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Stochastic theory for clustering of quenched-in vacancies— 1. General mathematical properties

G ANANTHAKRISHNA
Reactor Research Centre, Kalpakkam 603 102

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Abstract. The problem of clustering of quenched-in vacancies into various types of extended defects is considered. A master equation for the evolution of the concentration of clusters of various sizes is written down with general transition rates. It is shown that this model represents a continuous time non-stationary Markoff process. A particular choice of transition rates corresponding to the formation of vacancy loops and stacking fault tetrahedra is considered in some detail. It is shown that this choice of transition rates allows us to obtain the solution for the concentration of the single vacancy units, and hence yields some information on the nucleation time. Further, the transition matrix becomes stationary and doubly stochastic due to the short time constant of the concentration of single vacancy units. This in turn leads to an unphysical stationary state. Finally we show how the rate equations for the irradiated situation can be written down and derive the phenomenological rate equations that are conventionally used.

Keywords. Vacancy units; vacancy loops; stacking fault tetrahedra; Markoff process; master equation.

1. Introduction

Clustering of vacancies into various configurations has been observed when a material is quenched. The nature and the kind of defect configurations that are produced depend on the precise conditions of quenching such as the rate of quenching, the quenching and ageing temperatures, the medium of quenching, etc. (Kiritani *et al* 1964; Kiritani 1964; Westmacott 1966). The defects observed include vacancy loops, stacking fault tetrahedra and voids. These defects are also formed in the case of irradiated samples. In addition, one can have interstitial configurations. There are sinks for both vacancies and interstitials such as grain boundaries, dislocations, and the surface of the specimen. In addition to the recombination of vacancies and interstitials, the interstitials are known to diffuse to these sinks preferentially. Thus there will be an excess of vacancies in both cases (quenched and irradiated samples). It is the excess vacancy over and above the equilibrium concentration that leads to vacancy clustering in both instances.

The purpose of this work is to evolve a model for clustering of supersaturated system of vacancies induced by quenching. Clustering of vacancies in irradiated samples is clearly a more complicated situation due to the presence of another kind of an elementary defect, namely the interstitials and will be the object for future investigation. We shall however touch upon some aspects of this problem. There have been some theoretical attempts to understand the formation of vacancy loops and

voids. Most of these theories treat nucleation and growth separately. In addition, as for the growth part, the equations describe the growth of a cluster of an average size only (Katz and Weidersich 1971; Weidersich 1974; Harkness and Li 1969; Norris 1972). Our line of attack differs considerably from these studies both in content and in spirit. In our theory nucleation and growth are treated on the same footing, in the sense that both the formation of small clusters (nucleation) and their growth, are described by the same set of equations, with the growth of large clusters resulting from a continuous evolution of small clusters. Indeed, there is no well-defined demarkation between the nucleation of small clusters and the growth of large clusters. From this point of view, our approach is closely similar to that of Kiritani (1973) and Hayns (1976). Another basic difference is that we consider the problem as one wherein statistical methods have a natural role to play unlike the previous theories which take a deterministic approach. The support for this view is clear. Primarily the problem is a many body problem wherein fluctuation in the number of clusters at any instant is a natural consequence of the subsystem (i.e., the entire configuration of vacancy clusters and the vacancies) being in ' contact ' with its surroundings. The underlying physical cause may be varied; for instance, the fluctuations may be thermal or due to the diffusive motion of the elementary defects, and so on. So the number of vacancies contained in a cluster is considered as a random variable, with N_n representing the distribution function of the clusters with n vacancy units.

The basic idea is to set up a general model for clustering of vacancies starting from a microscopic point of view. We shall only be interested in the statistical aspects of clustering. The physical input is incorporated in the transition rates of association and dissociation. The present paper is the first of a series of papers which addresses to the general problem of clustering. In order to present the logical sequence of long winding modelling undertaken in this series of papers, we would like to give at the outset an outline of how we go from a general model of clustering to a particular continuum model. In the present paper to be referred to as paper I, we introduce a general model of clustering described by a master equation for the evolution of the clusters. A natural step would be to specialise the model to the formation of specific kinds of extended defects. Solving the rate equations for the formation of any kind of extended defect starting from small clusters (nucleation) and following the growth of clusters until the formation of stationary distribution of the clusters is an extremely complex problem. For this reason we attempt a much simpler problem which we have outlined below.

The problem of formation of extended defects can be viewed as a composition of the formation of small clusters (nucleation) and the growth of these clusters. This means all the clusters are formed within the nucleation period. This is valid in many interesting situations. The first one-namely nucleation, may in principle be understood by solving the appropriate rate equations on a computer. The difficulty here is one of putting the information about the binding energy, the impurity content, sources, sinks, etc. Since the nuclei are expected to form in a short period, there is no difficulty in solving these equations on a computer (see Wiberg and Vingsbo 1977; Kiritani 1973 and Hayns 1976). Often the problem of nucleation can be treated starting from a thermodynamic basis (Katz and Weidersich 1971; Weidersich 1974). However, obtaining closed form expressions for the nucleation, starting from kinetic rate equations, is very difficult due to the fact that the transition rates are complicated functions of the number of vacancy units, impurity concentration, etc. On the other

hand, the problem of growth has the difficulty of handling a very large number of equations and hence is difficult to solve on a computer as we have already mentioned. But, since the evolution of clusters after the initial incubation or nucleation period, is expected to be smooth, it is expected that the dependence of transition rates on the number of vacancy units is much simpler. Therefore we expect that it may be simpler to solve the problem of growth if the initial distribution of nuclei can be obtained in some way. It is this simplified problem that forms the subject matter for this series of papers. More specifically, our aim would be to evolve a model in which we can obtain the above information by calculating the concentration of single mobile units in a some-what idealised situation which provides just sufficient information for solving the growth problem. This involves decoupling of the equation for the decay of the concentration of single vacancy units from that of growth. That such a decoupling is possible comes from the physical consideration that the time constant for the decay of the concentration of single vacancy units should be small compared to the time scale involved for the growth of clusters of large size.

We have achieved the above objective in two stages. We first introduce a model which deviates considerably from the actual physical situation as far as the concentration of single vacancy units is concerned, but yields a closed form expression and therefore allows the decoupling mentioned above. This also gives us sufficient information to proceed with the problem of growth. This model corresponds to a particular choice of the transition rates leading to a solvable model. In this model the probability of emission is regarded as constant for clusters of all sizes. In a real situation however, the probability of emission x_2, is a function of n, the number of vacancy units in the cluster, i.e., $x_2=x_2(n, T)$. This is expected to lead to somewhat unphysical results as far as the concentration of single vacancy units is concerned. However, the results that we use for the problem of growth are reasonably consistent with the computer calculation of Kiritani (1973). *Although it appears that we have disregarded the dependence of x_2 on n, it turns out that this parameter in the final analysis depends upon $\langle n\rangle$, where the angular brackets refer to the average over the distribution N_n, i.e.,* $x_2=x_1$ ($\langle n\rangle$ T). Thus it should be regarded as a parameter to be determined from experiments. Therefore this parameter can indirectly take care of some idealisations (see discussion in Ananthakirshna 1979a and 1979c which are referred to as papers II and IV respectively). The main advantage is that it is a solvable model and gives a hint as to how the inadequacies of this model can be removed. The solution of this model forms the content of the paper II. The solution in closed form is only possible due to the choice of the number of sites for absorption and emission and the assumption about constant binding energy. Although some comparison is possible with experiments, the model has two inadequacies, namely, the highly peaked distribution and the non-evolution of the peak of the distribution (when transformed into the space where the radius of the loop rather than the number is measured.) In order to preserve the solvable nature of this model and to remove the inadequacies we attempt to construct a continuum model based on the above model. The idea here is to go to the continuum limit and construct an equation for growth of clusters consistent with the equation for the single vacancy concentration. This has been successfully carried out in the third paper of this paper (Ananthakrishna 1979b, referred to paper III). We then apply this continuum model to the formation of vacancy loops and stacking fault tetrahedra. This forms the subject matter of the fourth paper.

The plan of the present paper (paper I) is as follows. In § 2, we introduce a model with two principal idealisations, namely the absence of sinks and the existence of only one mobile species. These two idealisations make the problem transparent and easily tractable. We provide justification for these idealisations. (Relaxing these two idealisations only complicates the problem and gives no better insight. However, we do remark on the master equation with more than one mobile species. We also hint on how the existence of sinks can be included when we briefly touch upon the irradiated situation.) In this model the total number of vacancy units is conserved. The process is shown to be a continuous time non-stationary Markoffian process. A discrete time Markoffian process is argued to be unphysical. In § 3, we introduce a model for the formation of vacancy loops and stacking fault tetrahedra where we make a slightly unphysical assumption which allows us to decouple the equation for the rate of change of the concentration of single units from the equations for the rate of growth of other clusters. This gives us a closed form expression for the concentration of single vacancy units and allows us to obtain some informationn about the nucleation time which is in agreement with the computer calculation of Kiritani (1973). From this we prove some general properties about the stationary state of the system. The predicted state is nearly the same as the solution obtained via the generating function method (see paper II). Some features about the averages can also be seen in this result. Finally, in § 4, we write down the rate equations for the irradiation situation. The phenomenological rate equations for the total number vacancy units contained in a cluster is derived after averaging and shown to be nearly the same as written by Bullough *et al* (1975).

2. Formulation

We first sum up a few results on clustering in quenched metals which are of relevance and which give a physical feel of the problem. Specimens are taken in the form of thin ribbons and annealed. The quenching temperature T_Q is usually about two thirds the melting point. The specimen is quenched at a certain quenching rate (in an environment determined by the nature of the study) to a temperature T_A at which the specimen is aged. The concentration of single vacancies between these two temperatures differ by nearly ten orders of magnitude. The quenched-in vacancies cluster into various configurations such as vacancy loops stacking fault tetrahedra, etc. There is an energy ϵ_n associated with the formation of such tetrahedra and loops as a function of the number n of vacancies (Cotterill 1965). We shall not be interested in the exact form of the energy of formation but we shall note that the binding energy b_n of a vacancy in a cluster with n vacancy units, given by

$$b_n = E_v^F - (\epsilon_n - \epsilon_{n-1}), \tag{1}$$

is a rapidly saturating function of n. In the above expression E_v^F is the energy of formation of a single vacancy (for more details see paper II, Ananthakrishna 1979a). A slight modification is necessary while the unit of vacancy is not single.

We assume as mentioned in § 1, that there is only one kind of mobile unit (the mobile units in some systems like gold and aluminium are the divacancies). Thus

the growth of clusters is assumed to proceed via the absorption and emission of single mobile units. This assumption is justified in most cases. For example, the mobility of monovacancies in aluminium and gold is nearly three orders less than that of the divacancies near room temperature. (For additional support of this assumption see Kiritani 1973, Kiritani *et al* 1969; Jain and Siegel 1972b). It is expected that the next mobile species may become important only at late stages of clustering. (In any event it is possible to write down a model where several species can be considered as mobile.) As a second idealisation we consider a system in which sinks are excluded. This idealisation is not serious since as far as the phenomenon of clustering is concerned, only supersaturation of vacancies is required. (We refer the reader to paper II for additional justification.)

Now we can write down the rate equations for the growth of clusters. Let $N_1, N_2 \ldots, N_n, \ldots$ be the concentrations of 1-, 2-, ..., n-unit clusters. These clusters evolve by absorbing and emitting vacancy units. The rate equations are

$$\frac{dN_1}{dt} = -\sum_{i=2} W_{i1} N_1 N_{i-1} + \sum_{i=2} W_{1i} N_i, \tag{2}$$

for the change in concentration of single vacancy units and for $n=2$

$$\frac{dN_2}{dt} = \frac{W_{2\,1}}{2} N_1^2 - \frac{W_{1\,2}}{2} N_2 - W_{3\,1} N_1 N_2 + W_{1\,3} N_3. \tag{3}$$

For $n \geqslant 3$

$$\frac{dN_n}{dt} = W_{n\,1}\, N_1\, N_{n-1} - W_{n+1\,1}\, N_1\, N_n - W_{1\,n} N_n + W_{1\,n+1}\, N_{n+1}. \tag{4}$$

In the above equations $W_{n\,1}$ is the rate at which single units collide with clusters with $(n-1)$-unit clusters to form clusters with n-units, $W_{1\,n}$ is the rate of dissociation of clusters with n-units. For $n=2$, the rate of association and dissociation are $\frac{1}{2} W_{2\,1}$ and $\frac{1}{2} W_{1\,2}$ respectively. Now for any $W_{1\,n}$ and W_{n1} the above equations conserve the total number of vacancies. It is physically clear that this should be so because we do not have any sinks, and the above equations have been written with this in mind. To see this consider

$$\sum_2 n \frac{dN_n}{dt} = \sum_3 n\, W_{n\,1}\, N_1\, N_{n-1} - \sum_3 n\, W_{n+1\,1}\, N_1\, N_n$$

$$- \sum_s n\, N_n\, W_{1\,n} + \sum_s n\, W_{1\,n+1}\, N_{n+1}$$

$$+ W_{2\,1} N_1^2 - W_{1\,2} N_2 - 2 W_{3\,1} N_1 N_2 + 2\, W_{1\,3} N_3.$$

By appropriate manipulation we find

$$\sum_2 n \frac{dN_n}{dt} = \frac{df(t)}{dt} = \sum_2 W_{n\,1}\, N_1\, N_{n-1} - \sum_2 W_{1\,n}\, N_n = -\frac{dN_1}{dt}. \tag{5}$$

Thus $N_1(t) + f(t) = c.$

Using the fact that at $t=0$, $f(t)=0$ and $N_1(0)=N_0$ we get, $c=N_0$, and

$$f(t) = N_0 - N_1, \tag{6}$$

where N_0 is the concentration of quenched-in vacancies. The above expression simply means that whatever amount of single vacancy units are lost from N_1 should be in the form of clusters. This result is independent of the form of W's.

Now we shall show that the process of clustering as we have modelled is a continuous time discrete non-stationary Markoff process. We shall rewrite equations (2), (3) and (4) with the probabilities (unnormalised) namely $p_n=nN_n$ which are the concentration of vacancies in a cluster with n-vacancy units. (This step would be essential since the Markoff property applies to probabilities only.)

$$\frac{dp_1}{dt} = -\sum_2 \frac{W_{n\,1}}{(n-1)} p_1\, p_{n-1} + \sum_2 \frac{W_{1\,n}}{n} p_n, \tag{7}$$

$$\frac{dp_2}{dt} = W_{2\,1}\, p_1^2 - \tfrac{1}{2} W_{1\,2}\, p_2 - W_{3\,1}\, p_1\, p_2 + \tfrac{2}{3} W_{1\,3}\, p_3, \tag{8}$$

$$\frac{dp_n}{dt} = \frac{n}{n-1} W_{n\,1}\, p_1\, p_{n-1} - W_{n+1,\,1}\, p_1\, p_n$$

$$- W_{1\,n}\, p_n + \frac{n}{n+1} W_{1\,n+1}\, p_{n+1}. \tag{9}$$

These three equations can be cast into an equation representing the rate of change of probability vector $\mathbf{p}$ with M components, M being the total number of quenched-in vacancies. Since $M \sim 10^{18}$ to 10^{19}, for all practical purposes it can be considered infinite.

$$\frac{d\mathbf{p}}{dt} = \tilde{\mathbf{W}}\, \mathbf{p},$$

or

$$\frac{dp_n}{dt} = \sum_{m=1}^{M} \tilde{W}_{n\,m}\, p_m \tag{10}$$

and $\tilde{W}_{n\,m}$ can be easily written down. Now we can identify $\tilde{W}$ with the transition matrix connecting different states of a non-stationary Markoffian system. For the sake of completeness we have outlined in Appendix 1, the derivation of a master equation similar to (10) starting from the Smoluchowski equation governing the conditional probabilities of a stationary Markoffian process. In the case of non-stationary Markoffian process the transition matrix connecting different states of the system with the master equation in such a case reads

$$\frac{dP}{dt}(n/m, t) = \sum_{m'} W(m, m', t)\, P(n/m', t). \tag{12}$$

$P(n/m, t)$ is the conditional probability which in a general case has to satisfy an initial condition

$$\lim_{t\to 0} P(n/m, t) \to \delta_{n\,m}. \tag{13}$$

The dependence on the initial state enters only this way. The transition matrix obeys

$$\sum_{m'} W(m/m', t) = 0. \tag{14}$$

It is clear that $\tilde{W}_{m\,m'}(t)$ corresponds to $W(m/m', t)$ and $p_m(t)$ to $P(n/m, t)$. (The index n in $P(n/m, t)$ gets suppressed due to the particular form of the initial condition in the present problem as seen below.) The fact that such a matrix would satisfy the condition (14) has been proved in deriving (5). We shall not write down the explicit form of the transition matrix for the case when general $\tilde{W}$'s are involved since we consider a special case in detail. The explicit time dependence comes from the dependence of $\tilde{W}$ on p_1. Since the material is quenched at $t=0$ and at $t=0$, only single vacancy units exist, the initial condition obeyed is

$$\lim_{t\to 0} p_n(t) \to p_1(0)\,\delta_{n\,1}.$$

Thus the conditional probability $P(n/m, t)$ reduces to a column vector. (Note that $p_n(t)$ we have defined are not normalised and therefore the additional multiplicative factor $p_1(0)$.) Thus the model we have introduced is non-stationary Markoffian in character. From this analysis it is clear that by relaxing the assumption that there is only one mobile unit introduces more non-zero off-diagonal elements and more rows in the upper triangle of the transition matrix. It is also clear that a discrete time Markoff process of the type generally introduced (see for instance Wang and Uhlenbeck 1945) is not physical, since the number of jumps a vacancy unit has to make in order to reach a cluster is not correlated with the jump time.

3. Constant binding energy model

It is physically clear that the concentration of quenched-in vacancies should rapidly decrease with time at temperatures of interest (near room temperature). However, this feature cannot be seen except in some special choices of $W_{1\,n}$ and $W_{n\,1}$. There appears to be only one choice and this choice also leads to a solvable model for the growth of clusters and is the subject matter of paper II. In this section we will only use some preliminary results of this model to investigate stationary state of the model based on the principle of entropy maximum. In a general situation the form of $W_{1\,n}$ and $W_{n\,1}$ are complicated enough to spurn attempts at solution in closed form. Their general forms can be taken as

$$W_{n\,1} = \nu\,\psi(n)\,Z_1 \exp(-E^M/kT), \tag{15}$$

and $$W_{1n} = \nu\, \bar{\psi}(n)\, Z_2 \exp\,[-(E^M + b_n)/kT], \tag{16}$$

where E^M is the energy of migration of the mobile unit, b_n the binding energy of single vacancy unit in a cluster with n-units, ν is the attempt frequency, Z_1 and Z_2 are the co-ordination numbers for hopping, and $\psi(n)$ and $\bar{\psi}(n)$ the number of absorption and emission sites respectively. As mentioned in §1, b_n is a complicated function of n, and it saturates fast. For the case of stacking-fault tetrahedra and vacancy loops, $\psi(n)$ and $\bar{\psi}(n)$ can be taken to be linear in the number of vacancy units in the cluster. (In other situations like void formation these are not linear in n.) We shall take $\psi(n)=n-1$ and $\bar{\psi}(n)=n$. This choice is not arbitrary but has been chosen to facilitate decoupling. Since b_n is a complicated function of n, equations (7), (8) and (9) cannot be solved. We have earlier introduced and solved a model which involves a slightly unphysical assumption (Ananthakrishna 1977). This model assumes that the binding energy of a vacancy unit in a cluster with n-units is independent of n and is a constant. Although this assumption is unphysical, the model is solvable in closed form. Further, in the final analysis as we will show in paper II this parameter x_2 which originally is a function of n, in this model, is a function of $\langle n\rangle$. We shall not go into details of justification of the assumption (which are given in paper II, Ananthakrishna 1979c) but consider some properties of this model relevant for obtaining the stationary state of this system. With this assumption and with these choices of $\psi(n)$ and $\bar{\psi}(n)$, (15) and (16) take the form

$$W_{n1} = (n-1)\, \nu\, Z_1 \exp\,[-E^M/kT], \tag{17}$$

and $$W_{1n} = n\, \nu\, Z_2 \exp\,[-(E^M + b)/kT]. \tag{18}$$

Using these and equation (6) in (2) we get

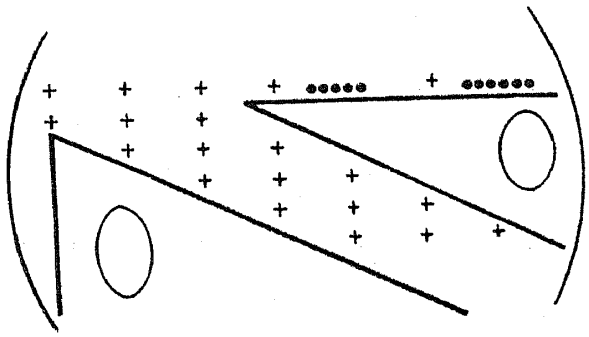
$$N_1(t) = p_1(t) = \frac{N_0}{N_0+x_2}\left[x_2+N_0 \exp\left\{-x_1(x_2+N_0)t\right\}\right]. \tag{19}$$

This equation tells us that the single vacancy concentration decreases rapidly. (This follows from the fact that $x_2 \ll N_0$, $x_2 \sim 10^{-8}$ and $x_1 \sim 10^6$ and $N_0 \sim 10^{-5}$. The value of x_2 is related to $\langle n\rangle$ which can be determined by solving (4). See paper II for details about the values of various parameters used.) If we define the time required to reduce the concentration of N_1 to a fraction (say 10%) of its original value to be the nucleation time τ' (i.e., on an average there are a few vacancies in a cluster) then $\tau' \sim 10^{-2}$ sec at 280°K and 300°K for vacancy loops in aluminium and for stacking fault tetrahedra in gold respectively. This value agrees quite well with the computer calculations of Kiritani (1973) for the case of aluminium. (In the case of aluminium, both the computer calculations and experiments of Kiritani (1973 and 1969) indicate that there is no nucleation barrier and is interpreted as due to gradual increase in the binding energy of the clusters. See for more details paper II.) This analysis further tells us that

$$\sum_2 N_n = \bar{N} = \frac{N_0^2\,[1-\exp\left\{-x_1\,(x_2+N_0)\,t\right\}]}{\langle n\rangle\,(N_0+x_2)}, \tag{20}$$

and therefore, there will be only redistribution of vacancy units among the various clusters after N_1 has reached its near asymptotic value. The average $\langle n \rangle$ is over the distribution N_n has a slow time dependence as we will show (paper II, Ananthakrishna 1979c). What comes out of the above equation is that as $t \to \infty$ the temperature dependence of $\langle n \rangle$ and $\overline{N}$ are opposite. Now we can write down the matrix explicitly:

$$\tilde{W} = \tag{21}$$



The matrix has entries wherever + is marked. Thus the transition matrix is mainly a tridiagonal one with additional entries in the first row. The entries are:

first row: $(-A, B-A, B-A, \ldots, B-A, \ldots)$
second row: $(A, -B-2A, 2B, 0, \ldots, \theta, \ldots)$
main diagonal: for $n \geqslant 3$: $-n(A+B)$
lower diagonal for $n \geqslant 3$: $n A$
upper diagonal for $n \geqslant 3$: $n B$.

where $A = x_1 p_1$ and $B = x_1 x_2$. Several interesting features follow. After the short initial transient during which the concentration of single vacancy units decreases rapidly attaining quasi-equilibrium with rest of the clusters with a value of $N_1 \sim N_0 x_2/(N_0 + x_2)$, all the elements in the first row except the first element are nearly zero. Thus after this short initial transient, the elements along the rows as well as columns add up to zero (to within an accuracy determined by the value of N_1 at the end of the transient). This immediately allows us to determine the final stationary state on the basis of a theorem concerning the increase of entropy for such systems. The theorem states that if the transition matrix which connects the probability vector with its rate of change has the property that elements along the rows and columns add up to zero, then the stationary solution of p in the most probable value (N_0/M) (1, 1, ..., 1), where M is the dimension of the matrix. This theorem has been outlined in Appendix B. (Ananthakrishna *et al* 1975; Okubo and Ishihara 1971). It may be noted that when M is taken to be finite, we have to write down two more equations for clusters with $M-1$ units and M units. Thus

$$p_n = n N_n \to N_0/M = 1/Z, \tag{22}$$

where Z is the number of atoms per cm^{-3}. Then

$$Z N_n = 1/n. \tag{23}$$

Thus the stationary distribution is highly peaked at the origin. The distribution that we obtain for this model via the generating function approach (see Ananthakrishna 1979a, paper II) is

$$N_n \sim \text{const} \times [N_0/(N_0 + x_2)]^n (1/n). \tag{24}$$

This model tells us that the elements along rows of the transition matrix should not add to zero, if we wish to obtain a physically reasonable distribution. Although the model introduced can be solved in closed form it gives rise to the unphysical distribution (see paper II). In the next paper we will show that any other choice of $W_{1\,n}$ and $W_{n\,1}$ render the problem intractable. For this reason we attempt to evolve a continuum model for the problem of clustering (paper III). We will try to retain some features of this model in building a continuum version of this model.

4. Derivation of phenomenological rate equations for irradiated materials

In this section we introduce rate equations for irradiated situation and show that the phenomenological equation that are usually written can be derived by performing an average. We explicitly write down the various choices for the transition rates that could be used.

In the case when a material is irradiated there are two species namely vacancies and interstitials. As we have mentioned in § 1, these recombine removing equal number of vacancies and interstitials, but it is the preferential loss of interstitials to the sinks that produces supersaturation of vacancies. It is this supersaturation of vacancies that leads to clustering. We shall assume that there is only one mobile unit in vacancies and interstitials. However, we can relax the assumption about the non-existence of sinks. The rate equations are

$$dN_1/dt = K - \sum_2 W_{i\,1}\, N_1\, N_{i-1} + \sum_2 W_{1\,i}\, N_i$$

$$-(D_I/a^2)\, N_1\, N_I - \rho_D\, N_1\, D_v + \tfrac{1}{2} W_{2\,I}\, N_I N_2, \tag{25}$$

$$dN_I/dt = K - (D_I/a^2)\, N_1\, N_I - \rho_D\, D_I\, N_I$$

$$- \sum_2 W_{n\,I}\, N_n N_I + \tfrac{1}{2}\, W_{2\,I}\, N_I\, N_2, \tag{26}$$

$$dN_2/dt = \tfrac{1}{2}\, W_{2\,1}\, N_1^2 - W_{3\,1}\, N_1\, N_2 + W_{1\,3}\, N_3$$

$$-\tfrac{1}{2}\, W_{1\,2}\, N_2 - \tfrac{1}{2} W_{2\,I}\, N_I\, N_2 + W_{3\,I}\, N_3 N_1, \tag{27}$$

and for $n \geqslant 3$

$$dN_n/dt = W_{n\,1}\, N_1\, N_{n-1} - W_{n+1\,1}\, N_1\, N_n - W_{1\,n+1}\, N_{n+1}$$

$$- W_{1\,n}\, N_n - W_{n\,I}\, N_I\, N_n + W_{n+1\,I}\, N_{n+1}\, N_I. \tag{28}$$

In the above equations, N_I is the concentration of interstitials, K is the rate at which the vacancies and interstitials are produced, ρ_D is the dislocation density, D_V and D_I are the diffusion constants of the vacancies and interstitials respectively, a is the lattice

parameter and $W_{n\,I}$ is the transition rate for the interstitial capture by a vacancy cluster with n-units (we have ignored the emission of interstitials by vacancy clusters since this process has a very low probability. Inclusion of this term does not complicate the situation for the aspects considered here.) Using the above equations, we get

$$df/dt = W_{2\,1}\, N_1^2 + \sum_2 W_{n+1\,1}\, N_1\, N_n - \sum_2 W_{1\,n}\, N_n$$

$$- \sum_2 W_{n\,I}\, N_n\, N_I. \tag{29}$$

We can now consider the growth of loops as an illustrative example.

Choose $W_{n\,1} = (n-1)^{1/2}\, D_V/a^2$,

$$W_{1\,n} = \sqrt{n}\,(D_V/a^2)\exp(-b_n/kT),$$

and $W_{n\,I} = \sqrt{n}\,(D_I/a^2)$. (30)

Normally the phenomenological equations are written in terms of the average radius $\langle r \rangle$ of the loop. Therefore we shall consider converting n into r. Using $n=\pi r^2/a^2$ and

$$\bar{N} = \sum_2 N_n = 2\pi \int N(r/a)\,\frac{r\,dr}{a^2} = \int \bar{N}(r/a)\,\frac{dr}{a}$$

we have

$$\pi \frac{d}{dt}\langle r^2 \rangle \bar{N} = D_V N_1^2 + N_1\, D_V \frac{\langle r \rangle}{a}\bar{N}\sqrt{\pi} - D_I N_I \bar{N}\langle r/a\rangle \pi$$

$$- D_V \bar{N}\sqrt{\pi}\left\langle \frac{r}{a}\exp(-b\,(r/a)/kT)\right\rangle, \tag{31}$$

where the average is with respect to the distribution $\bar{N}(r/a)$. Also we have converted the binding energy b_n to $b\,(r/a)$. We note the form of $b(r/a)$:

$$b(r/a) = E_V^F - [\gamma + F_{el}(r)]\,\mathbf{b}^2,$$

where $\mathbf{b}$ is the Burgers vector, γ is the stacking fault energy and F_{el} is the elastic energy stored in a loop of radius r. To compare with the equations normally written, we have to make the following approximation

$$\left\langle r/a \exp\left\{-\frac{b(r/a)}{kT}\right\}\right\rangle$$

$$\simeq \langle r/a\rangle\, C_V \langle \exp[\gamma\,\mathbf{b}^2 + F_{el}(r)\,\mathbf{b}^2]\rangle,$$

$$\simeq \langle r/a\rangle\, C_V \exp[\gamma\,\mathbf{b}^2 + F_{el}(\langle r\rangle)\mathbf{b}^2],$$

$$= \langle r/a\rangle\, C_V\, p_e. \tag{32}$$

If the above approximation is made, with $\rho=\bar{N}\sqrt{\pi}\,\langle r\rangle$, we get

$$\frac{d}{dt}\pi\langle r^2\rangle\bar{N}=\rho\left[\frac{D_V N_1^2}{\rho}+N_1\frac{D_V}{a}-\frac{D_I N_I}{a}-D_V C_V p_e\right]. \tag{33}$$

The above equation is very similar to the equation written for the number of vacancies contained in a vacancy loop (see for instance equation (8) of Bullough *et al* 1975; the term ϵK does not arise in the situation at hand.) The first term is an extra term which presumably is not written down in their approach since they are interested in a situation when the vacancy and interstitial concentrations have reached a steady state. Similar equations can be derived for the voids, and interstitial loops.

5. Summary and conclusions

In this paper we have introduced a general rate equation model for the problem of clustering of supersaturated system of vacancies. For the case of quenched-in vacancies, the model was shown to conserve the number of vacancy units. It was also shown that the model represented a non-stationary Markoffian process. A particular modelling of the transition rates for the case of the formation of vacancy loops and stacking fault tetrahedra was considered in some detail. The choice of transition rates was made in a way that the equation for the rate of change of single vacancy unit concentration could be decoupled from the equations for the growth of other clusters. This yields some information about the nucleation time of small clusters which agrees well with the computer calculations of Kiritani (1973). It was then shown that after a short transient the transition matrix is doubly stochastic which therefore leads to an unphysical distribution. For the irradiated situation, the phenomenological equation normally used for the number of vacancies contained in a cluster is derived starting from the microscopic rate equations. This equation is very similar to that written down by Bullough *et al* (1975).

The model introduced for the clustering of quenched-in vacancies into vacancy loops and stacking fault tetrahedra, although gives an unphysical distribution, has the feature that it is nearly exactly solvable. (See paper II). The unphysical nature of the distribution, namely the peaked nature of the distribution probably results from the particular choice the number of absorption and emission sites and the assumption of constancy of binding energy. This choice however is essential for obtaining closed form solution. We shall attempt to construct a continuum model, which retains some of the features of this model, in a following paper.

Appendix A

In this appendix we show that the phenomenon of clustering of quenched-in vacancies can be modelled as a continuous time non-stationary Markoff process. For the sake of completeness, we start out from the continuous time Markoff process and derive an equation which gives the rate equations that we have written when a particular choice for the transition rate is made. (The derivation of the differential-

difference equation for the conditional probability is well known. See Wang and Uhlenbeck 1945.) The discrete version of Smoluchowski equation is

$$P(n/m, t+\triangle t) = \sum_{m'} P(n/m', t)\, p(m'/m, \triangle t). \tag{A.1}$$

As for this derivation, we shall consider a stationary process. $P(n/m, t)$ has to be determined once $P(n/m, \triangle t)$ is given where $P(n/m, t)$ is the probability that the random variable takes on a value m after a time t given that it has a value n initially. Generally

$$\lim_{\triangle t \to 0} P(n/m, \triangle t)/\triangle t$$

is given from physical considerations. We shall use a new symbol for the basic probability

$$P(n/m, \triangle t) = Q(n/m, \triangle t). \tag{A.2}$$

This satisfies

$$\sum_{m} Q(n/m, \triangle t) = 1. \tag{A.3}$$

Following Wang and Uhlenbeck (1945) and taking the limit as $\triangle t \to 0$ we get

$$\frac{dP}{dt}(m, t) = \sum_{m'} W(m, m')\, P(m', t) - \left[\sum_{m'} W(m', m)\right] P(m, t), \tag{A.4}$$

where we have suppressed the index designating the initial state i.e., $P(n/m, t) = P(m, t)$ as the dependence of $P(n/m, t)$ on n enters only through the initial condition

$$\lim_{t \to 0} p(n/m, t) \to \delta_{nm}.$$

The elements of the transition matrix are given by

$$W(m, m') = \lim_{\triangle t \to 0} \frac{Q(m'/m, \triangle t)}{\triangle k}, \tag{A.5}$$

and

$$W(m, m) = -\lim_{\triangle t \to 0} \sum_{k}{}' \frac{Q(k/m, \triangle t)}{\triangle t}, \tag{A.6}$$

where the prime on the summation denotes that $k \neq m$

Appendix B

In this appendix we shall state a theorem concerning the entropy increase for a system which connects the two states of the system by a *doubly stochastic matrix.* We shall relate this theorem to our present situation. Let P be the probability vector and A_{ij} be the elements of the doubly stochastic matrix, then

$$P_i(t+\Delta t) = \sum_j A_{ij}(\Delta t)\, P_j(t)\,, \tag{B.1}$$

with $$A_{ij} \geqslant 0, \tag{B.2}$$

$$\sum_i A_{ij} = \sum_j A_{ij} = 1. \tag{B.3}$$

The matrix **A** is called a doubly stochastic matrix. Defining entropy by

$$s = -\sum P_i \ln P_i. \tag{B.4}$$

Then $s=0$ when **p** is pure (B.5)

and $s = \ln M$ when **P** is most impure i.e.,

$$s = \ln M \text{ for } \mathbf{P} = 1/M\,(1, 1, \ldots 1). \tag{B.6}$$

For any probability vector **P**, this quantity has a value bounded by these two limits (Fano 1957). We shall now state the theorem.

If the states of a system described by a probability vector **P** with M components are connected by a matrix **A** with the property given by (B.2) and (B.3) then $s(t') \geqslant s(t)$ for all $t' \geqslant t$.

The proof of the theorem is well known (Ananthakrishna *et al* 1976; Okubo and Ishihara 1971). As a consequence of this theorem the entropy should reach its maximum value $\ln M$ as $t \to \infty$. This implies that

$$\lim_{t\to\infty} p_n \to \frac{1}{M}, \tag{B.7}$$

or with appropriate identification of p_n, we get

$$\lim_{t\to\infty} N_n \to \frac{N_0}{M}\cdot\frac{1}{n}$$

The connection of (B.1) with the present situation comes by identifying $A_{ij}(\Delta t)$ with $Q(j/i, \Delta t)$ of Appendix A. We have indicated how $Q(i/j, \Delta t)$ is related to the elements of the transition matrix $W(i, j)$ in Appendix *A*.

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