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## LETTER TO THE EDITOR

# The kinetics of colloid formation in solids under irradiation

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**Abstract.** Results of the first-principles study of diffusion-controlled aggregation of Frenkel defects—interstitial atoms and vacancies—under irradiation of solids are presented. A novel theory is based on the discrete-lattice formalism for the single-defect densities (concentrations) and the coupled joint densities of similar and dissimilar defects, treated in terms of the Kirkwood superposition approximation. Conditions for the efficient aggregation of vacancies and interstitials are studied and the cooperative character of the aggregation process is discovered.

It was observed long ago that the primary radiation defects in ionic solids, the F centres (electrons trapped by anion vacancy) and the H centres (interstitial halide atoms), begin to aggregate under intensive irradiation and at high enough temperatures (typically around 100 °C), which leads to the formation of alkali metal colloids and gas bubbles (see [1, 2] and references therein); a similar process occurs in heavily irradiated metals [3]. The intensive experimental studies of the conditions for the defect aggregation and further colloid formation (temperature interval, dose rate, etc) continue now for alkali halides [4] and technologically important ceramics [5]. This problem is also interesting from a fundamental point of view, being an example of *pattern formation* and *self-organization* in reaction–diffusion systems far from equilibrium [6].

Existing theories of radiation-induced defect aggregation and colloid formation could be classified, in terms of the mathematical formalism used, into three categories: macroscopic [7], mesoscopic [8, 9] and microscopic [10]. These latter are first-principles theories using no fitting or uncertain parameters, but only several basic defect parameters such as the diffusion constants and interaction potentials. However, the continuum approximation used in [10] has led to the non-physical problem of the cutting off of the interaction potentials at the nearest-neighbour (NN) distances, and large gradients of the correlation functions at these distances. The first point makes results very sensitive to the manner in which the potentials are defined at distances shorter than that of the NN and the second requires us to use very small coordinate increments in the calculations which strongly restricts the time interval that realistically reached using such an approach. It should be stressed that metal colloid formation is a very slow process which in real experiments often lasts several weeks or more; another reason why this problem is difficult for direct computer (Monte Carlo) simulations is that the mobilities of the two kinds of defect involved—interstitials and vacancies—differ typically by 15 orders of magnitude!

In this letter we discuss the idea of the first microscopic *discrete-lattice* theory of diffusion-controlled aggregation during the bimolecular annihilation,  $A + B \rightarrow 0$ , under the permanent particle source and present its results for the study of cooperative kinetics of colloid formation under irradiation.

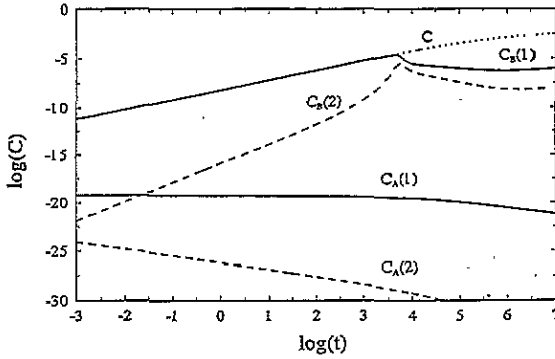
The *physical model* includes the creation of the interstitials and vacancies (hereafter called defects A and B), with the (dose) rate  $p$ ; AB pairs are not spatially correlated at 'birth' and recombine when they approach each other to within the NN distance during their migration. Therefore, their macroscopic concentrations always coincide,  $C = C_A = C_B$ . Isolated (single) defects hop with the activation energy  $E_\lambda$  and are characterized by the diffusion coefficients  $D_\lambda = D_0 \exp(-E_\lambda/k_B T)$ ,  $\lambda = A, B$ . When several defects are closely spaced, the hop rate of a given defect to the nearest empty lattice site is determined by both the local defect configuration and the interaction between defects; this can change its *effective* diffusion coefficient  $D_\lambda^{eff}$  by many orders of magnitude compared to that for a single defect. It affects the effective reaction rate  $K$  of the A and B recombination; for the diluted system in the continuum approximation is well known that  $K_0 = 4\pi r_0(D_A + D_B)$ , where  $r_0$  is the recombination radius.

As follows from previous theoretical studies [8–10], defect attraction plays a decisive role in the aggregation process. It is incorporated in our model via three types of NN attractions between the two kinds of NN defect (in the spirit of the Ising model):  $E_{AA}$ ,  $E_{AB}$  and  $E_{BB}$ . Note that up to now only a few theoretical studies have been devoted up to now to the effects of particle interaction (especially for similar particles) in the kinetics of the bimolecular diffusion-controlled reaction  $A + B \rightarrow 0$ , with the emphasis on fluctuation phenomena; rare exceptions are [11, 12]. The effect particle interactions make the kinetic equations essentially non-linear and thus able to manifest the self-organization (pattern formation) under the irradiation.

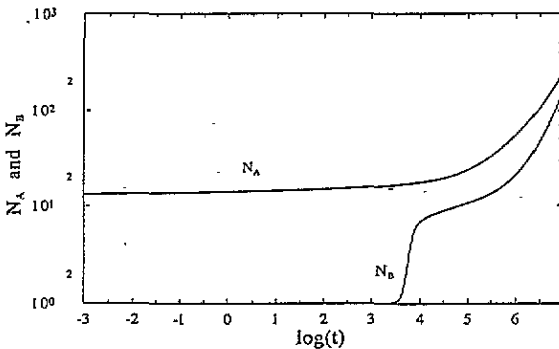
The *mathematical formalism* and the relevant computer program *Kinetica* will be described in detail elsewhere [13]. This is a generalization of our previous microscopic many-point density approach [10, 14, 15] for the discrete-lattice case which allows us to avoid the above-mentioned limitations of a continuum model and to increase the computation speed thus allowing us to study the aggregation kinetics in a very long time interval of up to  $10^7$  s. The theory is based on the Kirkwood superposition approximation for the three-particle densities [14] and thus operates with a set of coupled kinetic equations for the lattice defect densities (concentrations)  $C_\lambda(t)$ ,  $\lambda = 0, A, B$  and the joint correlation functions  $F_{\lambda\nu}(|r_\lambda - r_\nu|, t)$  where  $r_\lambda$  and  $r_\nu$  are coordinates of two lattice sites and  $t$  is time. Since defect correlations are short range,  $F_{\lambda\nu}(r, t)$  strives for its asymptotic value of unity (random particle distribution), as the relative coordinate  $r \rightarrow \infty$ . That is, if some joint density  $F_{\lambda\nu}(r, t)$  considerably exceeds the unity value, it means a surplus of the defect pairs  $\lambda\nu$  at a given relative distance compared to the their random (Poisson) distribution, and vice versa. The simultaneous analysis of the joint correlation functions for similar (AA, BB) and dissimilar (AB) pairs, as well as for OA, OB pairs (empty site-defect) permit to study the *spatio-temporal* evolution of a strongly non-equilibrium system—in particular, crystals with radiation defects [10, 11, 13–16].

It is also convenient to characterize the aggregation process by monitoring the concentrations of *single* defects  $C_\lambda(1)$  (no other defects in NN sites) and *dimer* defects  $C_\lambda(2)$  (two similar defects are NNs) which could be calculated from the joint densities in the standard cluster approximation [17]. Lastly, large aggregates could be characterized by the integral values of the number of particles  $N_A$ ,  $N_B$  therein and their sizes (radii)  $R_A$  and  $R_B$ . Let us now apply our theory to the set of parameters typical for alkali halides (e.g. NaCl crystals); they are given in the caption to figure 1. The first conclusion from figure 1 is that at room temperature (RT) starting from the very short times,  $t \leq 10^{-3}$  s, most interstitials are already aggregated; the concentrations of single and dimer interstitials,  $C_A(1)$  and  $C_A(2)$ , are about 10 orders of magnitude less than the macroscopic (total) concentration  $C = C_A = 10^{-10}$ , i.e. most of interstitials belong to larger aggregates. This is a direct result

of high mobility of interstitials A (the activation energy for hops is 0.1 eV only) when even moderate mutual attraction leads to the formation of large aggregates. In contrast, low-mobility vacancies B ( $E_B = 0.9$  eV) exist for a much longer times predominantly as single defects—up to some characteristic time  $t_0$  ( $= 10^4$  s at RT). As  $t > t_0$ , the concentrations of single and dimer defects become similar, and at longer times we see growth of more complex aggregates (trimers etc).



**Figure 1.** The time development of defect concentrations of interstitials (A) and vacancies (B). The  $C$  are macroscopic concentrations whereas  $C_\lambda(1)$  and  $C_\lambda(2)$ ,  $\lambda = A, B$  are single defect and dimer defect concentrations respectively. Concentrations are in dimensionless units ( $n_\lambda a_0^3$ ), time ( $t$ ) is in seconds,  $T = 300$  K, and the dose rate (irradiation intensity)  $p = 10^{14}$   $\text{cm}^{-3}\text{s}^{-1}$ . The migration and attraction energies are chosen to be typical for alkali halide crystals:  $E_A = 0.1$  eV,  $E_B = 0.9$  eV,  $E_{AA} = -0.2$  eV,  $E_{AB} = -0.2$  eV,  $E_{BB} = -0.1$  eV.  $D_0 = 10^{-3}$   $\text{cm}^2 \text{s}^{-1}$  [7, 8, 10].



**Figure 2.** Evolution in time of a mean number of particles in A and B aggregates. Note the cooperative effect of their abrupt simultaneous growth at  $t > 10^4$  s.

Figure 2 shows that below the critical time  $t_0$  mean number of interstitials in an A aggregate is practically constant,  $N_A \approx 15$ , whereas  $N_B \approx 1$  (single vacancies dominate). However, as soon as  $N_B$  shows a sharp increase at  $t > t_0$ , so too does  $N_A$ . That is, the aggregation of vacancies greatly enhances that of interstitials—we observe the *cooperative process* of the simultaneous aggregation of the two kinds of defects. This conclusion is supported by similar behaviour as regards size of these two kinds of aggregate (figure 3). The physical background of this effect is clear—at  $t > t_0$  most of the interstitials are already aggregated and their further growth is restricted by the recombination with low-mobility single vacancies. When the latter begin to aggregate too, they no longer the control behaviour (and prevent additional aggregation) of interstitials. As a result, we have

a positive back-coupling of the two kinds of aggregation process, which we called the *cooperative effect*. Here it is important to stress the great similarity between two kinds of aggregate in size and number of particles. This means that despite the fact that the mobilities and interaction energies differ greatly between single interstitials and vacancies, their aggregates start to reveal properties common for conglomerates of any kinds of particle.

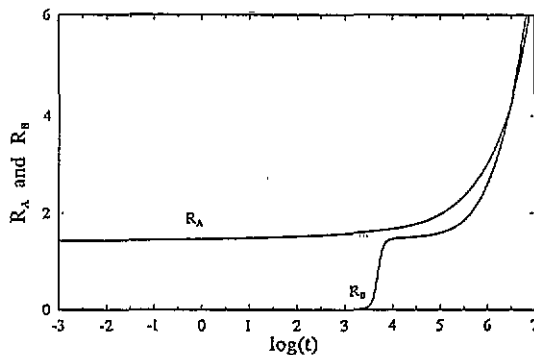


Figure 3. As figure 2 but for the aggregate radii (in units of the lattice spacing,  $a_0$ ).

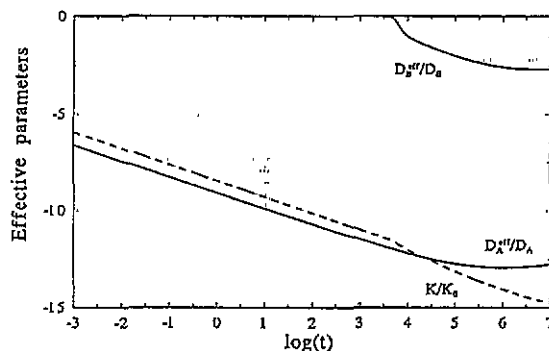


Figure 4. Time development of the relative effective coefficients  $D_\lambda^{eff}$ ,  $\lambda = A, B$  of interstitials A and vacancies B and the relative recombination rate  $K$ .

A very interesting condition of this cooperative aggregation of interstitials and vacancies can be learnt from figure 4. At  $t < t_0$  the effective diffusion coefficient of vacancies,  $D_B^{eff}$ , practically coincides with that for single vacancies,  $D_B$ , whereas that for the interstitials,  $D_A^{eff}$  dramatically decreases in time by many orders of magnitude due to effective interstitial aggregation. (A similar effect has been observed recently for the diffusion in an interactive adsorbate *without* reaction [18].) This continues up to the moment  $t_0$  when  $D_A^{eff}$  becomes close in magnitude to the small diffusion coefficient of single vacancies,  $D_B \approx 10^{-21} \text{ cm}^2 \text{ s}^{-1}$ . After the mobilities of the two kinds of defect become comparable,  $D_A^{eff}$  is stabilized but in its turn,  $D_B^{eff}$  begins to decrease, thus indicating the effective aggregation of vacancies. The broken line in figure 4 shows that the effective reaction rate  $K$  also decreases by many orders of magnitude, being closely correlated with the  $D_A^{eff}$  behaviour.

The relative spatial distribution of defects at the late aggregation stage ( $t = 10^7 \text{ s}$ ) is seen in figure 5. The joint correlation functions of similar defects,  $F_{AA}$  and  $F_{BB}$ , demonstrate

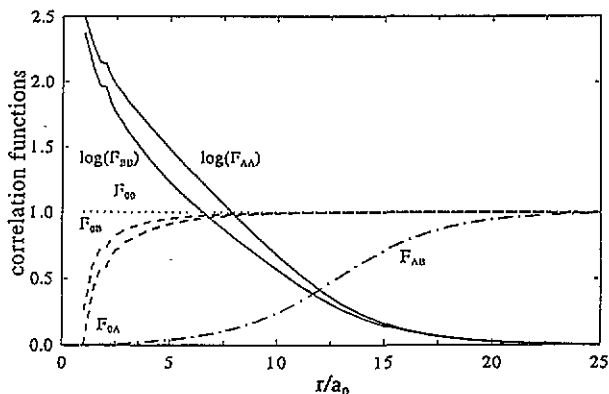


Figure 5. The joint correlation functions at the long time  $t = 10^7$  s versus the relative distance between particles; see the explanation in the text. Note that  $F_{AA}$  and  $F_{BB}$  are plotted on the semi-logarithmic scale.

the strong aggregation of *both* interstitials and vacancies. The relative distance of  $r \approx 15a_0$  where they approach the asymptotic value of unity agrees with a qualitative estimate of the radius of the aggregate plotted in figure 3. Another important conclusion is suggested from this figure—despite very different mobilities and interaction energies of interstitials and vacancies, the cooperative effects in their aggregations lead to the quite similar final aggregates observed at the end of irradiation. The correlation function for the dissimilar defects,  $F_{AB}(r)$ , is anti-correlated to  $F_{AA}$ ,  $F_{BB}$ , i.e. it increases from almost zero at  $r \leq 7a_0$  up to unity at  $r \approx 15\text{--}20a_0$ , which gives us an estimate of the average distance between aggregates of *dissimilar* particles (defects). Lastly, the ‘empty site-defect’ joint correlation functions,  $F_{0A}$  and  $F_{0B}$ , show that these aggregates have small, dense cores (there are almost no empty sites in their centres) but are quite loose on their periphery,  $r \geq 3a_0$ . This agrees with the fact that colloid growth is well pronounced in NaCl crystals at higher temperatures,  $T \geq 60^\circ\text{C}$  [4]. Our saturation concentration and time are close to those observed experimentally whereas for a proportion of dimer  $F_2$  (M) centres they exceed the values experimentally observed at RT, probably due to the non-exact defect interaction parameters. A study of the effects of the dose rate and the temperature on the aggregation kinetics is now in progress.

In conclusion, we presented the first-principles theory of colloid formation through the aggregation of similar *interacting* particles during the bimolecular reaction  $A + B \rightarrow 0$  (annihilation) with a permanent particle source and applied it successfully to the discrete-lattice description of the kinetics of the aggregation (colloid formation) in ionic solids under irradiation. This process includes several initial stages (a reduction of the mobility of interstitials via their aggregation and then vacancy aggregation) and demonstrates at the final stage essentially *cooperative behaviour* in the aggregation of the two kinds of particle/defect leading to quite similar aggregates.

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