\alpha}] \) so that the time dependence of the SDAR flux is of inverse power type:
\[
J_r(t) \sim (w_\alpha t)^{-(1+\alpha)} \quad \text{for } 1 < w_\alpha t < \gamma^{-2/\alpha}, \tag{3.19}
J_r(t) \sim (w_\alpha t)^{-(1+\alpha/2)} \quad \text{for } w_\alpha t > \gamma^{-2/\alpha}. \tag{3.20}
\]

Interestingly the expressions for steady state characteristics like the total SDAR yield \( Y_r^{\infty} = Y_r(t \to \infty) \) are fairly similar to those derived above (see Sec.II) for the case of conventional DAR, though with \( w_{\varepsilon_+} \) and \( w_{\varepsilon_-} \) replaced by \( w_{\alpha_+} \) and \( w_{\alpha_-} \), respectively. In particular,
\[
Y_r^{\infty} = \int_0^{\infty} dt J_r(t) = \tilde{J}_r(0) = \frac{w_{\alpha_+}}{w_{\alpha_-} + w_{\alpha_+}}. \tag{3.21}
\]

C. First order reaction in the well

In the case of first order reaction in the well the SDAR kinetics is described by more complicated non-Markovian stochastic Liouville equation (2.14) which is the non-Markovian analog of eq. (2.11). In what follows, however, for simplicity we will restrict ourselves to the more simple two-state model whose subdiffusive variant is represented by eqs. (3.11). With the use of the method recently proposed in ref. [7] the corresponding two state non-Markovian kinetic (stochastic Liouville) equation for the vector \( \tilde{R} = (\tilde{n}, \tilde{c})^T \) can be derived in the following form:
\[
(\tilde{\Omega} + \tilde{\Lambda}^{1-\alpha}) \tilde{R} = \tilde{R}_i, \quad \text{where } \tilde{R} = (\tilde{n}, \tilde{c})^T, \tag{3.22}
\]
$\tilde{R}_i = (1, 0)^T$ is the initial condition,

$$\tilde{\Omega} = \epsilon + \tilde{W}_{r_f}, \text{ and } \tilde{W}_{r_f} = \begin{bmatrix} w_{r_f} & 0 \\ 0 & 0 \end{bmatrix}$$  \hspace{1cm} (3.23)

with $w_{r_f}$ defined in eq. (2.23).

Solution of this equation (in the limit $K^2 - K^2 \rightarrow \infty$ with $K^2 / K^2 = Z_w$) yields for the population of the well

$$n(t) = \frac{1}{2\pi i} \int_{-i\infty+\epsilon_j}^{i\infty+\epsilon_j} \frac{d\epsilon}{\epsilon^{1-\alpha}} \exp[(\epsilon - \epsilon_j)(w_{r_f} t)] \left[ 1 + \frac{\epsilon^\alpha + \gamma_j (\epsilon - \epsilon_j)\alpha/2}{1 + \epsilon^\alpha + \gamma_j (\epsilon - \epsilon_j)\alpha/2} \right].$$  \hspace{1cm} (3.24)

where

$$\epsilon_j = w_{r_f} / w_{e_s} \text{ and } \gamma_j = (T^2 w_{e_s}^2 / D_s)^{1/2}.$$  \hspace{1cm} (3.25)

Naturally, in the model of first order reaction the SDAR flux $J_r(t)$ is proportional to the well population:

$$J_r(t) = w_{r_f} n(t)$$  \hspace{1cm} (3.26)

similarly to the case of conventional diffusion.

Expressions (3.24) and (3.26) show that in the first order reaction model the SDAR kinetics differs from that obtained in the activated rate model [eqs (3.11) and (3.13)]. In particular, in the most interesting limit of small $\gamma_j \ll 1$ and for weak reactivity $w_{r_f} \ll w_{e_s}$ at short times $t < 1/(\gamma_j^{1/\alpha} w_{e_s})$

$$J_r(t) = w_{r_f} n(t) \approx w_{r_f} e^{-w_{r_f} t} L_\alpha[-(w_{e_s} t)^\alpha].$$  \hspace{1cm} (3.27)

More detailed analysis allows one to conclude that for $\gamma_j \ll 1$ over a wide region of times the time dependence of the SDAR flux is of inverse power type given by:

$$J_r(t) \sim t^{-\alpha} \text{ for } 1 < w_{e_s} t < \gamma_j^{-2/\alpha}, w_{e_s} / w_{r_f};$$

$$J_r(t) \sim t^{-1+1/\alpha} \text{ for } \gamma_j^{-2/\alpha} < w_{e_s} / w_{r_f}, \gamma_j^{-2/\alpha}.$$  \hspace{1cm} (3.28)

In other words, the long time behavior of $J_r(t)$ is similar in both models of reactivity, however at intermediate times the first order reaction model predicts slower kinetics than the activated rate one.

It is of certain interest to note that despite this difference in the SDAR kinetics the formula for the SDAR yield in the first order reaction model appears to coincide with that in the the activated rate model [see eq. (3.21)]:

$$Y_{r,v} = w_{r_f}^2 / (w_{r_f}^2 + w_{e_s}^2).$$

IV. ELECTRON-HOLE RECOMBINATION KINETICS

Here we will apply the obtained results to describing the kinetics of photoluminescence decay in amorphous semiconductors $a$-Si:H governed by subdiffusion assisted geminate recombination of photogenerated charge carries: electrons ($e$) and holes ($h$) [23,24,25]. The geminated $e$-$h$ recombination is strongly influenced by the attractive interaction $u(r)$ of $e$- and $h$-quasiparticles. At $e$-$h$ distances $r$ much larger than the size $l_{bh}$ of these quasiparticles the potential $u(r)$ is of the Coulomb form

$$u(r) \sim -l_c/r, \text{ with } l_c = e^2/(\epsilon_s k_B T),$$  \hspace{1cm} (4.1)

where $l_c$ is the Onsager radius [see eq. (2.1)] and $\epsilon_s \approx 10$ is the static dielectric constant for the semiconductor $a$-Si:H. Note that $l_{bh}$ is probably of order of the mean spacing in this semiconductor. Is also worth noting that at short distances $r \sim r_s < l_{bh}$ the potential is expected to be somewhat flattened because of the effect of finite size of charge distribution at these distances resulting in the finiteness of e-$h$-interaction at $r < l_{bh}$.

This effect can qualitatively be understood by considering the potential of interaction between point-like charge with the homogeneously changed sphere which is known to be of parabolic shape and finite at the center of the sphere. In the case of quantum particles the qualitatively same effect is also expected as one can see from the analysis of the electronic terms of the simplest molecules $H_2$ and $H_2^+$.

However, independently of behavior of the potential at short distances this potential is of the shape of the potential well (see Fig. 1) and in the deep well limit the theory proposed is valid independently of the well shape, as it has been mentioned above. The characteristic features of well shape manifest themselves only in the value of the partition function $Z_w$ and thus in values of rates $w_r$ and $w_e$ which are considered as adjustable parameters anyway.

It is worth noting that the Onsager radius $l_c$ is fairly large for the systems considered (with the dielectric constant $\epsilon_s \approx 10$) for the temperatures of experiments, $100 < T < 170$ (K), we get $140 > l_c > 80$ (A). In such a case the assumption that the geminate $e$-$h$ pairs are initially created within the well, i.e. at $r < l_c$ looks quite reasonable. The large value of the Onsager radius $l_c > r_s \sim l_{bh}$ implies the large depth of the potential well. In addition, large value of $l_c$ also ensures the validity of the diffusion approximation for description of the jump like motion of electrons applied in our analysis.

The exact shape of the potential and the mechanisms of jump-like motion at short distances $r \sim d < l_{bh}$, which, according to the above discussion, determines the mechanism of reaction in the well, can hardly been found explicitly. One of the goals of this section is the selection of the proper model of recombination process in the well, i.e., actually, selection of mechanism of reactivity, by comparison of predictions of the models with experimental results. In our analysis we will consider two of them discussed above:

a) First order reaction model. This model assumes that $e$-$h$ recombination in the well is the first order reaction whose rate is determined by the direct charge-transfer exchange interaction $X$ [the model implies the exponential distance dependence of the reaction rate $k_r(r) \sim$
exp(−r/rd]). This model is traditionally applied to describing the kinetics of condensed phase recombination. 

b) Activated rate model. The activated rate model is based on the mechanism of diffusive passing over a barrier which can be considered as kinetically controlled reaction (i.e., reaction controlled by mobility of particles). This model is quite realistic as applied to charge recombination in polar liquids in which the mean-force interaction potential of charges is known to have a fairly high potential barrier at short distances r ∼ d3/2. As for solids, one can hardly expect similar barrier in them, in general. Note, however, that the activated passing over the barrier is only one example of kinetically controlled reaction processes. Another example is the reactions limited by jump-like migration with small jump rates at short distances (naturally, one should take into account the discreteness of space at short distances). In such a case, these jumps of small rate can control the rate of reaction. The small value of jump rates at short distances can result from large difference in energy (energy gap) between the states of migrating electron and the final electron state in the ion pair. Moreover, the rate of jumps into this final reacting state (this jumps are probably irreversible) can be small both for positive and negative energy difference (of large absolute value). In the case of small values of rates of irreversible jumps into the final state the kinetics of the processes is correctly described by the Smoluchowski-like equation with partially reflective boundary condition, in which the reflective term is determined the above-mentioned small (reactive) rate of jump in the final state. Analysis of this equation shows that the two-state representation of this equation (for the Laplace transform R) is also of the form (2.23) and (3.4) in the cases of normal diffusion and subdiffusion, respectively. It is important to emphasize that in the subdiffusion variant of the two-state model the term, describing the kinetically controlled reaction in the well, is represented in the form ε1−αWα, i.e. contains the factor ε1−α describing the long time memory effects caused by anomalous migration. In other words, the kinetic equations (2.23) and (3.4) derived in the activated rate model appear to be valid for a number of models of kinetically controlled reactions in the well, some of which are quite applicable to solid state recombination reactions.

To apply these models one needs to specify the kinetic scheme of the process under study which allows one to relate the calculated kinetics functions with the observed dependences. The scheme was, actually, implied in the analysis made in refs. [21] and [26]. We assume that the e-h recombination results in the formation of the fluorescing product (P) whose population will be hereafter denoted as np(t). The luminescence intensity I(t) can easily be determined from the simple kinetic scheme:

\[ e + h \xrightarrow{J_e(t)} P \xrightarrow{w_{f}+w_{d}} P_0 \] (4.2)

which takes into account formation of the product P with the rate Je(t) within the well, radiationless deactivation into the ground state P0 with the rate w_d and fluorescence with the rate w_f.

In a quite realistic limit of fast fluorescence and deactivation when w_d + w_f ≫ w_r, w_r, the kinetic equation for the population np(t)

\[ \dot{n}_P = -(w_d + w_f)n_P + J_e(t), \] (4.3)

corresponding to the scheme (4.2), predicts

\[ I(t) \sim w_f n_P(t) \sim \left[w_f/(w_d + w_f)\right]J_e(t). \] (4.4)

This formula shows the time dependence of the observed luminescence intensity I(t) is proportional to that of the recombination (DAR) flux discussed above and therefore gives the direct information on the kinetics of geminate e-h recombination.

Noteworthy is that usually in the interpretation of experimental results radiationless deactivation is not taken into consideration. We mentioned this process only for the sake of completeness and because typically it is faster than fluorescence transitions. It is seen from the proposed kinetic scheme that the considered experiments
The observed fairly substantial difference between predictions of the two models allows for selecting the most realistic model by comparison with experimental results. Close inspection shows that the very smooth experimental dependences \( J_r(t) \) are much closer to those predicted by the activated rate model rather than by the first order reaction one. This means that the activated rate model seems to be closer to reality as applied to the process under study.

The fitting of theoretical \( J_r(t) \)-dependences to experimental data (see Fig. 3) enables one to obtain corresponding parameters of the activated rate model: \( \alpha \), \( w_0 \), and \( \gamma_a \). Unfortunately, because of the very smooth shape of the kinetic dependences these parameters can be determined fairly approximately. The results can be summarized as follows:

1. The obtained values of \( \alpha \) increase approximately linearly with the increase of \( T \) in agreement with results of earlier analysis.\(^{25}\) As for absolute values of the parameter \( \alpha \) they are about 10 – 15% lower than those known for the same system from time-of-flight experiments.\(^{25}\) This deviation, however, is quite within the accuracy of our method (estimated to be \( \sim 20\% \)).

2. The rate \( w_0(T) \) increases with temperature \( T \), as expected: \( w_0(105K) \approx 3.3 \cdot 10^4 \text{s}^{-1} \), \( w_0(145K) \approx 1.3 \cdot 10^4 \text{s}^{-1} \), and \( w_0(170K) \approx 3.3 \cdot 10^3 \text{s}^{-1} \).

3. The parameter \( \gamma_a \) is found to depend on temperature and \( \gamma_a(T) \) increases with \( T \): \( \gamma_a(105) \approx 0.2 \), \( \gamma_a(145) \approx 0.3 \), and \( \gamma_a(170) \approx 0.4 \) (the estimated accuracy of these values is about 30%). This behavior of \( \gamma_a(T) \) can be qualitatively interpreted within the proposed model. Under quite reasonable assumption of small reaction rate in the well, \( w_{ra} \ll w_{es} \) when \( w_{ra} \approx w_{es} \), one gets for the ratio

\[
\frac{\gamma_a(T)}{\gamma_a(T_0)} \approx \left( \frac{T}{T_0} \right) \left( \frac{w_{es}(T)}{w_{es}(T_0)} \right)^{\alpha}.
\]

In deriving this relation we took into account that \( \ell_e(T)/\ell_e(T_0) = T_0/T \) and assumed that \( D_s \) depends on temperature weaker than other (rate) parameters. In any case the temperature dependence \( \gamma_a(T) \) is mainly determined by that of \( w_{es}(T) \).

Estimation [using eq. (4.5)] yields: \( \gamma_a(170)/\gamma_a(105) \approx 1.40 \) and \( \gamma_a(145)/\gamma_a(105) \approx 1.31 \). The corresponding values, obtained from fitting kinetic curves, are given by: \( \gamma_a(170)/\gamma_a(105) = 1.6 \pm 0.2 \) and \( \gamma_a(145)/\gamma_a(105) = 1.4 \pm 0.2 \). Unfortunately low accuracy of extracted parameters of the model does not allow unambiguous test of predicted characteristic dependences.

Concluding this section it is worth discussing the results of our analysis and comparing them with those obtained in the early work \cite{24} (see also ref. \cite{23}), in which the kinetics of the same process, geminate e-h recombination in amorphous semiconductors a-Si:H, is investigated both experimentally and theoretically in a fairly wide region of temperatures: \( 8 < T < 150 \text{K} \).

One of principle differences of the interpretation, presented this work, from our study lies in the applied model of migration of recombining charges in the disordered semiconductors. In the work \cite{23} the analysis has been made within the Markovian model implying the conventional Smoluchowski equation of type of eq. (2.14) for the PDF, whereas in our study the migration is assumed to be non-Markovian and is described with the use of the subdiffusion model. The difference between these two descriptions, evidently, shows itself in the long time behavior of the recombination kinetics. Both models predict the inverse power type dependence of the reaction yield on time \( J_r(t) \sim 1/t^{1+\alpha/2} \), however in the Markovian case \( \alpha = 1 \) while in the non-Markovian (subdiffusion) one \( \alpha < 1 \). Analysis of recent experimental measurements of the recombination kinetics\(^{25}\) shows that as applied to charge migration in amorphous a-Si:H semiconductors the subdiffusion model is more realistic than the Markovian model. This conclusion is strongly supported by recent time-of-flight measurements of transient currents in these semiconductors.\(^{25}\) Moreover, it is worth
mentioning that close inspection of experimental results presented in the work [24] indicates some deviation of the long time part of the recombination kinetics from the predicted dependence \(1/t^{3/2}\). It is also seen that at temperatures \(T \geq 60\) K the long time part is better described by the function \(1/t^{1+\alpha/2}\) with \(\alpha < 1\).

The intermediate part of the luminescence decay (i.e. \(e - h\) recombination) kinetics is described in ref. [24] by equation of type of eq. (2.13) with \(u(r) = l_e/r\) and \(k_r \sim e^{-r/r_c}\). This complicated equation is solved approximately by reducing it to the free diffusion one (which in turn is solved within the prescribed diffusion approximation) and then evaluating the effect of the Coulomb potential perturbatively. The weakness of the effect of the interaction results from the assumed fairly strong reactivity at short distances, i.e. fast reactive disappearance of pairs which is expected to be insignificantly affected by the potential. This assumption is, however, very restrictive because in the process under study the Coulomb interaction is quite strong: even at highest temperatures studied, \(T \approx 150\)K, for realistic values of the contact distance \(d \approx 10\)A and dielectric constant \(\varepsilon \approx 10\) the dimensionless well depth is fairly large, \(u(d) = U(d)/(k_BT) \approx 10\). As for lower \(T \approx 10\)K, the dimensionless well depth at these temperatures is even much (15 times) larger than that at \(T \approx 150\)K.

The observed reasonable accuracy of the perturbative solution of the Smoluchowski equation is due assumed fairly strong and long distant tunneling rate \(k_r \sim \exp(-r/r_c)\), with the tunneling length \(r_c \approx 11\)A. So large tunneling length corresponds to a very small electron localization energy \(E_l \approx 0.094\) eV in amorphous a-Si:H, which can easily be estimated by the relation \(r_c \approx r_B \sqrt{E_H/E_l}\) where \(r_B \approx 0.5\) A and \(E_H \approx 13.5\) eV are the Bohr radius and the ionization energy of hydrogen atom, respectively. The localization energy obtained appears to be very close to the thermal energy \(E_{th} = 0.026\) eV corresponding to room temperature \(T = 300\) K. Such a small value of \(E_l\) does not look quite realistic though some arguments in favor of this estimate have been presented in ref. [24].

In our interpretation, instead of assuming very small value of \(E_l\) we properly described the effect of the well resulting from the attractive Coulomb interaction and treated the reactivity suggesting it to be weak enough to neglect its manifestation during the time of population relaxation within the well. Because of long life time of pairs in the well, however, this relatively weak reactivity strongly manifests itself in the recombination kinetics leading to more smooth recombination kinetics at intermediate times than that predicted by free diffusion model in agreement with experimental results.

The analysis and comparison with results of experiments at relatively high temperatures \(T \geq 100\) K demonstrate that the proposed subdiffusion variant of the two-state model makes it possible to reproduce the behavior of the experimental luminescence decay kinetics (i.e. \(e - h\) recombination kinetics) both at intermediate and long times thus describing fairly accurately the kinetics in the whole region of experimentally investigated times.

Of certain interest is the observed luminescence decay kinetics at very low temperature \(T = 8\) K, the slope of which in a semilogarithmic scale [i.e. the slope of the dependence \(\ln(I(t))\) appeared to change non-monotonically with time at intermediate times. In ref. [24] such a behavior is described assuming the recombining pairs to be nearly immobile. In this case the kinetics is determined by the specific features of \(k_r \equiv k_r(r)\) dependence and the initial DPF \(\rho_0(r) = \rho(r, t = 0)\), which in ref. [24] is chosen to accurately fit the experimental kinetics.

It is worth noting that in the proposed two-state model similar non-monotonic behavior of the slope of \(\ln(I(t))\)-dependence is predicted in the first order reaction model (see Fig. 2). Such a behavior found without special assumptions on the initial PDF. However one has to assume that at low temperatures the first order reaction mechanism of reactivity becomes more efficient than the kinetically controlled reaction one (which seems to be of higher efficiency at high temperatures). In the interpretation within the first order reaction model one should also take into account possible distribution of coordinates of the bottom of the well which, for sure, will lead to the distribution of average recombination rates. This distribution can somewhat modify the kinetics as in the case of immobile reacting pairs.

V. CONCLUSIONS

This work concerns the analysis of the kinetics of geminate SDARs of interacting particles. The interaction potential is assumed to be attractive and of the well shape. The effect of this interaction is shown to reduce to the formation of the quasistatic state within the well (cage), which essentially controls the SDAR kinetics. The reaction is suggested to occur only in the well. Two models of reactivity in the well are discussed: the activated rate (or kinetically controlled reaction) and the first order reaction models. The results obtained have been used for the analysis of the geminate electron-hole recombination in amorphous semiconductors a-Si:H. This analysis have shown that the first (activated rate) model is able to describe the experimental recombination kinetics better than the second one and therefore can be considered as more appropriate as applied to the processes in amorphous a-Si:H semiconductors at not very low temperatures.

Comparison of experimental data with theoretical results have enabled us to obtain the values of characteristic parameters of the system under study within the proposed model. Unfortunately very smooth experimental kinetic time dependences does not allow for accurate enough determination of the parameters. In addition the experimental results presented in refs. [19] and [24] cover only relatively narrow temperature region in which parameters of the model do not change strongly.
For the same reasons it is, strictly speaking, hardly possible to make absolutely unambiguous conclusions in favor of any of two above-mentioned reactivity models. The specific features of the recombination kinetics at intermediate times predicted in the first order reaction model, which seemingly disagree with those found experimentally, can, nevertheless, be strongly smoothed in the presence of the distribution of kinetic parameters of the two-state model (average reaction rate $w_{r,j}$ and the escaping rate $w_{e,r}$). Such a distribution is quite natural for studied amorphous semiconductor.

The results of comparison show that more extensive experimental investigations in a wider temperature range are desirable. These studies would provide us with more detailed information on the mechanisms of migration and interaction of quasiparticles in amorphous semiconductors which would allow for making more reliable conclusions about these mechanisms.

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