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ON THE THEORY OF POINT DEFECT RECOMBINATION IN CRYSTALS

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A new approach to the diffusion-limited reaction kinetics for particles migrating by random walks on discrete lattice sites and reacting when two particles occupy the same site is extended to a more general case of a large reaction radius and applied to the problem of the recombination rate of point defects in cubic lattices. Numerical calculations correctly reproduce the analytic expressions in the limit cases considered in previous work and in the general case represent a step-wise dependence of the reaction rate on the recombination radius.

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1. INTRODUCTION

The kinetics of an irreversible diffusion-controlled bimolecular reaction $A + B \to C$ (where C does not affect the reaction) is described by the rate equation

$$\dot{n}_A(\mathbf{r},t) = \dot{n}_B(\mathbf{r},t) = -K_{AB} n_A(\mathbf{r},t) n_B(\mathbf{r},t), \qquad (1)$$

where n_A and n_B are the respective concentrations (numbers of particles per unit volume) of reacting A and B particles, which diffuse freely, and K_{AB} is the reaction constant [1]. This equation is also applicable to the reaction of point defects, vacancies, and interstitials ($V + I \to 0$) and annihilation in crystals produced by means of high-energy particles or electrons [2].

In the continuum approach, the reactant particles are represented as points or spheres undergoing spatially continuous Brownian motion, with chemical reactions $A + B \to C$ occurring instantly when the particles pass within a specified reaction radius R_{AB} between their centers. A method for calculating the reaction rate of reaction partners migrating by three-dimensional diffusion was developed in Refs. [3, 4] by generalizing the Smoluchowski theory for coagulation of colloids [5, 6]. In this method, which stipulates that the local reaction rate is equal to the diffusive current of particles, the radius of the activated complex (or the "reaction radius") corresponds to the "influence-sphere radius" in the Smoluchowski theory (equal to the sum of the radii of two colliding Brownian particles, $\tilde{R} = R_A + R_B$).

This traditional ("diffusion") approach was critically analyzed in our paper [7]. In particular, it was shown that the approach is applicable only to the special case of small A-particle trapping in large B-centres with a large trapping radius, $\overline{r} \ll R_{AB} \ll \overline{r}_B$ (where $\overline{r}_A \approx \approx n_A^{-1/3}$ and $\overline{r}_B \approx n_B^{-1/3}$ are the mean inter-particle distances), and becomes invalid for calculating the reaction rate in the case $R_{AB} \ll \overline{r}_A, \overline{r}_B$, which is most important for the reaction kinetics and, in particular, corresponds to comparable-size (or point-wise, owing to $R_{AB} \ll \overline{r}_A, \overline{r}_B$) particles A and B migrating by random walks. In order to resolve this inadequacy of the traditional approach, a new approach to the diffusion-limited reaction rate theory, based on a similar consideration of Brownian coagulation proposed in our papers [8–10], was developed in Ref. [7]. In the new ("kinetic") approach, point-wise particles tend to a homogeneous (in random) spatial distribution owing to their migration and mixing on the scale of the mean inter-particle distance $l \approx \overline{r}$, with the characteristic diffusion mixing time τ_d that is generally small in comparison with the characteristic reaction time τ_c, i. e., $\tau_d \ll \tau_c$.

Indeed, for instance in the simplest case $D_A \approx \approx D_B = D$ and $n_A \approx n_B = n$, reactions between A and B particles induce local heterogeneities in the spatial distribution of their probability densities on the length scale of the mean inter-particle distance $\overline{r} \approx n^{-1/3} \gg a$. However, such kind of heterogeneities quickly disappear owing to rapid diffusion relaxation on the length scale

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of the mean inter-particle distance $\overline{r}$ with the characteristic time $\tau_d \approx \overline{r}^2/6D$, which is generally much shorter than the characteristic time $\tau_c \approx (K_{AB}n)^{-1}$ of the particle concentration variation, $\tau_d \ll \tau_c$ (or equally, in terms of the mean free path λ of a particle between its two subsequent collisions, $\lambda \approx (6D\tau_c)^{1/2} \gg \overline{r}$, which has a clear physical sense and is valid under the basic "dilution" condition of the theory, $n^{1/3}R \approx R/\overline{r} \ll 1$).

In the opposite cases, $D_A \gg D_B$ or $n_A \gg n_B$, the mixing of slow particles (e. g., B) might be incomplete (if $\tau_d^{(B)} \approx \overline{r}^2/6D_B \geq \tau_c$). However, owing to the stochastic character of movement and collisions of particles A, the "surviving" particles B are still randomly distributed in space, whereas rapidly moving particles A heal up local heterogeneities in the A-particle distribution induced by reactions ("rarefied zones" in the vicinity of two-particle reactions) and thus uphold efficient mixing of the reaction system. This ensures the applicability of the kinetic approach to this case with a somewhat reduced, but reasonable accuracy.

This implies that a random distribution of particles is attained during a time step $\tau_d \ll \delta t \ll \tau_c$, chosen for calculation of the reaction rate, which can therefore be searched in the kinetic approach as the collision frequency of two particles (A and B) randomly located in unit volume. That value can be equally calculated as the rate of volume sweeping $\delta\langle V_{AB}\rangle/\delta t$ by the effective particle of the radius $R_A + R_B$ migrating with the diffusivity $D_A + D_B$.

The new approach (based on the "diffusion mixing" condition) was also generalized in Ref. [7] to the reaction kinetics of particles migrating by random walks on discrete lattice sites (with the lattice spacing a), and reacting when two particles occupy the same site, i. e., $R_{AB} < a$. Similarly to the continuum limit, it was shown that the original multi-particle problem can be readily reduced, owing to rapid diffusion mixing of particles between their mutual collisions, to the calculation of the collision probability between two particles randomly located in unit volume, which in turn can be related to the mean number of distinct sites visited by a k-step random walk of the effective particle (a discrete analogue of the swept volume).

The volume swept by a Brownian particle is known as the Wiener sausage [11]. In particular, this quantity equals the probability that a diffusing Brownian point-like particle is absorbed by a single trap of radius R_{AB} in time t (see, e. g., [12]). For this reason, the rate of volume sweeping coincides with the condensation rate constant for small particles sinking in a large trap, $\overline{r}_A \ll R_{AB} \ll \overline{r}_B$; for comparable-size particles (or $R_{AB} \ll \overline{r}_A, \overline{r}_B$), it eventually determines the Smoluchowski constant in Eq. (1), as is justified in the new kinetic approach [7, 8].

The discrete analogue of the Wiener sausage was related to the survival probability for a Brownian particle in the presense of random immobile traps in the Rosenstock approximation [13] or other related problems, e. g., the so-called "target annihilation by scavengers" [14]. In the latter problem, a single particle A (target) and $N_A = n_B N$ particles B (scavengers) of a finite concentration n_B are randomly located on $N \to \infty$ sites of a 3-dimensional regular lattice. Particle A is immobile, whereas particles B perform independent, homogeneous discrete-time random walks on the lattice sites (including sites occupied by other particles); particle A annihilates as soon as a particle B reaches it.

In fact, the kinetic approach (based on the diffusion mixing condition) allows extending the solution of the target annihilation problem to consideration of many-body effects in the diffusion-limited reaction kinetics. Indeed, since particles B moves independently from each other, the probability of the target annihilation between time t and $t + \delta t$ reduces to the probability of a two-particle (A–B) collision, $w_{AB}(t)\delta t$, times N_B. In the case of mobile particles A with a finite concentration $n_A(0)$, the problem also reduces to the analyzis of two-particle collisions, if rapid diffusion mixing of particles occurs between their mutual collisions. Actually, after each annihilation event (at a moment t) when a certain lattice position (where the collision occurred) becomes definitely unoccupied, the random (equiprobable) spatial distribution of particles over lattice sites is rapidly restored during the mixing time $\tau_d \ll \delta t$, and a configuration similar to the initial configuration (i. e., random location of particles A and B on lattice sites), but with the new (diminished) particle concentrations $n_{A,B}(t + \delta t) = n_{A,B}(t) - n_A n_B w_{AB}(t)\delta t$, can be considered in the subsequent time step, if $\delta t \ll \tau_c$. In the case $\delta t \gg \tilde{\tau} \approx 16R_{AB}^2/\pi D_{AB}$, which is generally valid because $\tau_c \gg \tilde{\tau}$ [7], a steady-state value of $w_{AB}(t) \approx w_{AB}(\infty) \equiv w_{AB}$ is attained in the time step δt, and thus the reaction rate equation takes the form of Eq. (1) with the rate constant $K_{AB} = w_{AB}$, which does not depend on time explicitly (as opposed to condensation of small particles in a large trap, considered in the diffusion approach).

It is important to note that in contrast to the target annihilation problem where sites can be occupied by several particles, two (or more) point-like defects (of the same type) cannot occupy the same site. However, under the basic assumption of the reaction rate theory, $n_A, n_B \ll 1$, the A–A and B–B "collisions" (i. e., occupation of one site by two identical particles) can be generally neglected in calculating the A–B reaction rate. Indeed, the incorporation of these events during the time step $\delta t \ll \tau_c$, which is used in the derivation of the rate equation and calculation of the reaction constant K_{AB} in the kinetic approach, requires considering two simultaneous or successive collisions (A–A and A–B, or B–B and B–A) in unit volume during δt, with the respective probabilities $w_{AAB}\delta t \propto n_A^2 n_B \delta t$ and $w_{ABB}\delta t \propto n_B^2 n_A \delta t$, which can be neglected, owing to $n_A, n_B \ll 1$, in comparison with the probability $w_{AB}\delta t \propto n_A n_B \delta t$ of a single pair-wise A–B collision during δt in unit volume. Therefore, the influence of the forbiddance for identical defects to occupy the same sites can be neglected in calculating the recombination rate.

2. REACTIONS ON DISCRETE LATTICES

As explained above, in both continuum and discrete limits, the original multi-particle problem can be reduced to the calculation of the collision probability between two particles, randomly located in unit volume, owing to the rapid diffusion mixing of particles between their mutual collisions. In the continuum limit, the probability of a collision between two particles randomly located in space, in the time interval between t and $t + \delta t$, was calculated as the mean volume swept in δt by an effective particle of the radius R_{AB} and diffusivity D_{AB}. In the discrete lattice limit (with $R_{AB} < a$), the collision probability should be calculated as the mean number of distinct sites visited by a k-step random walk of the effective particle (the so-called random walk range S_k), where $k = \delta t/\tau_{AB} = \delta t \cdot 6D_{AB}/a^2 \gg 1$.

For simple 3D and 2D lattices, this value S_k was analytically evaluated in the literature. For instance, in the case of a 3D simple cubic (sc) lattice, the mean of S_k was calculated in Refs. [15, 16] as $\overline{S}_k = 0.659 \cdot [k + O(k^{1/2})]$, which for the chosen time step $a^2/6D_{AB} \ll \overline{r}^2/6D_{AB} \approx \tau_d \ll \delta t_k \ll \tau_c$ corresponding to $k \gg 1$, can be reduced to

$$\overline{S}_k \approx 0.659k \tag{2}$$

and yields

$$K_{AB} \approx 3.96 D_{AB} a. \tag{3}$$

For fcc and bcc lattices, somewhat different values of $\overline{S}_k$ were calculated in Refs. [15, 16], approximately $0.744k$ and $0.718k$, respectively. These solutions can be applied, as assumed in Ref. [15], to the calculation of the rate at which point defects such as interstitials or vacancies diffusing by random walks on a lattice are annihilated at (immobile) point sinks of invariable concentration during the annealing (described by the Rosenstock trapping model [12]).

In the opposite case of the large reaction radius $R_{AB} \gg a$, the solution should converge to the continuum limit

$$\overline{S}_k = \frac{2\pi}{3} k, \tag{4}$$

which corresponds to the classical Smoluchowski expression for the reaction rate constant

$$K_{AB} = 4\pi D_{AB} R_{AB}. \tag{5}$$

This solution is widely used in the literature in the whole range of the ratio R_{AB}/a, including the consideration of point defects and impurities in crystals. Correspondingly, the reaction (or recombination) rate constant might be noticeably overestimated in the limit of pointwise collisions $R_{AB} < a$ as well in the transition range $R_{AB}/a \sim 1$.

Indeed, we should expect the reaction rate constant to vary in the transition range between two limits, Eq. (3), if $R_{AB}/a < 1$, and Eq. (5), if $R_{AB}/a \gg 1$. The reaction rate in this transition range can be calculated numerically, by modifying numerical algorithms developed by the authors in the continuum limit [9, 10]. The solution of this problem can be important in many practical cases.

For instance, the Frenkel pair recombination radius R_{iv} in fcc copper evaluated from the analysis of the resistivity damage rates smoothly varies from $4a$ to $3a$ (where $a \approx 0.36$ nm) in the temperature range from 50 to 110 K [17]. Extrapolating the correlation obtained in Ref. [17] for the temperature dependence of the recombination radius to room temperatures yields $R_{iv} \approx 2a$. Similar results were also obtained for other fcc metals [18]. These values of the recombination radius correspond to the transition range, and hence the new approach to calculation of the recombination rate (rather than the traditional expression, Eq. (5)) might be important.

In fcc lattices, the additional problem of the point defect site positions arises; in particular, interstitial atoms often reside in tetragonal positions with the highest symmetry, which form a simple cubic (sc) lattice for interstitial migrations. For simplicity, only such sc lattices are currently considered. This consideration can be readily generalized if the defect sites are specified more definitely (e. g., by atomistic calculations).

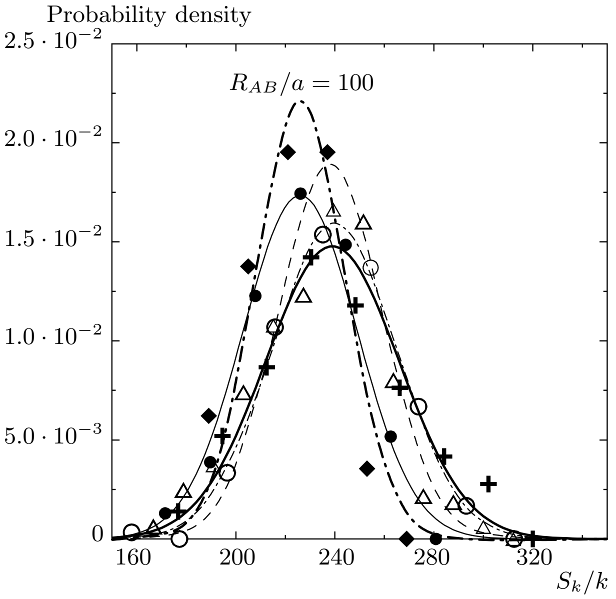

Fig. 1. Calculation of the probability density $f(x)$ for $x = S_k/k$ at $R_{AB}/a = 100$; for each number of hops k, 150–200 trajectories are generated resulting in calculation points, which are grouped in intervals of equal width L (about 10 % of the whole distribution width) and form normal distributions around the mean values (at a given k). The invariable mean value $\overline{S}_k/k \approx 226$ is attained at $k \geq 10^7$. Calculation points with the number of elementary hops: + — $3 \cdot 10^6$, ○ — $4 \cdot 10^6$, △ — $5 \cdot 10^6$, • — 10^7, ♦ — $2 \cdot 10^7$

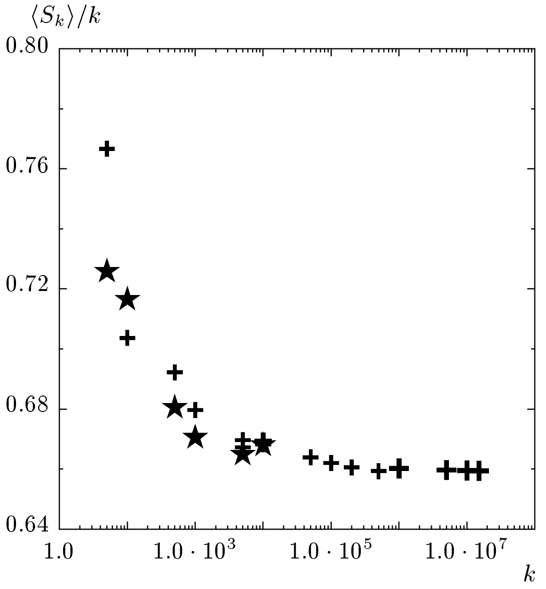

Fig. 2. Dependence of the mean number of visited distinct sites per one hop, $\overline{S}_k/k$, on the number of hops k in the discrete limit, $R_{AB}/a = 1/10$ (+), $R_{AB}/a = 1/20$ (★)

3. NUMERICAL CALCULATIONS

For the numerical evaluation of the mean number of distinct sites visited by a k-step random walk of the effective particle, $\overline{S}_k$, a random migration of a particle of the radius R_{AB} with the fixed hopping distance a on the sc lattice and the hopping frequency $v_{AB} = \tau_{AB}^{-1} = 6D_{AB}/a^2$ are numerically generated. The randomly generated data describe the subsequent positions of the particle center trajectory, which can be further used for calculating $\overline{S}_k$. Each lattice site visited by the particle is counted only once.

The number of visited distinct sites for each trajectory was calculated using an accelerated numerical algorithm, developed by the generalization and further improvement (with respect to the run time, which steeply increases with the trajectory length) of the original algorithm elaborated by the authors for the continuum-limit calculations [9, 10].

For each number of hops k, up to 100–150 random trajectories were generated, which allowed calculating a smooth distribution of the probability density $f(x)$ for $x = S_k/k$, Fig. 1. The number of hops $k = \delta t/\tau_{AB}$ was increased until $\overline{S}_k$ (averaged over the trajectories) attained a steady-state value, which in accordance with the above consideration has to converge to the analytically calculated values in the two limits $R_{AB}/a < 1$ (Eqs. (2)) and $R_{AB}/a \gg 1$ (Eq. (4)).

Similarly to the continuum limit, numerical calculations confirmed that the steady-state value of the mean number of visited distinct sites per unit time depends only on the ratio R_{AB}/a (rather than on R_{AB} and a separately). Besides, the general conclusion for 3D systems that the calculated value $\overline{S}_k/k$ smoothly decreases and reaches the steady-state limit, invariable under a further increase in the number of hops k, is justified. This conclusion is also illustrated in Figs. 2 and 3, where the results of calculations are presented for the two cases $R_{AB}/a < 1$ and $R_{AB}/a = 10$.

In particular, we see from Fig. 2 that the steady-state value $\overline{S}_k/k \approx 0.66$, numerically calculated for pointwise collisions ($R_{AB}/a < 1$), is in excellent agreement with the analytic prediction in Refs. [15, 16], $\overline{S}_k/k = 0.659$ (cf. Eq. (2)), which should therefore be used for calculation of the reaction rate constant $K_{AB} \approx 3.96 D_{AB} a$ in this limit.

The steady-state values $\overline{S}_k/k$ calculated in a wide range of the parameter values, $1 \leq R_{AB}/a \leq 100$, are shown in Fig. 4, with more detailed representa-

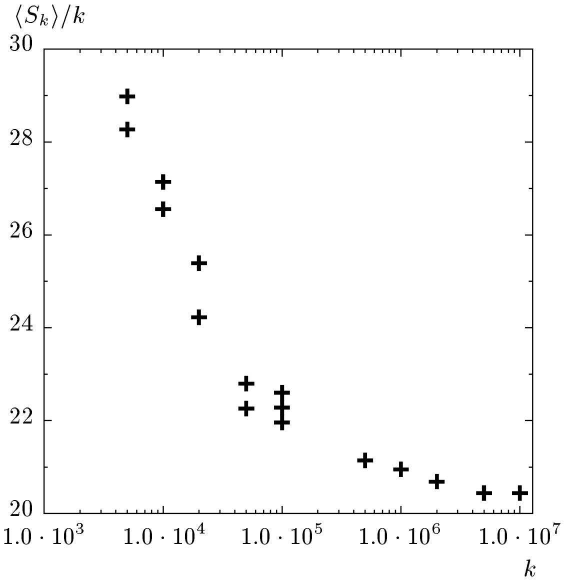

Fig. 3. Dependence of the mean number of visited distinct sites per one hop, $\overline{S}_k/k$, on the number of hops k in the case of $R_{AB}/a = 10$

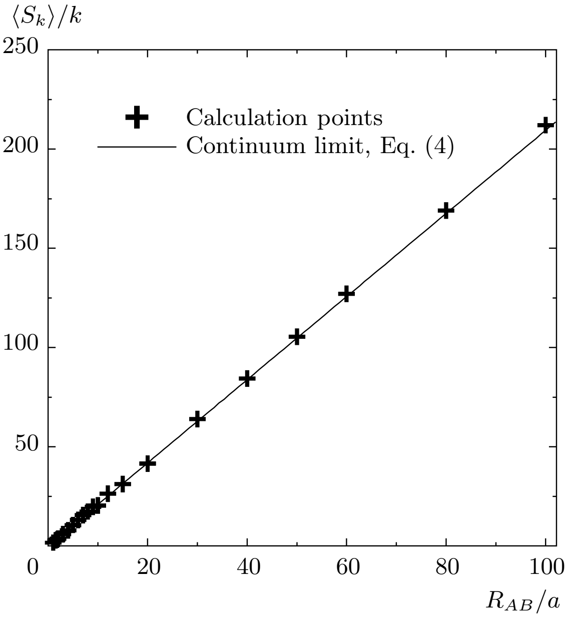

Fig. 4. Dependence of the mean number of visited distinct sites per one hop, $\overline{S}_k/k$, on the recombination radius R_{AB}/a in comparison with the theoretical curve calculated in the continuum limit, Eq. (4)

tion of the calculation results in the transition range $1 \le R_{AB}/a \le 4$ in Fig. 5.

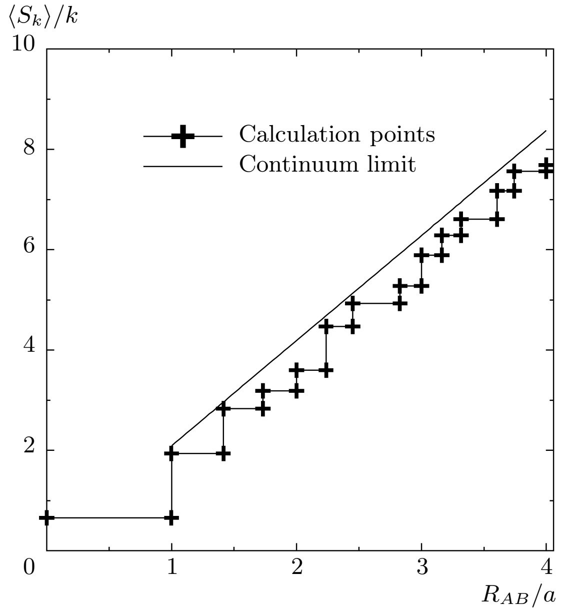

Fig. 5. The same as in Fig. 4 but for the reduced interval of R_{AB}/a

We see from Fig. 4 that at very large $R_{AB}/a \gg \gg 1$, the numerical results reasonably converge to the analytic value $\overline{S}_k = 2\pi k/3$, or $\overline{S}_k/\delta t_k = 2\pi R_{AB}/3a \approx \approx 2.094 R_{AB}/a$, calculated in the continuum limit (cf. Eq. (5)) and corresponding to the Smoluchowski expression for the reaction rate constant, $K_{AB} = = 4\pi D_{AB} R_{AB}$. In fact the calculated curve is a stepped rather than a straight line, as can be seen in Fig. 5; however, the ratio of the step height to the actual value of $\overline{S}_k/k$ smoothly decreases with the increase in the reaction radius R_{AB}, and therefore the calculated curve in Fig. 4 looks like a straight line at $R_{AB}/a \gg 1$. Nevertheless, the fine structure of the calculated curve with a step at each value $R_{AB}/a = \sqrt{h^2 + i^2 + j^2}$ (where $h, i, j = 0, 1, 2, \ldots$, run through the entire row of integers) becomes important for relatively small reaction radii, corresponding to the transition range $1 \le R_{AB}/a < 10$, Fig. 5. The maximum deviation factor (i. e., the ratio of the real value to that calculated in the continuum limit), approximately equal to 3, is attained at $R_{AB}/a \le 1$. The deviation factor gradually decreases and tends to 1 at larger R_{AB}/a.

Comparison of the new calculation results for the discrete lattice at large $R_{AB}/a \gg 1$ with the previous ones for the continuum model [9, 10] shows that although the steady-state values of the collision rate practically coincide in both cases, the number of hops necessary for the attainment of the steady state increases by several orders of magnitude. Indeed, in the continuum limit, the minimum number of necessary hops fairly agrees with the value $k_{min} \gg (96/\pi)(R_{AB}/a)^2$ derived from the assessment of the analytic solution, $\delta t \gg 16R^2_{AB}/\pi D_{AB}$. For instance, in the case $R_{AB}/a = 10$, the number of hops in the continuum model [9, 10], $k_{min} \approx 8 \cdot 10^4$, was approximately two orders of magnitude smaller than the minimum number of hops $\approx 5 \cdot 10^6$ in the discrete model. In the case $R_{AB}/a = 100$, the last value further increases and attains $\approx 10^7$, see Fig. 1. This value is generally much larger than that used in the molecular dynamics (MD) calculations and thus can therefore lead to a serious restriction on the applicability of atomistic calculations to large molecular clusters.

In these cases, the current approach might be rather effective, as will be shown elsewhere, for extrapolation of the reaction radii calculated by MD at relatively short times to the correct values corresponding to the steady-state values of the reaction constants K_{AB} in the reaction rate equation, Eq. (1).

4. CONCLUSIONS

Our new approach, based on the "diffusion mixing" condition, to the analysis of the reaction kinetics for particles A and B migrating by random walks on discrete lattice sites (with the lattice spacing a), and reacting when two particles occupy the same site, i. e., $R_{AB} < a$, was extended to the transition regime corresponding to $R_{AB}/a \geq 1$ and applied to the recombination rate of point defects in cubic lattices. In this approach, the reaction rate is reduced to the calculation of the mean number of distinct sites visited by the effective particle of the radius R_{AB}, which was calculated using a numerical algorithm generalizing and further improving the original algorithm elaborated by the authors for the continuum-limit calculations. As could be foreseen, the numerical calculations correctly reproduced the analytic expressions in the two limits $R_{AB} < a$ and $R_{AB} \gg a$ and represented a step-wise curve in the intermediate range of the parameter R_{AB}/a, which generally corresponds to the Frenkel pair recombination radius in many practical cases, e. g., for fcc metals.

REFERENCES

1. S. A. Rice, *Diffusion-Limited Reactions*, in: *Chemical Kinetics*, ed. by C. H. Bamford, C. F. H. Tipper, and R. G. Compton, Vol. 25, Elsevier, Amsterdam (1985).
2. J. W. Corbett, Sol. St. Phys. Suppl. **17**, 36 (1966).
3. F. Collins and G. Kimball, J. Colloid Sci. **4**, 425 (1949).
4. T. R. Waite, Phys. Rev. **107**, 463 (1957).
5. M. Smoluchowski, Z. Phys. Chem. **92**, 129 (1917).
6. S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
7. M. S. Veshchunov, JETP **141**, 723 (2012).
8. M. S. Veshchunov, J. Aerosol Sci. **41**, 895 (2010).
9. I. B. Azarov and M. S. Veshchunov, J. Engineer. Thermophys. **19**, 128 (2010).
10. M. S. Veshchunov and I. B. Azarov, J. Aerosol Sci. **47**, 70 (2012).
11. M. Kac, Rocky Mt. J. Math. **4**, 511 (1974).
12. A. M. Berezhkovskii, Yu. A. Makhnovskii, and R. A. Suris, J. Stat. Phys. **57**, 333 (1989).
13. H. B. Rosenstock, Phys. Rev. **187**, 1166 (1969).
14. A. Blumen, G. Zumofen, and J. Klafter, Phys. Rev. B **30**, 5379 (1984).
15. E. W. Montroll and G. H. Weiss, J. Math. Phys. **6**, 167 (2004).
16. G. H. Vineyard, J. Math. Phys. **4**, 1191 (1963).
17. R. Lennartz, F. Dworschak, and H. Wollenberger, J. Phys. F: Met. Phys. **7**, 2011 (1977).
18. G. Duesing, H. Hemmerich, W. Sassin, and W. Shilling, *Int. Conf. on Vacancies and Interstitials in Metals*, Vol. 1, Juelich, Germany (1968), p. 246.