Variability in atomic collision cascade distributions



2001 J. Phys.: Condens. Matter 13 5365

(http://iopscience.iop.org/0953-8984/13/22/326)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 5365–5375 www.iop.org/Journals/cm PII: S0953-8984(01)21659-2

# Variability in atomic collision cascade distributions

**M Hou**[1,4], **A Souidi**[2] **and C S Becquart**[3]

[1]Physique des Solides Irradiés CP234, Université Libre de Bruxelles, Campus de la Plaine, Boulevard du Triomphe, B-1050 Brussels, Belgium
[2]Centre Universitaire de Saida, BP138, En-nasr, Saida 20000, Algeria
[3]Laboratoire de Métallurgie Physique et Génie des Matériaux, UMR8517, Université de Lille 1, F-59655 Villeneuve d'Ascq Cédex, France

E-mail: mhou@ulb.ac.be

Received 5 February 2001, in final form 9 March 2001

**Abstract**

The origin of the variance in several properties characterizing atomic collision cascades in crystals and polycrystals is investigated by full molecular dynamics and its binary collision approximation. The critical dependence of the cascade development on the initial conditions is evidenced. In the case of internal irradiation, as a consequence of this instability, atomic thermal displacements from equilibrium lattice sites are sufficient to induce a complete loss of correlation with the initial conditions before the end of the cascade development. Thermal disorder turns out to be the leading factor determining the spatial configuration distributions of induced stable point defects, which are particularly broad and skewed. In contrast with spatial distributions, the frequency distributions of Frenkel pairs are known to be particularly narrow. An explanation is suggested, based on the vacancy–interstitial distance distributions which are also found to be uncorrelated from the initial conditions.

## 1. Introduction

When a large amount of kinetic energy is provided to an atom in a solid, this atom, the so-called primary knock-on atom (PKA), generates an atomic collision cascade. The PKA may be an ion of an energetic beam slowing down on a surface, an atom at an interstitial or at a lattice site in a crystal or a fission fragment. It is well known that spatial correlations in crystalline materials may have a significant influence on the atomic motion and the correlation of this motion with the initial conditions. Channelling [1] and low energy focused collision sequences along close packet rows (see [2] for a review) are well known examples of lattice effects on the atomic motion. Other lattice effects are discussed in [3]. When a PKA is initiated at a lattice site, its channelling is prevented. The question addressed in this paper

[4] Corresponding author.

  

is to what extent, the critical sensitivity of collision cascades to the initial conditions may be the driving factor which governs the spatial distributions of the point defects produced in a single crystal. This would have the consequence of de-correlating the cascade development from the initial conditions and inducing a large variability in the final defect configurations. The lifetime of collision cascades is short (typically less than one thermal vibration). If the de-correlation time is still shorter, thermal displacements of atoms from their lattice sites may be expected to represent a sufficient perturbation to induce stochasticity.

We calculated the spatial point defect distributions produced by elastic collision cascades. As expected for systems where evolution is dominated by an instability, we show that, because of thermal disorder, these distributions are fully de-correlated from the direction of the PKA with respect to the lattice orientation. Spatial configuration distributions were estimated quantitatively and display a huge variability. In contrast with their spatial distributions, the Frenkel pair frequency distributions (frequency distributions of stable vacancy–interstitial pairs) display little variability. This was already predicted by simulations in the binary collision approximation [4] or by full molecular dynamics (MD) in this work as well as by others [5]. Such a small variance was also predicted analytically [6] in structureless materials. In this work, we show that a vanishingly small variance of the Frenkel pair frequency distributions is a natural consequence of the de-correlation from the initial conditions.

The atomic elastic collision cascades were initiated in iron by high-energy PKA using both full MD and its binary collision approximation (BCA). Iron was selected as a case study, generic to other crystalline and polycrystalline solids.

Full MD has the advantage of modelling the time evolution of a box of atoms as a whole. However, accumulating statistics over large samples of collision cascades by MD is nowadays still not practical in the energy range of interest in radiation damage studies. This drawback is drastically reduced in the BCA, at the expense of an approximate treatment of multiple simultaneous interactions. The BCA is indeed several orders of magnitude less computer time consuming than MD, therefore it allows for reasonably significant statistics in case of widespread statistical distributions. The discussion of the measure of the model approximations used is beyond the scope of the present work. However, since the consequences of the approximations are not all fully identified, the BCA needs to be grounded on full MD predictions as much as possible.

The next section is devoted to a brief description of the MD and BCA models used. The concepts derived from component analysis used to study spatial point defect distributions are reviewed. Evidence for trajectory instabilities is given in section 3 and their consequences are shown. The origin of the variance of stable point defect frequency distributions is discussed in section 4.

## 2. Atomic scale models

### *2.1. Full molecular dynamics*

The MD code used, DYMOKA [7], is a slightly modified version of CDCMD [8]. The Newton equations of motion are integrated using a fifth-order Gear predictor–corrector algorithm. The neighbour search is done with a linked cell method combined with a Verlet list so that the code is fully linear with the number of atoms [9]. The interatomic potentials are tabulated and the interpolation of the potential is made through a fifth-order Lagrange polynomial. In this work, we used the EAM potential developed in [10].

The effect of electron excitation was neglected. Periodic boundary conditions were used with a choice of the simulation box size depending upon the energy of the PKA.

At the beginning of the simulation, the system of particles was allowed to equilibrate for 5 ps at the desired temperature (600 K in the present case study). When the lattice was at thermal equilibrium, one PKA was given a momentum corresponding to energies from 1 to 30 keV. The discussion below is exemplified with 20 keV PKA only. The actual time step was 'manually' adapted to the PKA velocity, and it can be as low as $10^{-17}$ s. As soon as the extreme collisions are over, a much longer time step is adequate, i.e. $10^{-16}$ to $10^{-15}$ s. More detail on the procedure can be found in [11].

### *2.2. The binary collision approximation of molecular dynamics*

The Marlowe program was used to model atomic collision cascades in the binary collision approximation. The model is particularly flexible and described through an extensive literature. A basic reference is given in [12]. Collision cascades in bulk materials are described as sequences of binary encounters between which atoms move freely along their scattering asymptotes. Individual collisions are governed by pair potentials that may have an attractive component [13]. We used the repulsive potential form given in [14] because, at small separation distances, its slope is close to that of the repulsive branch of the EAM potential employed in the full MD calculations. The potential function is used to estimate the scattering angle and the time integral in each binary collision. Integration is achieved by means of a Legendre quadrature, the accuracy of which may be tuned. Particles are considered to move along their asymptotic path. The binary collisions are chronologically ordered so that time represents the driving parameter in the cascade development. Electron excitations were neglected to compare with the full MD model described above. The number of collisions undergone by the moving atoms was limited by a maximum impact parameter value selected a little smaller than the first neighbour distance in iron. Energy parameters are available to model the binding of atoms and others to cut off their trajectories. Their adjustment is discussed in section 2.4.

### *2.3. Component analysis of point defect distributions*

Component analysis is an efficient technique to uniquely associate an ellipsoid with each individual displacement cascade. Such ellipsoids account for the spatial extension and the morphology of the displacement cascades [15]. The information provided by this method is the direction of three orthogonal axes that are associated with the spatial point defect distribution and the variance of this distribution projected onto them. The major axis has the direction maximizing the variance, the second maximizes the variance of the distribution projected onto a plane perpendicular to the first and the third one has the direction minimizing the variance.

The major axis has the direction of a unit vector $\boldsymbol{u}$, such that the quantity

$$S^2 = \sum_{k=1}^{n} |f_k|^2 = \sum_{k=1}^{n} (\boldsymbol{u} \cdot \boldsymbol{r_k})^2 = \boldsymbol{u} \cdot \boldsymbol{R}\boldsymbol{u} \tag{1}$$

is maximal. $f_k$ is the projection of the position vector $\boldsymbol{r_k}$ of the point defect $k$ on the major axis. $n$ is the number of point defects considered and $S^2$ is thus the variance of the point defect distribution projected on directions $\boldsymbol{u}$. $\boldsymbol{R}$ is proportional to the covariance matrix of the point defect positions. By expressing the fact that the derivative of $S^2$ with respect to $\boldsymbol{u}$ is zero, one obtains:

$$\boldsymbol{R}\boldsymbol{u} = \alpha^2 \boldsymbol{u}. \tag{2}$$

The second and third directions are found in a similar way and they are thus parallel to the directions of the eigenvectors of the covariance matrix of the point defect distributions. The

associated eigenvalues are the variances of the distribution projected onto the directions of the eigenvectors. The problem is thus limited to the diagonalization of a $3 \times 3$ symmetrical real and positive matrix, which is quite straightforward. These eigenvectors and eigenvalues allow us to associate with each cloud of point defects an ellipsoid for which the axis lengths are given by the standard deviation of the distributions projected onto the directions of the eigenvectors. Such ellipsoids define the *cascade cores*. Using this technique, cascade core volume distributions were constructed. The anisotropy of each cascade core was measured from the ratio between the lengths of the axes maximizing and minimizing the projected distribution variance. A more elaborate approach is developed in [16], which allows accounting for cascade inhomogeneities and subcascade formation, thus associating possibly more than one ellipsoid per cascade. Such a detailed description is not necessary for the present discussion.

### *2.4. Consistency between the BCA and MD models*

The binary collision approximation is several orders of magnitude faster for collision cascade calculations than full MD. This is a significant advantage for predicting statistical distributions requiring the calculation of a large number of events. However, since BCA predictions are sensitive to several parameters that are not relevant to MD, the consistency between the two approaches needs to be established. This is the purpose of the present section.

The dynamics of atomic collision cascades was studied in the case of low-energy cascades in copper and gold [17] using full MD and its BCA. The mean number of moving atoms was measured against time. An excellent agreement between full MD and its BCA was found in elemental metals, even for atoms having total energies as low as 0.5 eV. In order to reach this agreement, lattice atoms had to be considered as bound to their lattice sites with a binding energy equal to the material cohesive energy. In replacement collisions however, since both the initial and final situations consist of a moving interstitial and a lattice atom, the binding energy to the lattice site had to be drastically reduced and a value of 0.2 eV used. This order of magnitude was consistent with the comparison between various models made in [2]. In the present work, the same energy parameter adjustment was used.

To determine the number of Frenkel pairs formed in the BCA, one often uses a displacement energy threshold around several 10 eV. Atoms recoiling with less energy are thus considered to produce no further displacements. We prefer to account for an instability volume [18]. In this work, a Frenkel pair is thus considered to be stable if and only if its vacancy–interstitial separation distance is larger than this instability or recombination radius. Within the range of PKA energies considered, the BCA provides good agreement overall with MD for the number of Frenkel pairs formed if $3\,a_0 < r_c < 3.5\,a_0$. $a_0$ is the lattice distance and $r_c$ the recombination radius. With this model, about 90% of the Frenkel pairs are produced by replacement sequences in a single crystal at 600 K.

## 3. Sensitivity of collision cascades to the initial conditions

The critical sensitivity of a system on initial conditions is a classical problem of statistical physics, often discussed in terms of a Lyapunov exponent. A Lyapunov exponent characterizes most of the physical systems where evolution in phase space can be described by a set of first-order differential equations [19]. The exponent characterizes the temporal evolution of a perturbation to the solution of this set of equations. When it is negative or zero the solution is stable and the evolution of the perturbed system converges to the unperturbed solution. When it is positive, a divergence takes place which grows exponentially with time and the correlations with the initial conditions vanish. In computations a Lyapunov positive exponent

has two origins. One is numerical and results from the inaccuracy of the integration algorithm employed. That point is discussed in [9]. The second origin is physical and is discussed in [19]. A positive exponent is associated with a de-correlation from the initial conditions with time. When the integration algorithm is accurate enough, the associated de-correlation time is longer than the physical de-correlation time, and the latter can be identified. This applies to atomic collision cascades. The occurrence of such a divergence should thus imply a de-correlation of the cascade evolution from the initial conditions.

In what follows, we show that the physical de-correlation time is short enough compared with the cascade lifetime that the correlation between the initial conditions and the final point defect distributions has vanished. To this purpose we measure, in configuration space, the temporal evolution of the Euclidean distance between spatial configurations when the initial distances only differ by a small amount. In a $3N$-dimensional space (where $N$ is the number of atoms), this distance is defined by

$$d_N^2(t) = \sum_{i=1}^{N} \left[ (\boldsymbol{r}_i(t) - \boldsymbol{r}'_i(t) \right]^2 \tag{3}$$

where $\boldsymbol{r}_i(t)$ and $\boldsymbol{r}'_i(t)$ refer to the position vector of particle $i$ in the system at time $t$ after the PKA initialization from positions which differ from each other by a small distance $\Delta$. The same expression is used in [20].

With this definition, only particles that were moving earlier than $t$ contribute to the distance between configurations. Equation (3) can thus be evaluated in the BCA as well as in MD, even though the BCA does not use a finite simulation box. This Euclidian distance was measured as a function of time both by full MD and by its BCA for $\Delta/\sqrt{3} = \Delta_x = \Delta_y = \Delta_z = 0.005$ Å. The initial system temperature was 0 K, in such a way that all atoms initially sat at their geometrical lattice positions (except the PKA which was displaced by ($\Delta_x$, $\Delta_y$, $\Delta_z$)). The evolution of this distance versus time is shown in figure 1 in a semi-log representation (the evolution is shown as computed in the BCA, and similar curves were obtained by full MD).

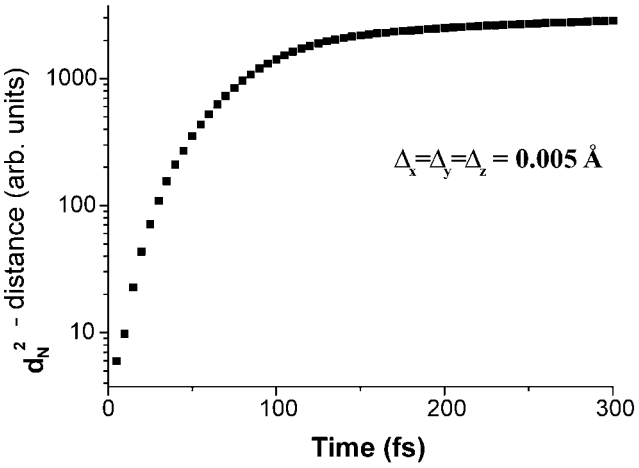


**Figure 1.** Euclidean distance, $d_N(t)$ (see (3)), between spatial configurations generated by PKA initiated at one lattice site and at the site situated $\Delta = (0.005$ Å, 0.005 Å, 0.005 Å) away from this lattice site. The initial energy was 20 keV and the PKA momentum direction was parallel to the same ⟨135⟩ direction.

The time dependence of the distance much resembles that expected in the case of an instability characterized by a positive Lyapunov exponent. It is indeed close to exponential in the early stage of the cascade development. This exponential behaviour is moderated by a saturation effect, induced by particles coming to rest while the cascade evolves. The accuracy of the scattering integrals estimated in the BCA was considered to be good enough so that higher accuracy does not bring any sizeable difference in the temporal evolution obtained. Hence, this instability is not of numerical origin.

The consequences of this instability on atomic displacements are significant. To show this, the simulations in figure 1 were repeated for different small values of $\Delta$ by full MD, recording the number of occurring vacancies as a function of time. The results are presented in figure 2 for three $\Delta$-values. The initial temperature was again 0 K. It appears clearly that a very small difference in the initial conditions leads to a significant difference (more than 30%) in the number of vacancies formed after 300 fs. Thus the initial conditions profoundly influence the development of the collision cascades.

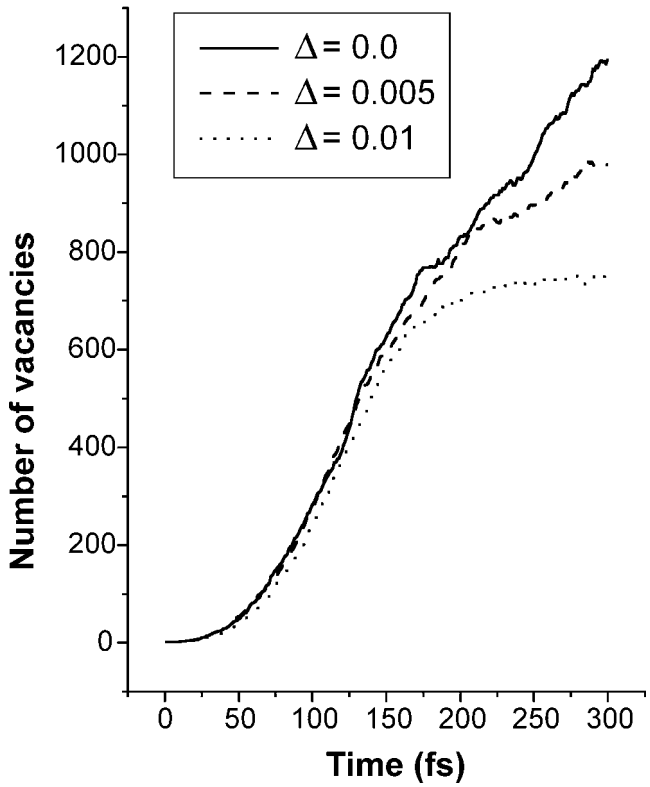


**Figure 2.** Number of vacancies as a function of time obtained for three slightly different values of $\Delta$. Calculations performed by full MD for 20 keV PKA oriented along the same $\langle 135 \rangle$ direction.

The $\Delta$-values used in the preceding discussion are more than one order of magnitude smaller than the root mean square thermal vibration amplitude in iron at room temperature [21]. Consequently, thermal vibrations of atoms around their equilibrium lattice positions are expected to generate such an instability, and therefore to affect the spatial configurations of the final defects.

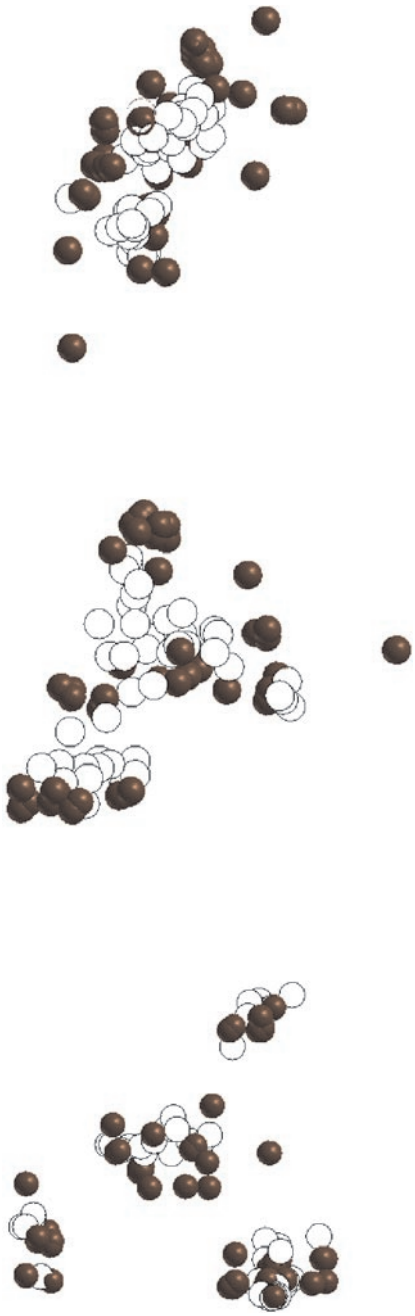

**Figure 3.** Three examples of stable vacancies (open circles) and interstitials (dark spheres) obtained by full MD with a PKA oriented in the same ⟨135⟩ direction with 20 keV initial energy. The iron temperature was 600 K. The only difference between the three cases is the initial thermal configuration of the crystal.

This is what can be observed in figure 3 which displays three examples of residual vacancy and interstitial final configurations at the end of three different 20 keV collision cascades modelled by MD at 600 K. The simulations were done with a PKA directed in the same ⟨135⟩ direction. The only difference when launching the PKA was the initial instantaneous thermal configuration. All other initial conditions were identical. The final vacancy and interstitial configurations appear to depend substantially on the initial thermal

configurations, and significant configuration variability in the final state of the system is qualitatively observed. The differences observed in figure 3 are typical of all the cascades investigated by both MD and its BCA. Vacancies are seen to cluster into cores surrounded by the interstitials, consistently with the pioneering schematic picture of Brinkman [22]. Subcascade formation is also found.

The divergence evidenced by figure 1 enhances the variance of the configuration distributions as time evolves. This enhancement is limited by the fact that, after a time which is finite, moving atoms come to rest. The balance between both effects is illustrated by the results in figure 4 which shows typical distributions of core volumes and anisotropies

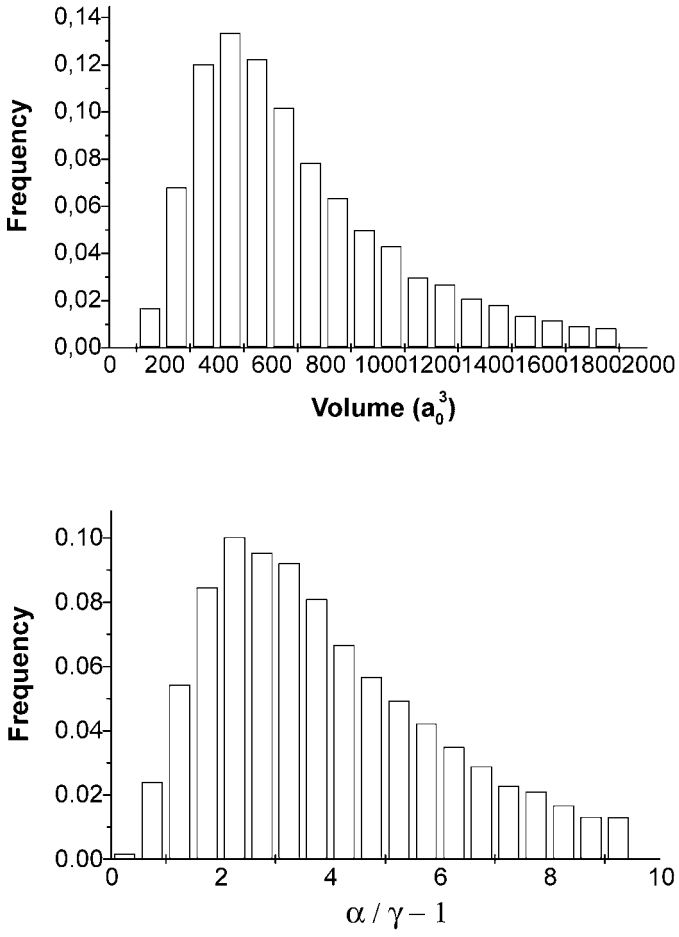


**Figure 4.** Frequency distributions of cascade volumes (a) and anisotropies (b) for cascades calculated in the binary collision approximation and initiated in the same conditions as those shown in figure 3. The statistics were accumulated over 5000 cascades. The tail distributions have been truncated. Simulations using other PKA momentum directions as well as using isotropic and random momentum direction selection provide similar statistical distributions.

obtained with the component analysis method described above. All the cascades were initiated from a lattice site by 20 keV PKA in a crystal at 600 K. Statistics were accumulated in the BCA over 5 to 15000 cascades. The cascade core anisotropy was measured by $\alpha/\gamma-1$, where $\alpha$ and $\gamma$ are the lengths of the major and minor axes of the ellipsoids respectively. The

distributions are quite broad and the widths relative to modal values are over 100%. They are pronouncedly skewed toward high values and subsequently the most probable and mean values differ significantly.

The same distributions as in figures 4(a) and 4(b) were found with initial directions in the ⟨135⟩ and ⟨235⟩ directions, as well as when the PKA directions were selected isotropically and at random. It can thus be concluded that final cascade configurations are not correlated to the initial conditions. This is a direct consequence of the instability revealed by figure 1, of which the physical origin is thermal disorder.

## 4. Frequency distributions of Frenkel pairs

As already noticed in the introduction, the variance of the frequency distributions of Frenkel pairs obtained both in the BCA and by MD is quite small, despite the effect of the divergence shown in figure 2. Subsequently, the mean number of Frenkel pairs produced by collision cascades can be determined accurately on the basis of limited sampling. It was estimated in [4] that, in the case of copper, at 10 keV, a sample of 20 cascades should yield no more than 1% uncertainty in the value of the mean number of Frenkel pairs produced. This is qualitatively confirmed by the MD calculations performed here as well as in [5]. Ten to twenty cascades were sufficient to limit the uncertainty to a few per cent. This uncertainty is consistent with the variance of the frequency distributions of the Frenkel pairs analytically calculated in [6] for a Kinchin and Pease model [23].

The Kinchin and Pease theory is based on an energy partition model among the atoms in the solid via binary collisions and the occurrence of a displacement energy threshold. It does not take into account the spatial configuration of the point defects produced. Consequently, point defect distributions, as predicted by the Kinchin and Pease model, are not subjected to the instability discussed above. In the BCA displacement model used here, the criterion for the production of Frenkel pairs is based on a vacancy–interstitial threshold distance. A stable Frenkel pair is considered to be produced if the vacancy–interstitial separation is larger than 3.5 lattice units. The number of Frenkel pairs thus depends on the spatial configurations of the vacancies and interstitials produced, that are affected by the instability evidenced by figure 1.

The question is now to understand why Frenkel pair frequency distributions only display small variances although their spatial configuration distributions are subjected to divergence. Figure 5 shows the mean number of Frenkel pairs produced with this model as a function of the recombination radius. The simulations were performed in the BCA, in the same conditions as those used to establish the configuration distributions in figure 4. As was found for these distributions, the vacancy–interstial distance distributions obtained by selecting the PKA momentum in a ⟨135⟩ direction, a ⟨235⟩ direction and isotropically at random, are indistinguishable. The distribution in figure 5 is thus not correlated with the initial conditions for a given PKA energy. The curve drawn in figure 5 passes through 24 mean frequency values corresponding to 24 different values of the recombination distance ranging from 1 to 7.5 lattice units. Statistics were accumulated over 1000 trajectories for each initial condition. The estimated standard deviation of each frequency is lower than 3% of the mean. This small variance is a consequence of de-correlation. Consequently, the number of vacancy–interstitial pairs separated by a distance larger than a well defined recombination radius is independent of the initial conditions. In the present simulation, the standard deviation of the frequency distributions is lower than 3% for any recombination radius. It would become still smaller with a larger sampling.

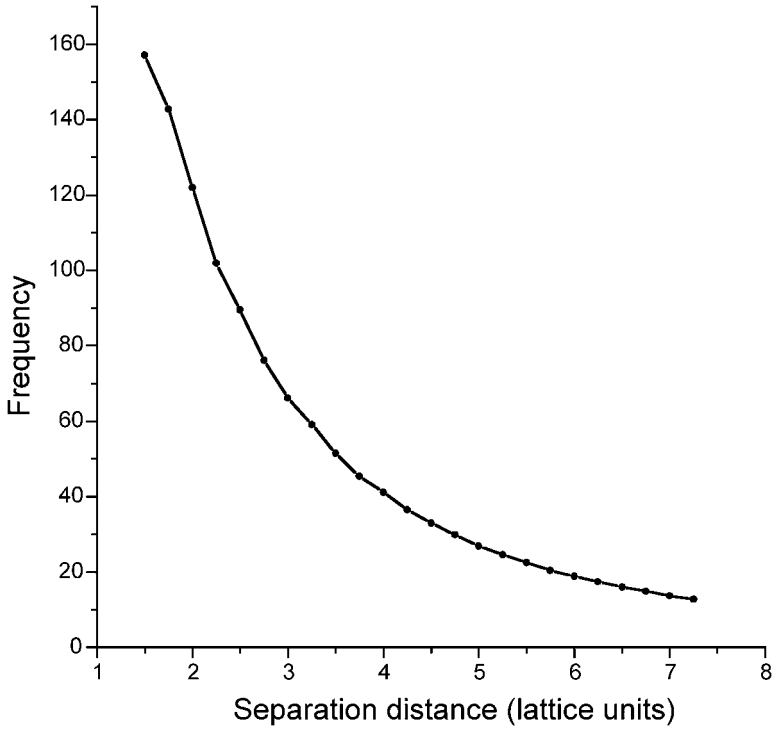


**Figure 5.** Mean number of Frenkel pairs produced as a function of the vacancy–interstitial recombination radius. The simulation conditions are the same as in figure 4. Distributions obtained with ⟨135⟩, ⟨235⟩ PKA momentum directions and with isotropic random direction selection differ by less than the size of the points plotted in the figure.

## 5. Conclusion

To summarize, we showed for internal irradiation that the collision cascade development is critically dependent on the initial conditions. A perturbation in the initial position of the PKA, one order of magnitude smaller than a typical root mean square thermal displacement, is sufficient to induce a difference larger than 30% in the number of vacancies produced after a few hundred femtoseconds. Consequently, and as predicted for systems characterized by a positive Lyapunov exponent, the point defect distributions are not correlated with the initial conditions. They display large variance and skewness. It thus turns out that the cascade lifetime in the present simulations is larger than the time required for de-correlation. It should be noticed that the situation may be different in the case of lower energy PKA. Indeed, the cascade lifetime decreases with decreasing PKA energy and de-correlation may not take place fully. This suggestion is supported by recent MD simulations in iron with PKA starting with an energy of a few hundred eV [24].

We also found that the vacancy–interstitial distance distributions in cascades are independent on the initial conditions. We show that this is the reason why, in a Frenkel pair model involving a recombination threshold distance, the variance of the frequency distribution of Frenkel pair is extremely small. In the present work, this recombination threshold is isotropic and thus independent of the crystallography. Deviations from isotropy may result in broader Frenkel pair frequency distributions.

To initiate PKA at a lattice site inhibits the primary channelling. In the case of external irradiation, channelling may be quite efficient and represents a strong correlation with the initial conditions which is thus not affected by the instability discussed here. The consequences for the Frenkel pair configuration and frequency distributions may be quite significant. More generally, the consequences of a combination between correlation and de-correlation in atomic collision cascades is a question still almost unexplored, and considered for future work.

## Acknowledgment

This research is partially conducted under contract IUAP 4/10- with the Belgian Federal Government.

## References

[1] Lindhard J 1965 *Mat. Fys. Medd. Kon. Dan. Vid. Selsk.* **34** 14
[2] Robinson M T 1981 *Sputtering by Particle Bombardment* vol I, ed R Behrisch (New York: Springer)
[3] Hou M and Eckstein W 1990 *Phys. Rev.* B **42** 5959
[4] Robinson M T and Torrens I M 1974 *Phys. Rev.* B **9** 5008
[5] Stoller R 2000 *J. Nucl. Mater.* 746 283–287
[6] Leibfried G 1965 *Bstrahlungseffekte in Festkörpern* (Stuttgart: Teubner)
[7] Becquart C S, Decker K M, Domain C, Ruste J, Souffez Y, Turbatte J C and Van Duysen J C 1997 *Radiat. Eff. Defects Solids* **142** 9
[8] A C version of CDCMD can be found at http://www.ims.uconn.edu/centers/simul/index.htm#xmd.
[9] Allen M P and Tildesley D J 1987 *Computer Simulation of Liquids* (Oxford: Oxford Science)
[10] Ludwig S M, Farkas D, Pedraza D and Schmauder S 1998 *Modelling Simul. Mater. Sci. Eng* **6** 19
[11] Becquart C S, Domain C, Legris A and Van Duysen J C 2000 *J. Nucl. Mater* **280** 73
[12] Robinson M T 1989 *Phys Rev.* B **40** 10717
[13] Robinson M T 1997 *Radiat. Eff.* **141** 1
[14] Nagakawa S T and Yamamura Y 1988 *Radiat. Eff.* **105** 239
Nagakawa S T 1991 *Radiat. Eff.* **116** 21
[15] Hou M 1985 *Phys. Rev.* B **31** 4178
[16] Hou M 1989 *Phys. Rev.* A **39** 6
[17] Hou M and Pan Z-Y 1997 *Radiat. Eff.* **142** 483
[18] Scholtz A and Lehmann C 1972 *Phys. Rev.* B **6** 813
[19] see e.g. Berger P, Pomeau Y and Vidal C 1998 *L'ordre dans le Chaos* (Paris: Hermann)
Sagdeev R Z, Usikov D A and Zaslavsky G M 1988 *Nonlinear Physics* (New York: Harwood Academic)
[20] Frenkel D and Smit B 1996 *Understanding Molecular Simulation* (San Diego: Academic Press)
[21] Haworth C W 1960 *Phil. Mag.* **5** 1229
[22] Brinkman J A 1956 *Am. J. Phys.* **24** 246
[23] Kinchin G and Pease R 1955 *Rep. Prog. Phys.* **18** 1
[24] Stoller R 2000 *Proc. MRS Meeting (Boston)* at press