

DIFFUSION-CONTROLLED COLLOID FORMATION  
IN IRRADIATED SOLIDS: MICROSCOPIC THEORY

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The kinetics of diffusion-controlled aggregation of Frenkel defects (interstitial atoms and vacancies) under irradiation of solids is studied on a microscopic level. The theory is based on the discrete-lattice formalism for the single defect densities (concentrations) and coupled joint densities of similar and dissimilar defects treated in terms of the Kirkwood superposition approximation. The physical model takes into account random defect creation, diffusion, attraction, and bimolecular  $A+B\rightarrow 0$  recombination. Conditions of the efficient aggregation of vacancies and interstitials are studied. The cooperative character of the aggregation process is shown.

### I. INTRODUCTION

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) — begin to aggregate under intensive irradiation and at temperatures high enough (typically above the room temperature, RT). This 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 [3]. The intensive experimental studies of the conditions for defect aggregation and further colloid formation (such as the temperature interval, dose rate, etc) continue nowadays for alkali halides [4] and technologically important ceramics [5]. 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 [6].

Existing theories of the 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]. The microscopic are first-principle theories using no fitting or uncertain parameters but only several basic defect parameters such as diffusion constants and interaction potentials. However, the continuum approximation [10] has led to non-physical problems of cutting off the 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, the second one makes us apply very small coordinate increments to the calculations, which strongly restricts the time interval realistically reachable with such an approach. It should be stressed that usually the metal colloid growth is a very slow

process, which in real experiments often lasts several weeks or longer; another reason why this problem is difficult for the 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 briefly 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 prolonged irradiation of ionic solids.

## II. THE MODEL

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 during their migration when they approach each other within the nearest-neighbour (NN) distance. Therefore, their macroscopic concentrations always coincide, i.e.  $C=C_A=C_B$ . 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  $D_\lambda^{\text{eff}}$  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, which for dilute system in the continuum approximation is well-known to be  $K_0 = 4\pi r_0(D_A + D_B)$ , 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 into our model via three types of the NN attractions between the two kinds of NN defects (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 reaction  $A+B \rightarrow 0$ , with the emphasis on fluctuation phenomena (rare exceptions being [11, 12]). Namely, particle interactions make the kinetic equations essentially non-linear and thus able to manifest the self-organization (pattern formation) under the irradiation.

## III. CORRELATION FUNCTION FORMALISM

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 mentioned limitations of a continuum model, to increase the computation speed and thus to study the aggregation kinetics in a very wide time interval exceeding ten orders of magnitude. 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 the two lattice sites and  $t$  is time. Since defect correlations are short-range,  $F_{\lambda\nu}(r, t)$  strives for its asymptotic value of the unity (random particle distribution) as the relative coordinate increases,  $r \rightarrow \infty$ . That is, if some joint density  $F_{\lambda\nu}(r, t)$  considerably exceeds the unity value, it means surplus of the defect pairs  $\lambda\nu$  at a given relative distance compared to 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 0A, 0B pairs (empty site—defect) permits one to study the *spatio-temporal* evolution of the strongly non-equilibrium system, in particular, in crystals with radiation defects [10, 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 NN) that could be calculated from the joint densities in the standard *cluster approximation* [17]. Finally, 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  $R_B$ .

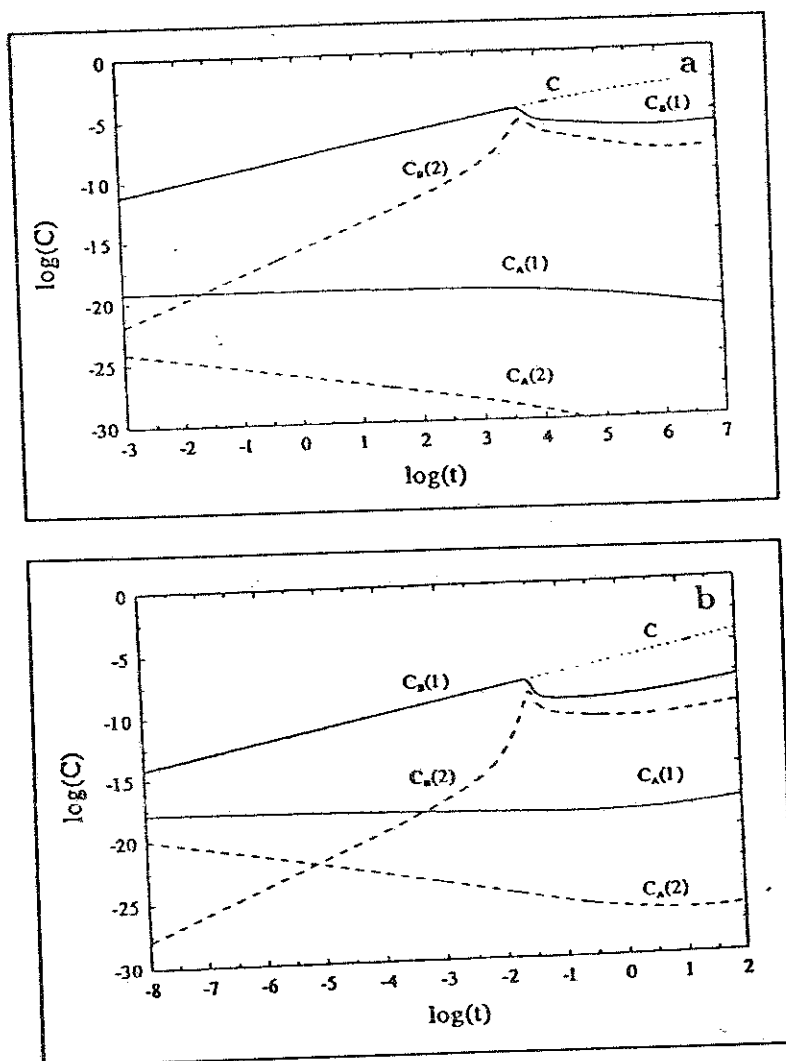


Fig. 1. The time development of defect concentrations of interstitials (A) and vacancies (B) at 300 K (a) and 500 K (b).  $C$  are macroscopic concentrations whereas  $C_{\lambda}(1)$  and  $C_{\lambda}(2)$ ,  $\lambda=A, B$  are single defect and dimer defect concentrations, respectively. Concentrations are in dimensionless units ( $n\lambda a_0^3$ ), time ( $t$ ) in seconds, 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:  $E_A=0.1 \text{ eV}$ ,  $E_B=0.9 \text{ eV}$ ,  $E_{AA}=-0.2 \text{ eV}$ ,  $E_{AB}=-0.2 \text{ eV}$ ,  $E_{BB}=-0.1 \text{ eV}$ .  $D_0=10^{-3} \text{ cm}^2 \text{ s}^{-1}$  [7, 8, 10]

#### IV. RESULTS

##### A. Concentration growth

Let us now study the kinetics of colloid growth at two different temperatures — 300 K (room temperature, RT) and 500 K (high temperature) in a model-like alkali halide crystal; its typical parameters are given in the caption to Fig. 1. The first conclusion from Fig. 1 is that at both temperatures starting from the very short times,  $t \ll 1$  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 hopping is only 0.1 eV) even when moderate mutual attraction leads to the formation of large aggregates. In contrast, slowly mobile vacancies  $B$

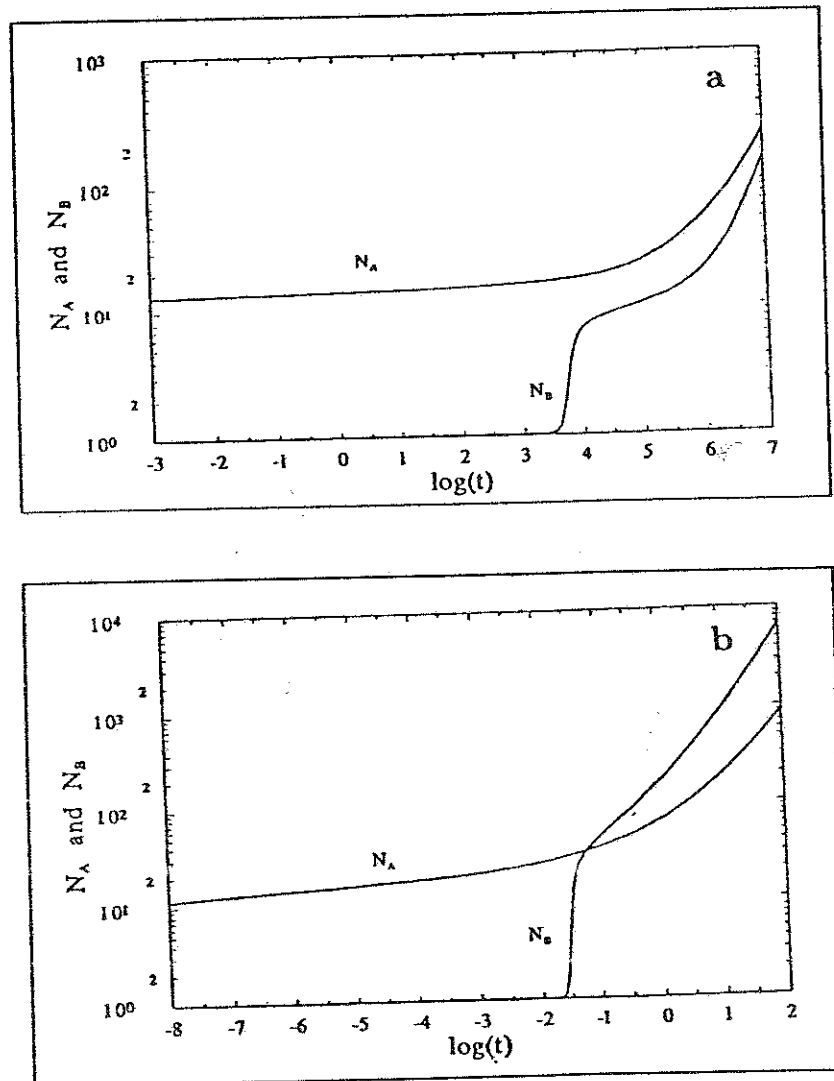


Fig. 2. Evolution in time of a mean number of particles in A- and B-aggregates. Note the cooperative effect of their abrupt simultaneous growth at long times;  $T = 300$  K (a) and 500 K (b)

( $E_B=0.9$  eV) exist for much longer times predominantly as single defects — up to some characteristic time  $t_0$ . This time  $t_0$  greatly depends on the temperature and decreases from  $10^4$  s at RT down to  $10^{-2}$  s at 500 K, i.e. by six orders of magnitude. As  $t > t_0$ , the concentration of single and dimer defects becomes similar, and at longer times we observe the growth of more complex aggregates (trimers, etc.).

### B. Aggregate characterization

Figure 2 shows that below the critical time  $t_0$  the *mean number* of interstitials in the A-aggregate is practically constant at both temperatures studied,  $N_A \approx 15$ , whereas  $N_B \approx 1$  (single vacancies dominate). However, as soon as  $N_B$  shows a sharp increase at  $t > t_0$ ,  $N_A$  does so, too. That is, the aggregation of vacancies greatly enhances that of interstitials — we observe a *cooperative process* of the simultaneous aggregation of the two kinds of defects. This conclusion is supported by similar behaviour of the *size* of these two kinds of aggregates (Fig. 3). The physical background

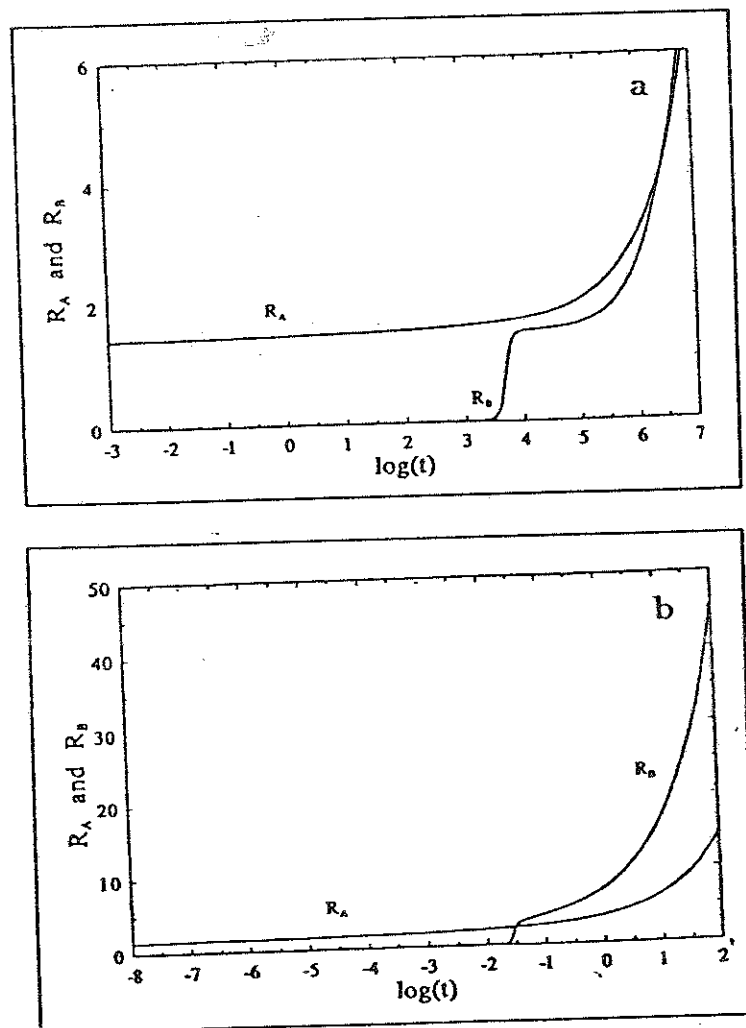


Fig. 3. Same as Fig. 2 but for the aggregate radii (in units of the lattice spacing,  $a_0$ )

of this effect is clear: at  $t > t_0$  most of interstitials are already aggregated and their further growth is restricted by the recombination with slowly mobile single vacancies. When the latter begin to aggregate, too, they control no longer the behaviour (and prevent additional aggregation) of the interstitials. As a result, we have a positive back-coupling of the two kinds of aggregation processes, mentioned above as the cooperative effect. At higher temperature and  $t > t_0$  the aggregate size is much greater. It is important here to stress the great similarity between two kinds of aggregates in sizes and number of particles. This means that, despite the fact that the mobilities and interaction energies of single interstitials and vacancies greatly differ from each other, their aggregates start to reveal properties common for large conglomerates of any kind of particles.

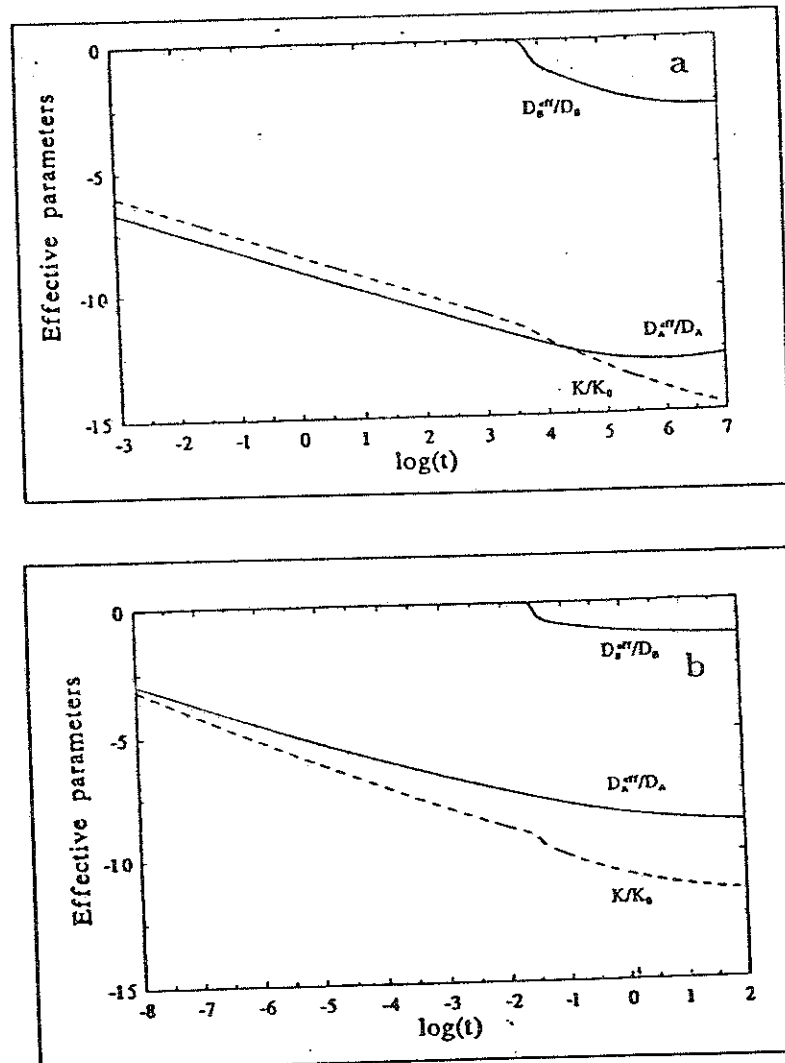


Fig. 4. Time development of the relative effective coefficients  $D_{\lambda}^{eff}/D_{\lambda}$ ,  $\lambda=A,B$  of interstitials A and vacancies B and the relative recombination rate  $K$  at 300 K (a) and 500 K (b)

### C. Conditions for colloid formation

A very interesting condition of the cooperative aggregation of interstitials and vacancies could be learnt from Fig. 4. At  $t < t_0$  the *effective diffusion coefficient* of vacancies,  $D_B^{\text{eff}}$ , practically coincides with that for single vacancies,  $D_B$ , whereas the diffusion coefficient for the interstitials,  $D_A^{\text{eff}}$  dramatically decreases with 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  $D_A^{\text{eff}}$  becomes close in magnitude to the small diffusion coefficient of single vacancies,  $D_B \approx 10^{-21} \text{ cm}^2 \text{ s}^{-1}$ . Only after the mobilities of the two kinds of defects become comparable,  $D_A^{\text{eff}}$  is stabilized; in its turn,  $D_B^{\text{eff}}$  begins to decrease, thus indicating the effective aggregation of vacancies. The broken line in Fig. 4 shows that the effective reaction rate  $K$  decreases also by many orders of magnitude, being well-correlated with the  $D_A^{\text{eff}}$  behaviour.

### D. Spatial distribution of defects

The relative *spatial distribution of defects* at the late stage of aggregation is seen in Fig. 5. Large magnitudes of the joint correlation functions of similar defects,  $F_{AA}$ ,  $F_{BB}$ , at short relative distances clearly demonstrate the strong aggregation of *both* interstitials and vacancies. At RT and a relative distance of  $r \approx 15a_0$  the correlation functions approach the asymptotic value of unity. This value of  $r$  is a qualitative estimate of the radius of the aggregates plotted in Fig. 3,a.

Another important conclusion could be suggested from this figure: despite 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 dissimilar defects,  $F_{AB}(r)$ , is anti-correlated with  $F_{AA}$ ,  $F_{BB}$ , i.e. it increases at RT from almost zero at  $r \leq 7a_0$  up to unity at  $r \approx 15-20a_0$ , which gives us an estimate of the average distance between aggregates of *dissimilar* particles (defects). Finally, 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 at their centers, but they are quite loosely packed on their periphery. This agrees with the fact that colloid growth is well pronounced in many alkali halides only at higher temperatures (e.g. at  $T \geq 60^\circ \text{C}$  in NaCl [4]).

At 500 K (Fig. 5,b) the aggregates are characterized by nearly the same small core but of a much greater radius  $r \approx 120a_0$ . Very large values of the joint correlation functions of similar defects,  $F_{AA}$ ,  $F_{BB} \approx 10^4$  as  $r \rightarrow 0$ , clearly demonstrate colloid formation at this temperature.

A detailed study of the colloid growth for several particular ionic solids (NaCl,  $\text{CaF}_2$  and LiF crystals) is now in progress.

### CONCLUSION

We have presented here results of the first-principles theory of colloid formation through the aggregation of similar *interacting* particles during the bimolecular reaction  $A+B \rightarrow 0$  (annihilation) with the permanent particle source, and applied new theory successfully to the discrete-lattice description of the kinetics of the aggregation

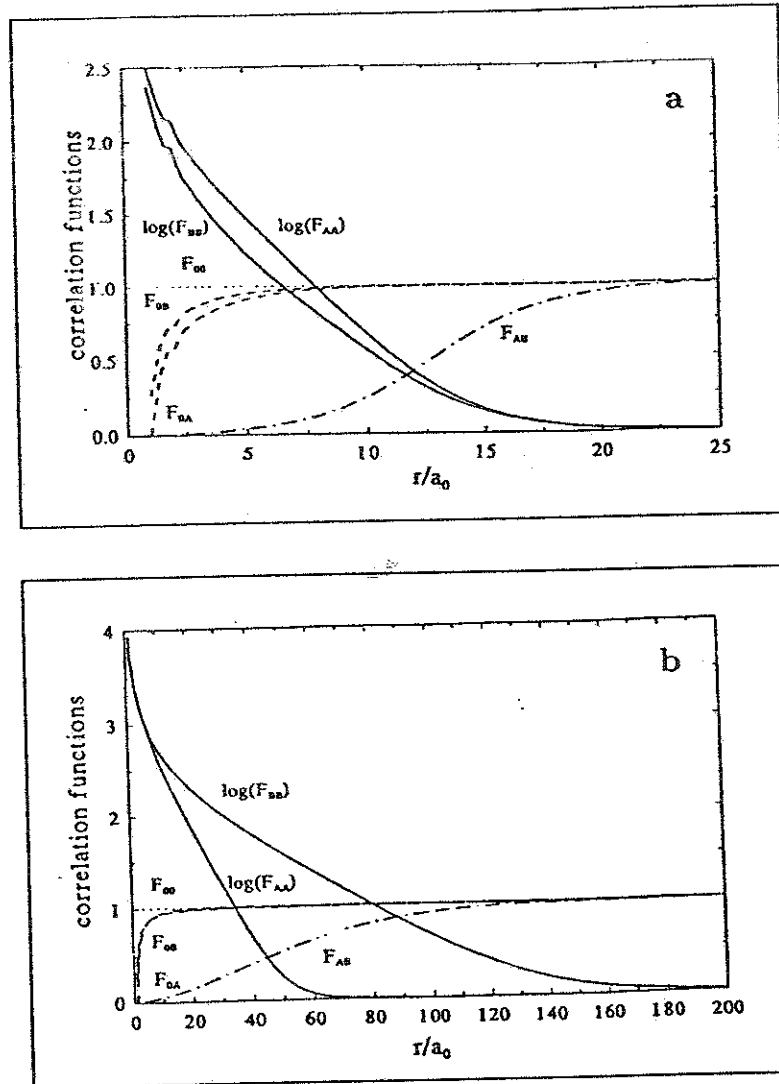


Fig. 5. The joint correlation functions at 300 K (a) and 500 K (b) for long times are plotted as a function of the relative distance between particles (see explanation in the text). Note that  $F_{AA}$  and  $F_{BB}$  are plotted in the semi-logarithmic scale

(colloid formation) in a model alkali-halide crystal exposed to irradiation. We have shown that this process includes several stages: it begins with a reduction in the mobility of interstitials via their aggregation, then vacancy aggregation is triggered, and at the last stage the essentially *cooperative behaviour* in the aggregation of the two kinds of Frenkel defects leads to quite similar their aggregates.

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DIFŪZIJAS KONTROLĒTĀ KOLLOIDU VEIDOŠANAS TEORIJA  
CIETĀS VIELĀS TĀS APSTAROJOT

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Anotācija

Mikroskopiskā līmenī aprēķināta difūzijas kontrolēta Frenkeļa defektu (starpmezglu atomu un vakanču) agregatizācija cietās vielās tās apstarojot. Teorija balstās uz režģa formalisma kopīgi saistītam pāru korelāciju funkcijām vienādiem un atšķirīgiem defektiem, iegūtām izmantojot Kirkvūda superpozīcijas tuvinājumu.

Modelis iekļauj defektu veidošanu, difūziju, pievilkšanu un komplementāro defektu bimolekulāro ( $A+B \rightarrow 0$ ) rekombināciju. Pētīti nosacījumi efektīvai defektu agregatizācijai. Parādīts agregatizācijas procesa kooperatīvais raksturs.