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on a disordered linear-chain lattice**

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To investigate the kinetics of photoexcited states in MX chain compounds the diffusion-controlled irreversible reaction of $A + A \rightarrow 0$ on a disordered linear lattice is examined by numerical simulation, where A and 0 denote the photoexcited state and its annihilation, respectively. The lattice disorder is introduced by irregular energy barriers of which the height obeys a Gaussian distribution around a given value. As the irregularity evolves the survival probability $S(\zeta)$, $\zeta = N_0^2 D t$, of A is transformed from Torney-McConnell's form or its modified one into the Kohlrausch form $S(\zeta) = \exp[-(\zeta/\zeta_{1/e})^\beta]$, so that $S(\zeta)$ becomes still more nonexponential, where N_0 , D , and t are the initial density, diffusion coefficient, and reaction time, respectively. The argument β is reduced as if the fractal dimension of the lattice is reduced from unity. Concurrently, the parameter $\zeta_{1/e}$ increases, so that the $1/e$ decay time τ at a given temperature increases significantly. As long as, however, the mean height of the barriers remains unchanged, the temperature dependence of τ is not altered by the irregularity. The present results are consistent in various respects with the decay properties of long-lived solitons observed in degenerated MX chain compounds.

I. INTRODUCTION

Nonequilibrium kinetics of quasiparticles states in nature often encounters the problem of an irreversible reaction of random walkers. To treat the diffusion-controlled irreversible reactions, one has to solve for the diffusion equation with adequate boundary and initial conditions incorporated. In conventional analyses of decay phenomena of electric excitations in solids we assume implicitly that the reaction in question is homogeneous during the whole course of the process. For bimolecular reactions in such a special situation, the survival probability S of a particle at time t after the start of reaction is given by¹

$$S(t) = \frac{1}{1 + N_0 \xi(t)}, \quad (1)$$

where N_0 is the initial density and $\xi(t)$ is the time integral of the rate coefficient of the reaction. If the rate coefficient is constant, being equal to c , Eq. (1) is reduced to a familiar form of $S(t) = (1 + N_0 c t)^{-1}$.

In a microscopic view, however, diffusion-controlled reactions are spatially nonhomogeneous and do not obey Eq. (1). There is no general approach to the nonequilibrium kinetics of diffusion-controlled reactions, and thus the problem of random walk has still been the subject of much recent interest.² Nonhomogeneous reactions are known to cause a distinct deviation of S from the t^{-1} power law which is postulated by Eq. (1). In fact, as for the bimolecular reactions of $A + A \rightarrow 0$, where A and 0 denote the reacting particle and its annihilation, respectively, taking place on an infinitely long, continuous medium of one-dimension, a good approximate solution is given by the Smoluchowsky-Noyes formula^{3,4}

$$S^{\text{SN}}(\zeta) = \frac{1}{1 + \sqrt{32\zeta/\pi}}, \quad \zeta = N_0^2 D t, \quad (2)$$

where D is the diffusion coefficient of a particle. Torney and McConnell have developed the stochastic theory for this reaction to show that S is given exactly by⁴

$$S(\zeta) = S^{\text{TM}}(\zeta) \equiv e^{8\zeta} \operatorname{erfc} \sqrt{8\zeta}, \quad (3)$$

where $\operatorname{erfc} x$ is the complementary error function defined as $1 - \operatorname{erf} x$. The nature of the kinetic process is manifested by the dimensionless time variable ζ that is proportional to N_0^2 and by a strongly nonexponential time evolution of $S(\zeta)$. Subsequently several groups of workers have extended the theory to the reactions taking place on a long periodic lattice.⁵⁻⁷

Another important ingredient for nonexponential temporal behavior is the disorder of the potential energy of the medium which governs the motion of reacting particles. In amorphous semiconductors, for instance, the photoluminescence and photoconduction intensities and/or the photoinduced dielectric relaxation obey the Kohlrausch decay law

$$S(t) = e^{-(t/\tau)^\beta}, \quad 0 < \beta < 1, \quad (4)$$

or the power law of

$$S(t) = C t^{-\alpha}, \quad 0 < \alpha < 1, \quad (5)$$

where τ and C are constants. These functions can be expanded by the Laplace transform into a continuous series of $e^{-\nu t}$ with a given distribution function of ν .⁸ This consequence tells us that a nonexponential behavior may result from superposition of exponential decay functions with different life times $1/\nu$'s. Theoretically, these decay laws are

realized by pseudomolecular reactions of excited charge carriers.⁹ In such reactions β and α depend on the dimensionality of the medium. Furthermore, if the medium has a fractal character, the fractal dimension is directly reflected in the values of β and α .¹ There are, however, not many studies on the physical roles of the randomness in nonequilibrium relaxation phenomena of electronic excitations in solids other than amorphous materials.

Photoexcited solitons and polarons in conjugated polymers¹⁰⁻¹⁶ and *MX* chain compounds¹⁷⁻¹⁹ exhibit strikingly nonexponential decay profiles. Here we are concerned with the solitonic excitations created by a continuous irradiation with a cw blue light in single crystals of a degenerated *MX* chain compound $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$, where (en) denotes ethylenediamine. Those excitations can be annihilated only through mutual collisions in the course of random walks on the linear chain lattice. Since the chain lattice has local disorders serving as energy barriers of the order of 0.5 eV, the nonequilibrium states have an exceedingly long lifetime: The $1/e$ decay time τ depends on samples but is typically of the order of 10 min at room temperature, becoming infinitely long below 150 K.¹⁷ When the barriers are uniform the observed $S(t)$ agrees with $S^{\text{TM}}(\zeta)$ given by Eq. (3) well. Interestingly, when the barriers are irregular, $S(t)$ is changed into the Kohlrausch form given by Eq. (4), and at the same time, τ is elongated by an order of magnitude regardless of temperature.^{17,19} Viewed from the fact that very similar characteristics of τ are observed also in $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$,^{20,21} the underlying kinetic mechanism is likely to be common to solitonic photoexcitations in degenerated *MX* chain compounds, particularly the PtCl compounds.

What is specific to the decay kinetics of solitonic photoexcitations in the degenerated *MX* chain compounds is that the spatial nonhomogeneity of potential energies due to lattice disorders is concurrent with the nonhomogeneity of reactions due to random walks. There have been a few attempts of numerical simulation of the power decay laws of photoexcitations in disordered CH_n polymers.^{22,23} To date, however, no theories which adequately describe the kinetics of the long-lived photoexcitations in the *MX* chain compounds are available. To obtain an insight, therefore, into the properties of those photoexcitations we perform a numerical simulation of $S(t)$ of the $A+A \rightarrow 0$ reaction on a locally disordered linear-chain lattice. Our concern is to investigate how $S(t)$ is influenced by the irregularity of the energy barriers. The model of the calculation is described in Sec. II. The results are discussed in Sec. III and are compared with experiments in Sec. IV. This study is summarized in Sec. V.

II. MODEL

We deal with the aforementioned bimolecular reaction $A+A \rightarrow 0$ of particles moving on a ring of a chain lattice of which all sites are divided by the intersite energy barriers as shown in Fig. 1(a). The lattice sites are periodically arrayed with a spacing of a . In addition the height of the energy barriers is assumed to be fluctuated with a Gaussian distribution around the central height E_0

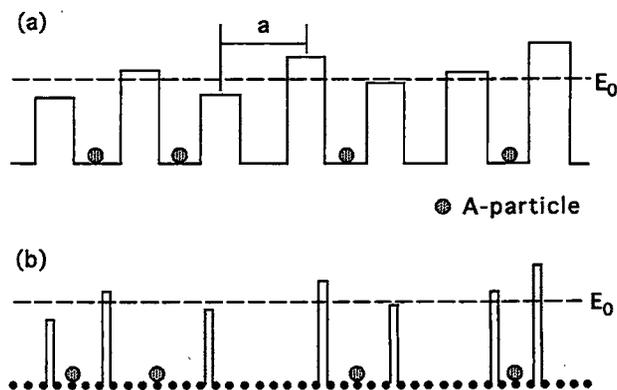


FIG. 1. (a) A model of a disordered linear-chain lattice and (b) a schematic representation of the *MX* chain lattice with local disorders. The solid circles in (b) denote *M* atoms.

$$g(E) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(1/2)[(E-E_0)/\sigma]^2}, \quad 0 \leq \sigma \leq E_0. \quad (6)$$

The particles hop from site to site across these barriers at the rate

$$w = w_0 e^{-(E/kT)}, \quad (7)$$

where w_0 is the hopping-rate constant, k is the Boltzmann constant, and T is the lattice temperature. For $\sigma=0$, the definition of the hopping rate by Eq. (7) gives the diffusion coefficient of a particle to be

$$D = D_0 = a^2 w_0 e^{-(E_0/kT)}. \quad (8)$$

To model the degenerated *MX* chain compounds we suppose that the *MX* chains are divided into segments physically by irregular energy barriers, as shown in Fig. 1(b), due to some local disorders of the chain bonds.¹⁷ We suppose furthermore that the photoexcitations move very quickly in the segments so that their kinetics is governed by their random walks of jumping over the energy barriers. This situation corresponds just to the model shown in Fig. 1(a). The average length of the chain segments gives the lattice constant a of the present model.

The calculation is carried out with respect to a lattice ring comprised of 10^4 sites by the standard method. Initially, an even number of particles are placed at random on the lattice sites on the basis of binomial occupation. The reaction is assumed to take place instantaneously when two particles collide with each other. Therefore, once two particles meet on the same site, they are removed immediately from the lattice ring. The hopping-rate constant w_0 and mean height E_0 of energy barriers are fixed to be 10^6 step^{-1} and 0.40 eV, respectively. To investigate general properties of the kinetics of particles, the initial density N_0 , lattice temperature T , and magnitude σ of fluctuations of energy barriers are each changed in a wide range as follows: $N_0 a = 0.05, 0.10, 0.20, 0.30$, and 0.40; $T = 200, 225, 250, 273, 300$, and 350 K; $\sigma = 0, 0.01, 0.03, 0.05$, and 0.10 eV. For $N_0 a = 0.05$, to reduce statistical errors, calculations are also carried out by increasing the number of lattice sites to 2×10^4 .

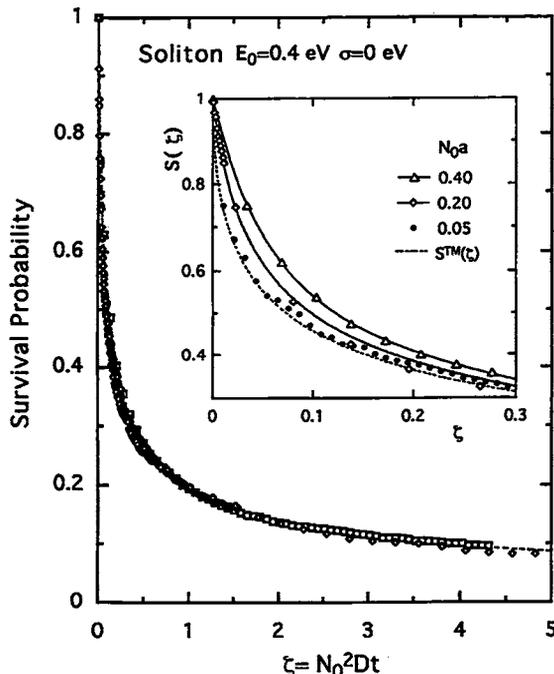


FIG. 2. $S(\zeta)$ in the uniform lattice ring. The markers are calculated values and the dotted line shows $S^{\text{TM}}(\zeta)$. The inset shows $S(\zeta)$ at different values of $N_0 a$ and $S^{\text{TM}}(\zeta)$ in a region $0 \leq \zeta \leq 0.3$.

III. RESULTS AND DISCUSSION

Previous theories, including the theory of Torney and McConnell, have mostly dealt with reactions in continuous media, although reactions of quasiparticles states in solids take place on lattice spaces. A continuous medium corresponds to a lattice with infinitesimal lattice constants. In a one-dimensional space, the reaction on a uniform and continuous ring, which is expressed by $S^{\text{TM}}(\zeta)$ given by Eq. (3), describes the reaction in the low-density limit $N_0 a \rightarrow 0$ on a discrete lattice ring. Lushnikov⁵ and Spouge⁶ have extended the theoretical treatment to a lattice medium and have shown exact solutions for $S(t)$ in special cases of $N_0 a = 0.5$ and 1.0 . Balding, Clifford, and Green have derived the general solution,⁷ but in the case of arbitrary $N_0 a$ their solution gives rise to the difficulty of evaluating a summation of an infinite number of terms consisting of modified Bessel functions at any values of t . Hence only little is known about the dependence of $S(\zeta)$ on $N_0 a$ in a lattice space. For this reason, we examine the reactions on the regular lattice of $\sigma = 0$ to begin with, and then proceed to irregular lattices of $\sigma \neq 0$.

A. Regular lattice

Figure 2 shows the plot of the results of calculation for various different values of $N_0 a$ and T to compare them with $S^{\text{TM}}(\zeta)$. The results of our calculation agree well with $S^{\text{TM}}(\zeta)$ in a wide range of ζ . Note that $S^{\text{TM}}(\zeta)$ falls vertically at $\zeta = 0$. This is because in a continuous ring there exist particles almost contacting each other even at $t = 0$. In a lattice ring, as shown in the inset of Fig. 2, the initial part of $S(\zeta)$ deviates significantly from $S^{\text{TM}}(\zeta)$. The deviation depends on $N_0 a$. As $N_0 a$ approaches zero, $S(\zeta)$ approaches $S^{\text{TM}}(\zeta)$ asymptotically. We note that the deviation is caused by the presence of a linear component at an early stage of decay.

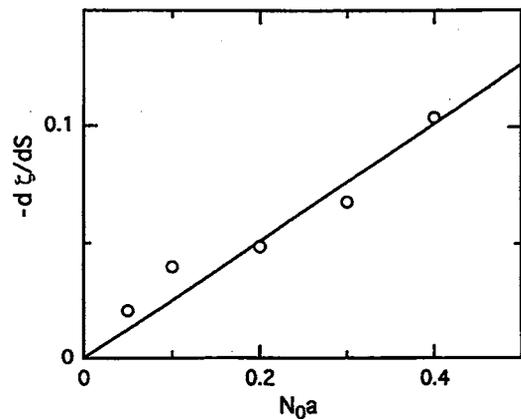


FIG. 3. Dependence of $-d\zeta/dS(\zeta)$ on $N_0 a$.

To quantify the linear component we employ a modified Smoluchowsky-Noyes formula

$$S(\zeta') = \frac{1}{1 + p\sqrt{\zeta'}}, \quad \zeta' = \frac{\zeta^2}{1 + q\zeta}, \quad (9)$$

where p and q are adjustable constants. Taking $q \rightarrow \infty$, while maintaining $p^2/q = 32/\pi$, one obtains the original formula given by Eq. (2). The solid lines in the inset of Fig. 2 show the best curves of $S(\zeta)$ calculated from Eq. (9). Figure 3 shows a plot of p^{-1} , which gives $-d\zeta/dS$ at the initial stage, as a function of $N_0 a$. The value of $-d\zeta/dS$ appears to be rather linear to $N_0 a$ with a coefficient of ~ 0.25 .²⁴ This finding implies that in a discrete lattice ring a finite waiting time is needed for particles residing on consecutive lattice sites to collide with each other and that the fraction of those closely assembling particles increases with increasing N_0 .

B. Irregular lattice

To extend our treatment to irregular lattices, we redefine $N_0^2 D_0 t$ as ζ . As the irregularity of energy barriers evolves, $S(\zeta)$ is found to become still more nonexponential. An example of the calculation on the σ dependence at $N_0 a = 0.1$ and $T = 250$ K is shown in Fig. 4. Figure 5, on the other hand, shows the results of calculations at various temperatures for the case of $(\sigma, N_0 a) = (0.03 \text{ eV}, 0.2)$.

Comparing Figs. 4 and 5 with Fig. 2, we note that the lattice disorder gives rise to the following striking effects.

(i) For a given value of $N_0 a$, the initial ζ -linear decay is faster than in the case of $\sigma = 0$, because the presence of barriers lower than E_0 promotes the reaction at an early stage. However, since the reactions at longer times are governed by the particles left between relatively high barriers, the $1/e$ decay parameter $\zeta_{1/e}$ increases from 0.195 ($\equiv \zeta_{1/e}^{\text{TM}}$) with increasing σ . As a consequence, $S(\zeta)$ can no longer be reproduced by $S^{\text{TM}}(\zeta)$ nor modified $S^{\text{SN}}(\zeta)$. Of course, as mentioned later again, the dependence of $\zeta_{1/e}$ on σ varies as $N_0 a$ increases.

(ii) Like the case of a regular lattice, the temperature effect on $S(\zeta)$ is manifested only by the temperature variation of ζ . Namely, the value of $\zeta_{1/e}$ and the functional form of $S(\zeta)$ are independent of temperature. The same is true for any set of σ and $N_0 a$ examined. Consequently, as shown in Fig. 6, regardless of the values of σ and $N_0 a$ an Arrhenius

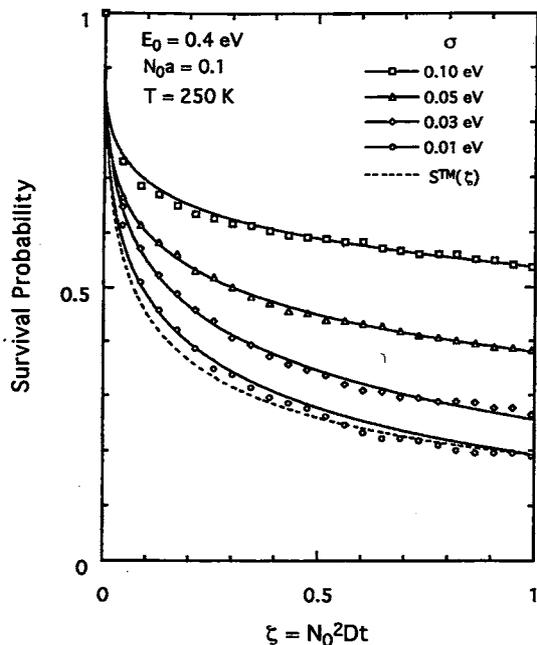


FIG. 4. $S(\zeta)$ at $N_0a=0.1$ and $T=250$ K in the irregular lattice ring of different values of σ . The dotted line shows $S^{TM}(\zeta)$.

plot of the temperature dependence of the $1/e$ decay time $\tau(\equiv \zeta_{1/e} N_0^{-2} D_0^{-1})$ yields a thermal activation energy that is almost identical with the value, 0.40 eV, employed for E_0 in the calculation.

Provided the particles do not react, it is expected from the distribution function $g(E)$ given by Eq. (6) that a particle has a mean diffusion coefficient of $D_0 \exp[(\sigma/kT)^2/2]$. The factor $\exp[(\sigma/kT)^2/2]$ depends strongly on temperature. In the case of $\sigma=0.05$ eV, for instance, $\exp[(\sigma/kT)^2/2]$ changes an order of magnitude upon a change in temperature from 200 to 300 K. When particles react, however, as manifested by our numerical calculation the irregularity of energy barriers yields no apparent influences on the diffusion coefficient of par-

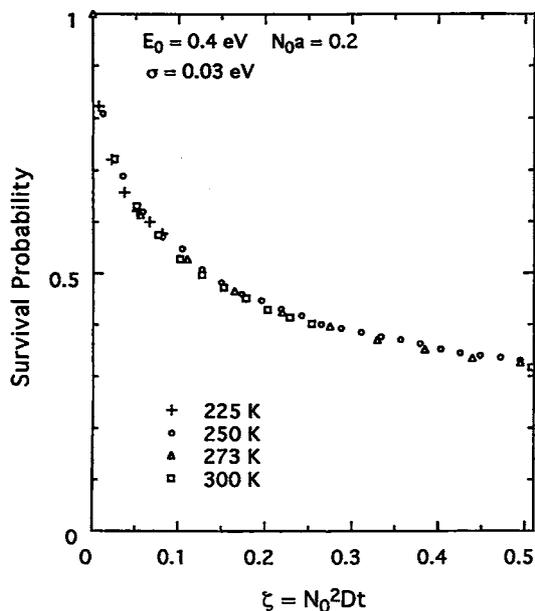


FIG. 5. $S(\zeta)$ at various temperatures in the irregular lattice ring in the case of $(\sigma, N_0a) = (0.03, 0.2)$.

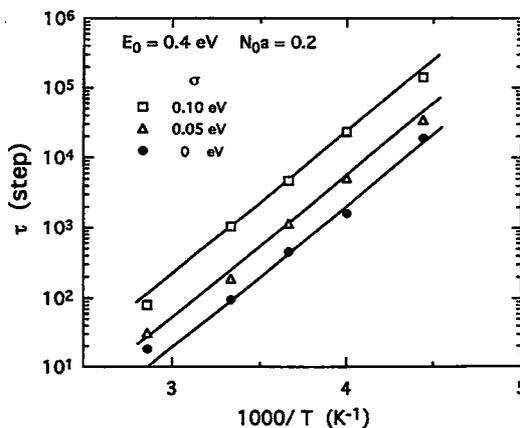


FIG. 6. Temperature dependence of τ at $N_0a=0.2$ and different values of σ .

ticles. Instead, the form of $S(\zeta)$ is changed. For $\sigma \geq 0.01$ eV, $S(\zeta)$ is found to be reproduced well by the Kohlrausch law of $S(\zeta) = \exp[-(\zeta/\zeta_{1/e})^\beta]$ in a wide range of ζ . Examples of the curve fits are shown in Fig. 4 along with the values of $S(\zeta)$ calculated for various σ at $N_0a=0.1$. For $\sigma \leq 0.03$ eV, the fits are yet imperfect, so that the fitted curves run below the true values as ζ goes beyond 1. For $\sigma \geq 0.05$ eV, however, $S(\zeta)$ can be reproduced very well by the Kohlrausch law up to $\zeta=5$ for any value of N_0a .

Figures 7(a) and 7(b) show the σ dependence of the relationships of $\zeta_{1/e}$ and β , respectively, to N_0a . For the above-mentioned reason, the fitting analysis for the cases of $\sigma \leq 0.03$ eV is made in a region of $0 \leq \zeta < 0.5$. We see from Fig. 7 that β , as well as $\zeta_{1/e}$, depends significantly on σ and N_0a . On increasing σ from 0.01 to 0.1 eV, β decreases distinctly from 0.4–0.5 to 0.2–0.3. The trapping process of a pseudomolecular reaction is known to obey the Kohlrausch law with $\beta = d^*/(d^*+2)$ in a space of the fractal dimension of d^* .^{1,25} It appears from the present calculation that β decreases with increasing σ as if the fractal dimension d^* is reduced by σ , even though the reaction treated here is strictly bimolecular and the disorder of the lattice is not necessarily fractal. In the present case we note that the dependence of β on σ is enhanced as N_0a increases.

The discrete-lattice effect discussed in the preceding subsection causes $\zeta_{1/e}$ to increase with increasing N_0a . A small but distinct increase seen for $\zeta_{1/e}$ at $\sigma=0.01$ eV in Fig. 7(a) is almost identical with that at $\sigma=0$ within errors of numerical calculations. The effect of σ on $\zeta_{1/e}$ becomes pronounced when σ is elevated from 0.01 eV. In Fig. 8 the values of $\zeta_{1/e}$ at various values of N_0a are plotted as a function of σ . This plot illustrates that if N_0a is given, $\zeta_{1/e}$ increases almost exponentially with σ . The increase in $\zeta_{1/e}$ leads to an enlargement of τ . Let us write the enlargement factor as

$$\gamma = e^{\eta\sigma/E_0}, \quad (10)$$

with a temperature-independent parameter η . Then Fig. 8 shows that if the initial density of particles is sufficiently small such that $N_0a < 0.1$, τ is enlarged by the order of 50 at $\sigma=0.1$ eV, yielding $\eta \approx 19$. As N_0a increases, since the average interparticle distance decreases, the probability that

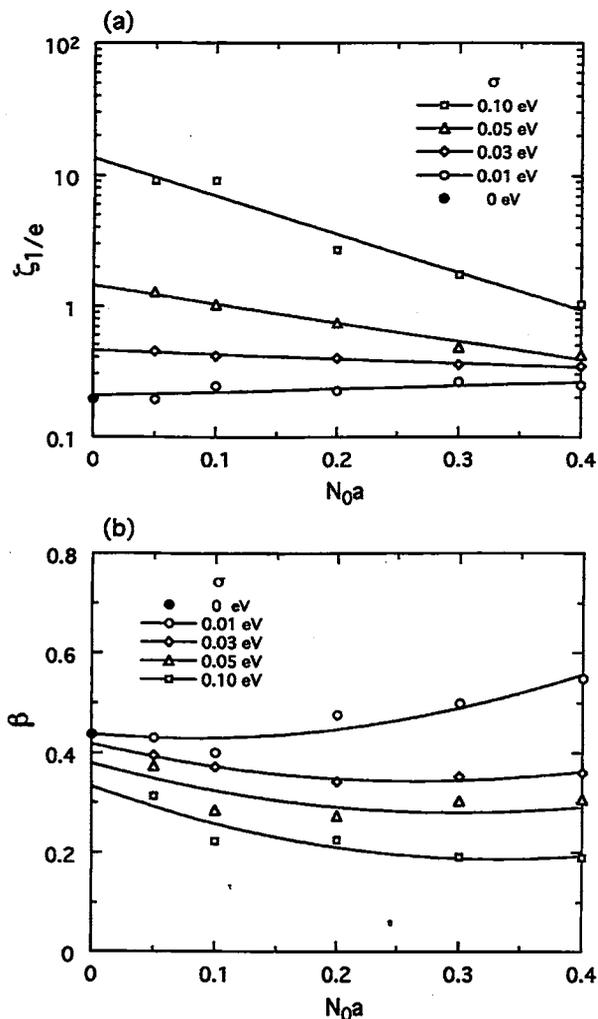


FIG. 7. Dependence of (a) $\zeta_{1/e}$ and (b) β on $N_0 a$ at different values of σ .

there are no barriers of $E > E_0$ between pairs of particles increases. Consequently, an increase in $N_0 a$ results in a reduction of η .

IV. COMPARISON WITH EXPERIMENTS

Crystals of $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$ can be classified in decay properties of long-lived photogenerated solitons

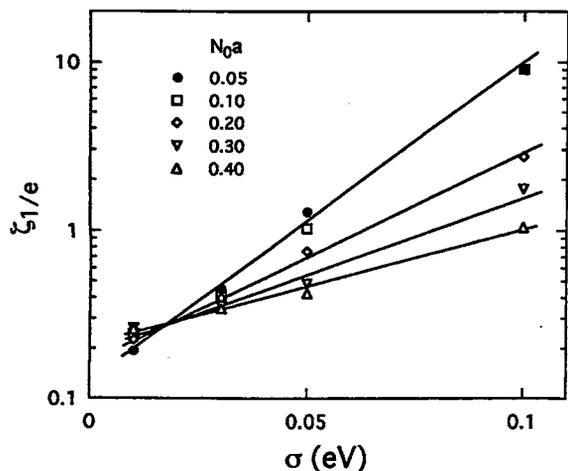


FIG. 8. Dependence of $\zeta_{1/e}$ on σ at various values of $N_0 a$.

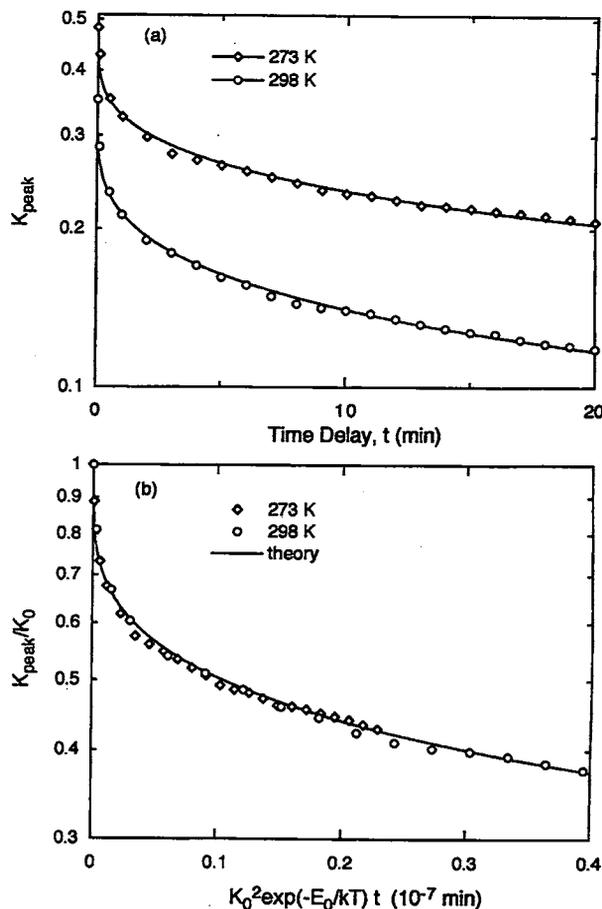


FIG. 9. (a) Time decay of peak absorbance K_{peak} of the photoinduced midgap band in $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$ at 273 and 298 K. (b) Normalized peak absorbance K_{peak}/K_0 versus $t' \equiv K_0^2 \exp(-E_0/kT)t$ with $E_0 = 0.45$ eV. The solid lines are the best fit of the Kohlrausch curve to the experimental data.

into two groups. In one group the decay obeys $S^{\text{TM}}(\zeta)$ given by Eq. (3) well,¹⁹ while in the other group the decay exhibits the Kohlrausch behavior.¹⁷ As for the former group of crystals it has been confirmed from measurements of the pumping power and temperature dependencies of the time decay that S is universal if the time variable is chosen as $\zeta \equiv N_0^2 D t$ with $E_0 \approx 0.45$ eV.¹⁹ This fact means that the crystals of the former group contain rather uniform energy barriers. Hence it is strongly suggested that the Kohlrausch behavior observed in the crystals of the latter group originates from random distribution of barrier height. The value of β of the Kohlrausch law is in a range 0.25–0.35. Viewed from the result of our numerical calculation [Fig. 7(b)] those crystals might contain irregular energy barriers of $\sigma/E_0 = 0.1$ –0.2.

Figure 9(a) shows typical examples of the experimental data¹⁷ on the time decay of the photoinduced midgap absorption in the irregular crystals. These data are obtained at 273 and 298 K by using a same sample. At both temperatures the decay of the photoinduced absorption is extremely nonexponential, slowing down so fast with time that it cannot be expressed by the Torney-McConnell and Sasaki-Nakagawa formulas. The point to observe is that the decay obeys the Kohlrausch law very well with $\beta = 0.26$ –0.28 at both temperatures and with $\tau = 35.7$ and 13.8 min at 273 and 298 K, respectively, as shown by solid lines in Fig. 9(a).

In Fig. 9(b) the experimental values of peak absorbance K_{peak} normalized by the respective initial value K_0 , being 0.48 and 0.35 at 273 and 298 K, respectively, are plotted as a function of $t' \equiv K_0^2 \exp(-E_0/kT)t$ with $E_0 = 0.45$ eV. Despite the large difference in the decay time τ , the data of K_{peak}/K_0 at the two temperatures lie on a single curve well. Consequently the Kohlrausch curve of S seems to be a universal function of ζ . This is consistent with our numerical calculation on the temperature dependence of $S(\zeta)$: As illustrated in Figs. 5 and 6, $S(\zeta)$ is insensitive to temperature and τ obeys the Arrhenius law well. Regarding the dependence on the initial density N_0 , we note that the difference in the value of K_0 by about 40% yields no significant influence on the observed $1/e$ decay parameter $\zeta_{1/e}$. This is also plausible from Fig. 7(a), because as far as $N_0 a$ is of the order of 0.1 or less a 40% change in N_0 gives only a small change in $\zeta_{1/e}$. On the other hand, $\zeta_{1/e}$ is sensitive to the irregularity of energy barriers. The present calculation on the σ dependence of S (Fig. 8) shows that in irregular crystals of $\sigma/E_0 = 0.1 \sim 0.2$, $\zeta_{1/e}$ should be significantly greater than the value $\zeta_{1/e}^{\text{TM}} = 0.195$ regardless of N_0 . Indeed, the experimental value of $\zeta_{1/e}$ at a given temperature is an order of magnitude greater than that of homogeneous crystals.¹⁹

V. SUMMARY

We have examined the kinetics of the diffusion-controlled reaction of $A + A \rightarrow 0$ on a disordered linear-chain lattice by numerical simulation. We have introduced irregular energy barriers between consecutive lattice sites. The A particles are rendered to perform thermally activated random walks on this lattice. In the present study the irregularity of energy

barriers is assumed to obey a Gaussian distribution around a central energy E_0 .

If the half width σ of the Gaussian distribution is sufficiently small, the survival probability $S(t)$ of a particle at a time t agrees well with the Torney-MacConnell formula or a modified Smoluchowsky-Noyes formula. As σ increases, $S(t)$ is transformed into the Kohlrausch form of $S(\zeta) = \exp[-(\zeta/\zeta_{1/e})^\beta]$ with $\zeta = N_0^2 D_0 t$, where N_0 and D_0 are the initial density and specific diffusion coefficient, respectively. The $1/e$ decay parameter $\zeta_{1/e}$ enlarges exponentially with increasing σ , while the argument β decreases to make $S(\zeta)$ still more nonexponential. The enlargement factor of $\zeta_{1/e}$ exceeds 50 if σ/E_0 exceeds 0.25. Nevertheless, both $\zeta_{1/e}$ and β are independent of temperature, so that the $1/e$ decay time is reduced with elevating temperature as $D_0^{-1} \sim \exp(E_0/kT)$.

These findings are consistent with experimental decay properties of long-lived photoexcited solitons in degenerated MX chain compounds. Since our model is not restricted to the MX chain compounds, the present results will be applicable to diffusion-controlled annihilation reactions of solitonic excitations in various disordered one dimensional systems.

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