

Microscopic theory 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—under irradiation of solids are presented. Conditions of the efficient radiation-induced aggregation of vacancies and interstitials are studied and the scenario of this process is presented.

Keywords: Frenkel defects; Alkali halides; Clusters; Defect formation; Diffusion; Nucleation

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

Recently [6] we presented the first microscopic formalism describing the process of radiation-induced defect aggregation and colloid formation. This theory uses 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 this study has led to non-physical problems of the cutting off of interaction potentials at the nearest-neighbour (NN) distance, 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 NN, and the second requires the use of very small coordinate increments in the calculations which strongly restricts the time interval reachable realistically 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 longer; another reason why this problem is difficult for direct computer (Monte Carlo) simulations is that the mobilities of the two kinds of defects involved—interstitials and vacancies—differ typically by 15 orders of magnitude!

In the present paper we describe results of the microscopic *discrete-lattice* theory of diffusion-controlled aggregation during the bimolecular annihilation, $A + B \rightarrow 0$, under the permanent particle source and with its help we study theoretically the cooperative effects in colloid formation under irradiation.

The *physical model* includes creation of the interstitials and vacancies (called hereafter defects A and B), with the (dose) rate p ; AB pairs are not spatially correlated at birth and recombine when during their migration they approach each other to within the NN distance. Therefore, their macroscopic concentrations always coincide, $C = C_A = C_B$. Isolated (single) defects hop with the activation energy E_λ and are characterized by the diffusion coefficients $D_\lambda = D_0 \exp(-E_\lambda/k_B T)$, $\lambda \equiv A, B$. When several defects are closely spaced, the hop rate of a given defect to the nearest empty lattice

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site is determined by both the local defect configuration and the interaction between defects; this can change its *effective* diffusion coefficients D_{λ}^{eff} by many orders of magnitude compared with 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 it 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 [6], defect attraction plays a decisive role in the aggregation process. It is incorporated in our model via three types of NN attraction between the two kinds of NN defect (in the spirit of the Ising model): E_{AA} , E_{AB} and E_{BB} . Note that 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 $A + B \rightarrow 0$, with the emphasis on fluctuation phenomena; rare exceptions are [7,8]. However, particle interactions make the kinetic equations essentially non-linear and thus able to manifest the self-organization (pattern formation) under irradiation.

The mathematical formalism will be described in detail elsewhere [9]; it is a generalization of our previous microscopic many-point density approach [6,10,11] for the discrete lattice case which allows us to avoid the mentioned limitations of a continuum model, to increase the computation speed and thus to study the aggregation kinetics in a very wide time interval, up to 10^5 s. The theory is based on the Kirkwood superposition approximation for the three-particle densities [10] and thus operates with a set of coupled kinetic equations for the lattice defect densities (concentrations) $C_{\lambda}(t)$, $\lambda \equiv 0, A, B$ and the joint correlation functions $F_{\lambda\nu}(|r_{\lambda} - r_{\nu}|, t)$ where r_{λ} and r_{ν} 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 $F_{\lambda\nu}(r, t)$ exceeds considerably the value of unity, there is a surplus of the defect pairs $\lambda\nu$ at a given relative distance compared with their random (Poisson) distribution, and vice versa. The simultaneous analysis of the joint correlation functions for similar (AA, BB) and disimilar (AB) pairs, as well as for 0A, 0B pairs (empty site-defect) allow study of the *spatiotemporal* evolution of the strongly non-equilibrium system, in particular, crystals with radiation defects [6,9–12].

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 NN) which could be calculated from the joint densities in the standard so-called cluster approximation. 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 NaCl crystals at 400 K when colloid formation is well pronounced. (The parameters used are given in the caption to Fig. 1.) The first conclusion from this figure is that at 130 °C starting from very short times, $t \leq 10^{-5}$ s, most interstitials are already aggregated; the concentrations of single and dimer interstitials, $C_A(1)$ and $C_A(2)$, are about 6 orders of magnitude less than the macroscopic (total) concentration $C = C_A = 10^{-11}$, i.e. most of the interstitials belong to larger aggregates. This is a direct result of the 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, slow mobile vacancies B ($E_B = 0.9$ eV) exist for much longer times predominantly as single defects, up to some characteristic time t_0 ($t_0 \approx 1$ s). As $t > t_0$, the concentrations of single and dimer defects become similar, and at longer times we see the growth of more complex aggregates (trimers, etc.).

Our calculations show that below the critical time t_0 the mean number of interstitials in an A-aggregate is practically constant, $N_A \approx 150$, whereas $N_0 \approx 1$ (single vacancies dominate). However, as soon as N_B shows a sharp increase at $t > t_0$ so 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 defect. This conclusion is supported by similar behavior of the calculated size of these two kinds of aggregate. 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 slow

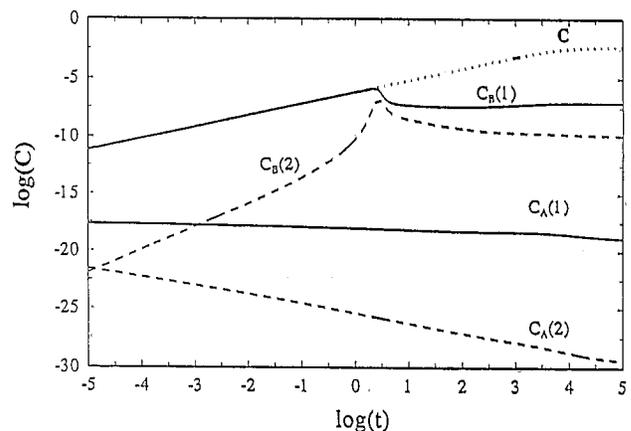


Fig. 1. The time development of defect concentrations of interstitials (A) and vacancies (B). C are macroscopic concentrations whereas $C_{\lambda}(1)$ and $C_{\lambda}(2)$, $\lambda = A, B$ are single defect and dimer defect concentrations respectively. Concentrations are in dimensionless units ($n_{\lambda} a_0^3$), time t in seconds, $T = 400$ K, the dose rate (irradiation intensity) $p = 10^{16} \text{ cm}^{-3} \text{ s}^{-1}$. 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, $E_{AB} = -0.1$ eV, $E_{BB} = -0.05$ eV; $D_0 = 10^{-3} \text{ cm}^2 \text{ s}^{-1}$.

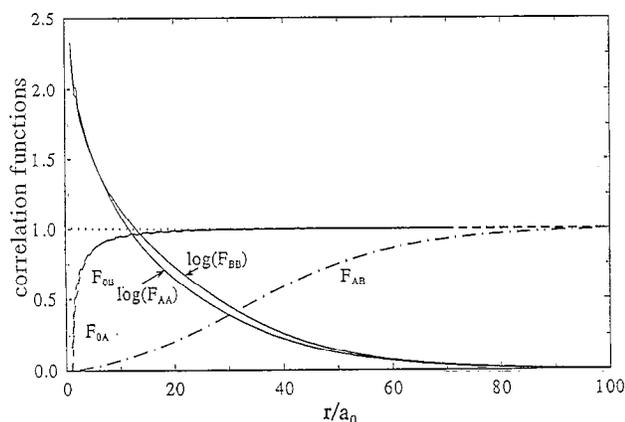


Fig. 2. The joint correlation functions at the long time $t = 10^5$ s vs. the relative distance between particles, see explanation in the text. Note that F_{AA} and F_{BB} are plotted on a semi-logarithmic scale.

mobile single vacancies. When the latter begin to aggregate too, they no longer control the behavior (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 the two kinds of aggregate in sizes and number of particles reaching 2000–3000 per aggregate. This means that despite the fact that the mobilities and interaction energies between single interstitials and vacancies differ greatly, their aggregates start to reveal properties common for large conglomerates of any kinds of particle.

A very important condition of this cooperative aggregation of interstitials and vacancies could be learnt from our calculations. 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} decreases dramatically in time by many orders of magnitude owing to effective interstitial aggregation. 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 . 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 relative spatial distribution of defects at the late aggregation state ($t = 10^5$ s) is seen in Fig. 2. The joint correlation functions of similar defects, F_{AA} , F_{BB} , demonstrate the strong aggregation of *both* interstitials and vacancies. The relative distance $r \approx 60a_0$ where they approach the asymptotic value of unity agrees with our qualitative estimate of the radius of the aggregate. Another important conclusion is suggested from this figure. Despite the very different mobilities and interaction energies of interstitials and vacancies, the cooperative effects in their aggregation lead to 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 short distances up to unity for r approximately $60a_0$ – $70a_0$, which gives us an estimate of the average distance between aggregates of *dissimilar* particles (defects). Lastly, the joint correlation functions “empty site-defect”, F_{0A} , F_{0B} , show that these aggregates have small dense cores (there are almost no empty sites in their centers, but they are quite loose at their periphery, $r \geq 5a_0$). This agrees with the fact that at this temperature colloid growth is indeed well pronounced in NaCl crystals [3]. A study of the effects of the dose rate and the temperature on the aggregation kinetics is now in progress.

In conclusion, we have presented results of the first-principles discrete-lattice 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 (permanent irradiation). We have shown that this process includes several intermediate stages (a reduction in the mobility of interstitials via their aggregation, then vacancy aggregation) and demonstrate at the latest stage the essentially *cooperative behavior* in the aggregation of the two kinds of particle/defect leading to quite similar aggregates.

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