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A stochastic theory for clustering of quenched-in vacancies—III. A continuum model

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Abstract. In continuation of our earlier investigation on the problem of clustering of quenched-in vacancies reported earlier, starting from the discrete model, we derive a second order partial differential equation for the growth of the clusters. The solution of this equation is shown to be in reasonable agreement with the solution of the discrete model proposed earlier. However, the total number of vacancies is not conserved under slightly less stringent conditions than the conditions dictated by the solution of the discrete model, suggesting a slightly modified differential equation for the concentration of the clusters. The solution of this modified differential equation has the required properties. The leading part of the distribution when transferred into the space designating the linear dimension of the cluster has a Gaussian form. This feature is shown to be consistent with writing a Langevin equation with the linear dimension of the cluster taking the role of the random variable. This permits the identification of the smallness of parameter. An alternate formulation is also given where the concentration of the vacancies stored in a cluster of a certain size is considered as the dynamical variable. The solution obtained in this alternate formulation is shown to be consistent with the other formulation.

Keywords. Continuum model; Fokker-Planck equation; dynamical variable; Gaussian distribution; random variable; Langevin equation.

1. Introduction

In our earlier papers (Ananthakrishna 1977; 1979 a, b referred to as papers I and II) we introduced the constant binding energy model for clustering of quenched-in vacancies. This model was introduced with a view to obtain the solution in closed form for the concentration of single vacancy units and the distribution for the cluster sizes. The model has several attractive features but the distribution has also two undesirable features. First, the peak of the distribution does not evolve in time when transformed to the space where the linear dimension of the defect is used as a measure of the size of the defect. Second, the distribution is rather peaked. It is possible to overcome the first drawback by appropriately changing $\psi(n)$ and $\bar{\psi}(n)$ from the choice given by equations (I. 17) and (I. 18). (the equations from papers I and II will be referred by their prefices.) But this poses some other problems. It is the purpose of this paper to evolve a continuum model, a model where the random variable takes on a continuum of values. This poses lot of problems and has to be carried out in a self-consistent manner.

We recall certain features of the constant binding energy model:

(i) Decoupling of the equation for rate of change of the concentration of single vacancy units and the equation for the growth of clusters is not possible

unless the number of absorption and emission sites are taken to be $(n-1)$ and n respectively, and the binding energy is considered independent of the number of vacancies contained in the clusters.

(ii) The quantity $x_2 = \exp(-b/kT)$, where b is the assumed constant binding energy, in the final analysis is related to $\langle n \rangle$ and therefore has to be considered as a parameter. Thus x_2 is a function of the average size.

(iii) A discrete time version of the model is not physically meaningful since the number of jumps a vacancy has to make to reach a cluster has no specific relation with jump time.

It is most likely that the non-evolution of the peak and the rather peaked distribution result from the feature given by (i). Regarding the non-evolution of the peak.we note that all the experimental distribution are measured in the r-space. So the evolution of the peak in the n-space is not necessary. It is sufficient to have a distribution in n-space which when transformed into r-space makes the peak evolve in r-space. When a continuum version of similar models is attempted, the procedure to be adopted is well known. There can be several limiting cases corresponding to different physical situations (See Kalrin and McGregor 1964). In general, there is a small or a large parameter which helps to take these limits. In the problem at hand, there is no such parameter. In some cases, one can start by regarding both the parameter of the random variable and the random variable to take on discrete values, and take appropriate limits as can be done in the case of problem of diffusion (Wang and Uhlenbeck 1945). This possibility is ruled out due to point (iii). In addition to these points, it is important to note that the dynamical variable in our problem is N_n the concentration of the cluster with n-units because of the fact that the model describes the growth of clusters and not the number of vacancies in the cluster. (The latter would have been the right choice if a Fokker-Planck equation had to be set-up. Since the normal methods available in literature cannot be used, we will have to rely on some other physical considerations.) There is an additional problem about the choice of the right dynamical variable. There are two choices one can make. One is the concentration of the clusters N_n and the other is the concentration of vacancy units p_n in a vacancy cluster of concentration N_n. If the latter is used a generalised Fokker-Planck can be set-up. As we will show, if we use some results available from the previous model about the short time constant for p_1 using N_n and p_n as the dynamical variable gives rise to consistent results. The basic physical assumption in the problem is that as for the growth of clusters after the initial incubation period, the effect of the variation in the binding energy is small and hence the growth of the clusters is smooth. As far as the construction of the continuum model, since the normal methods available in literature cannot be used, we will have to rely on the correspondence of the method of constructing the continuum limit to the original model and use other physical information. We will see that once the continuum limit of this model is constructed in the n-space, we can identify a small parameter by writing down a Langevin equation for the random variable r, the radius of the loop.

2. Continuum model

In cases where a Fokker-Planck equation has a small parameter, the Kramer-Moyal

expansion is truncated at the second order (see Stratonorich 1963.) This is indeed arbitrary because the fact that the Fokker-Planck equation is of second or infinite order depends on whether or not some even moment greater than the second vanishes. There is no guarantee that the truncated Fokker-Planck equation gives a solution which is consistent with the solution of the integral equation for the conditional probabilities (i.e., the Smoluchowski's equation). Yet in many cases the solutions of the truncated Fokker-Planck equation with the help of small parameter yield physically reasonable distributions. In the present case we will be guided by somewhat similar considerations.

First, we show that by regarding n as a continuous variable we can set up a second order partial differential equation which has nearly the same solution as that of the differential-difference equation given by eqs (II. 3) (II. 4) and (II. 5). This equation will be arrived at by arbitrarily truncating the Taylor series expansion of

$$p_{n\pm1} = (n\pm1)\, N_{n\pm1}$$

at the second order. By requiring that the total number of vacancies be conserved in this continuum model also, which in turn implies certain conditions of $N(n, t)$ as $n \to 0$ and $n \to \infty$ consistent with our earlier known results on the distribution obtained from via generating function approach for N_n (Ananthakrishna 1979b), we show that the differential equation should be slightly modified. This corresponds to a slightly different choice of the number of absorption and emission sites. The solution of this equation will be shown to be physically reasonable.

Consider equation (II. 5). Multiplying by n and using $n\,N_n = p_n$ gives an equation for p_n. We shall use Taylor series expansion for $p_{n\pm1}$ upto second order only. Using

$$p_{n\pm1} = p_n \pm \frac{\partial p_n}{\partial n} + \frac{1}{2}\frac{\partial^2 p}{\partial n^2} \mp \cdots$$

in equation (I. 5) we get

$$\frac{\partial p_n}{\partial t} = x_1 (x_2 - N_1) n \frac{\partial}{\partial n} p_n + \frac{n}{2} x_1 (x_2 + N_1) \frac{\partial^2 p_n}{\partial n^2}. \tag{1}$$

Using $p_n(t) = p(n, t) = nN(n, t)$ we get

$$\frac{\partial N(n, t)}{\partial t} = x_1 (x_2 - N_1) \frac{\partial}{\partial n} (nN) + \frac{x_1}{2} (N_1 + x_2) \frac{\partial^2}{\partial n^2} (nN). \tag{2}$$

Thus we have truncated the expansion at the second order. Some points can be noted here. The coefficients of this partial differential equation are functions of x_1, N_1 and x_2 ($\langle n \rangle$). Since N_1 is a very rapidly decreasing function of time, there will be a short transient superimposed on the time development of $N_n(t)$, the solution obtained in paper II. We note from the analysis of the previous paper, that the equation for N_1 and that of N_n get decoupled after N_1 has reached its asymptotic value which is of the order of tenth of a second. Since it will be very difficult to solve

the equation with the full time dependence of N_1, we shall solve the above equation after N_1 has reached its asymptotic value. By using the asymptotic value of N_1 in (2), we cannot expect the solution obtained in this fashion to be valid for shorter times. Also we assume that for shorter times, the evolution of clusters is smooth and using the actual physical boundary condition gives the correct distribution. We also wish to remark that x_2 will be related $\langle n\rangle$ (as was shown in the discrete model and will be shown to be true here also) and therefore should be regarded as a parameter. Indeed, when we started with the original equations (equations (I. 4), (I. 17) and (I. 18)) x_2 was a function of n. Now it has to be regarded as a function of $\langle n\rangle$. By considering $x_2 = x_2(\langle n\rangle)$ we can dump all unknown features into this parameter.

We shall rewrite (2) in the following manner

$$\frac{\partial N}{\partial t} = x_1\,[x_2 - N_1]\,\frac{\partial}{\partial n}(nN) + x_1\,(x_2+N_1)\,\frac{\partial N}{\partial n} + \tfrac{1}{2}\,x_1\,(x_1+N_1)n\,\frac{\partial^2 N}{\partial n^2},$$

$$= x_1\,(x_2-N_1)\,\frac{\partial}{\partial n}[(n-1)N] + 2\,x_1\,x_2\,\frac{\partial N}{\partial n} + \tfrac{1}{2}\,x_1\,(x_2+N_1)n\,\frac{\partial^2 N}{\partial n^2}.$$

Using $N_1 \to N_0\,x_2/(N_0+x_2)$, we get

$$\frac{\partial N}{\partial t} = \frac{x_1\,x_2^2}{N_0+x_2}\,\frac{\partial}{\partial n}[(n-1)N] + 2\,x_1\,x_2\,\frac{\partial N}{\partial n}$$

$$+ \tfrac{1}{2}\,x_1\left[x_2 + \frac{N_0\,x_2}{N_0+x_2}\right] n\,\frac{\partial^2 N}{\partial n^2}.$$

In the last term we could replace $N_0\,x_2/(N_0+x_2)$ by x_2 since $x_2 \ll N_0$ (as we will show later or see Ananthakrishna 1979b, paper II). Then we have

$$\frac{\partial N}{\partial t} = \frac{x_1\,x_2^2}{N_0+x_2}\,\frac{\partial}{\partial n}[(n-1)N] + x_1\,x_2\,\frac{\partial^2}{\partial n^2}(nN). \tag{3}$$

(The procedure of splitting the second term into a contribution that can be absorbed in the first term plus another one that can be absorbed in the term $n(\partial^2 N/\partial n^2)$ is expected to cause less error than directly using $N_1 \to N_0\,x_2/(N_0+x_2)$ in (2).)

In order to solve (3), we use methods of Laplace transforms. Define

$$\chi(s, t) = \int_0^\infty N(n, t)\,(\exp -sn)\,dn. \tag{4}$$

Here few comments are in order. First, the physical domain of definition of n does not extend upto zero. Thus by extending the domain of definition of n, we have to assume $N(0, t)=0$. Second, this integral does not have contribution from $n=1$, i.e., $N(1, t) \neq N_1(t)$. Third, equation (1) is expected to hold for $n=2$ for analytic calculations only. Indeed, due to the fact that we have used continuum approximation to obtain (2), it is probably not valid for small n. Further, we attempt a solution of (3) only with the asymptotic value of N_1. By this time several clusters with sizes in the

small n region would have formed. So the statements concerning $n=0$, 1 and 2 are for mathematical convenience. We shall also assume that

$$\frac{\partial}{\partial n} nN(n, t)\,|_{n=0} = 0.$$

Thus we assume

$$\left.\begin{aligned} & N_1(t) \neq N(1, t) = 0, \\ & N(0, t) = 0; \lim_{n \to 0} \frac{\partial}{\partial n} nN(n, t) = 0, \\ \text{and} \quad & \lim_{n \to \infty} N(n, t) = 0. \end{aligned}\right\} \tag{5}$$

With this we can write a differential equation for $\chi(s, t)$

$$\partial x/\partial t = -As\,\chi - s\,(A+Bs)\,(\partial x/\partial s),$$

where

$$A = x_1 x_2^2/(N_0 + x_2) \text{ and } B = x_1 x_2.$$

The method of obtaining the solution is shown in Appendix 1. The solution is given by

$$\chi(s, t) = (A/B)^{A/B} \left\{\exp - \frac{A\,s\phi}{B\,[A/B + s(1-\phi)]}\right\} \times$$

$$[(A/B)+s(1-\phi)]^{-A/B}, \tag{6}$$

with $\phi = \exp - At$.

$N(n, t)$ can be calculated by using the inverse laplace transform (The details are given in Ananthakrishna 1979c.) With $\nu_1 = A/B$, we get

$$N(n, t) = \frac{\left[\dfrac{\nu_1 n}{(1-\phi)}\right]^{\nu_1} \exp\left\{-\dfrac{\nu_1(n+\phi)}{(1-\phi)}\right\} I_{\nu_1 - 1}\left(\dfrac{\nu_1\sqrt{n\phi}}{1-\phi}\right)}{n\,[\nu_1\sqrt{n\phi}/(1-\phi)]^{\nu_1 - 1}}. \tag{7}$$

Since the leading term in

$$I_{\nu_1}(Z/2) \simeq (\tfrac{1}{2}Z)^{\nu_1}/\Gamma(\nu_1 + 1),\ \text{Re}\ \nu_1 > -1,$$

for small Z, we can use this to compare with our earlier result. With this we have,

$$N(n,t) \simeq \left[\frac{An}{B(1-\phi)}\right]^{A/B} \frac{\exp\left\{-\dfrac{A(n+\phi)}{B(1-\phi)}\right\}}{n\,\Gamma(A/B)}$$

$$\simeq \frac{k\,n^{-N_0/(N_0+x_2)}}{(1-\phi)^{[x_2/(N_0+x_2)]}} \exp\left\{-\frac{x_2(N+\phi)}{N_0+x_2(1-\phi)}\right\}$$

$$\simeq k'\,n^{-1} \exp\left\{-\frac{x_2 n}{(x_2+N_0)(1-\phi)}\right\}, \tag{8}$$

where k and k' are constants. (We have used $N_0/(N_0+x_2) \sim 1$ since $x_2 \ll N_0$.) The distribution function that we have obtained via the generating function approach gives two terms one of which identically vanishes as $t \to \infty$. The leading term is

$$N_n = \frac{x_2(2N_0+x_2)}{2(N_0+x_2)} \exp\left\{n \ln \frac{N_0(1-\phi)}{(N_0+x_2)\,[1-N_0\phi/(N_0+x_2)]}\right\}. \tag{9}$$

With the same approximation that $x_2 \ll N_0$.

$$\ln \frac{N_0}{N_0+x_2} \simeq -\frac{x_2}{N_0+x_2}$$

and

$$\ln \frac{1-\phi}{1-[N_0\phi/(N_0+x_2)]} \simeq \frac{\phi\,[x_2/(N_0+x_2)]}{1-[N_0\phi/(N_0+x_2)]},$$

gives

$$N_n \simeq \frac{x_2}{n} \exp\left\{-\frac{nx_2}{(N_0+x_2)\{1-[\phi N_0/(N_0+x_2)]\}}\right\}$$

or

$$N \simeq n^{-1}x_2 \exp\left\{-\frac{nx_2}{(N_0+x_2)(1-\phi)}\right\}. \tag{10}$$

Thus the leading behaviour in both cases is nearly the same. Therefore the expansion scheme that we have used appears to give consistent distribution as the one obtained for the differential-difference equation.

Now we remove the two inadequacies namely the highly peaked nature of the distribution and the non-evolution of the peak in the r-space. To avoid the later, we note that if $N(n, t)$ has a maximum at $n=0$,

$$\tilde{N}(r,t) = \frac{r}{a} N\left(\frac{r^2}{a^2}, t\right)$$

has a maximum at non-zero r. In order to achieve the above objectives, we note that in view of our earlier remarks about the absence of a small parameter or relevant time scale in the continuum model we should demand consistency between the decay

of the concentration of single vacancy units and the equation for the growth of clusters. This implies conservation of the total number of defects in the system. We do not have any reason to believe that this conservation of defects should hold even after the truncation of the differential equation at the second order by ignoring the higher order terms in the Taylor series. Further, since we need a nice behaviour at the origin for the distribution function $N(n, t)$ the boundary condition under which we expect to solve the growth of clusters is different. This is another reason why the conservation may not hold. We recall that the behaviour of N_n as $n\to 0$ is singular (if $n=0$ is considered as a point in the physical domain for n), even as $n\to 1$, N_n becomes highly peaked. So the least stringent conditions, on $N(n, t)$ are dictated by our earlier knowledge about N_n based on the solution of the discrete model. These lead to

$$\lim_{n\to 0} n^2 N(n, t) \to 0 \quad \text{and} \quad \lim_{n\to\infty} N(n, t) \to 0.$$

(This is due to the fact that $1/n$ factor contributes as $n\to 0$.) The behaviour of $N(n, t)$ as $n\to\infty$ in the parent model is sufficiently strong and we shall retain this feature. However, a slightly less stringent condition is required as far as the behaviour of $N(n, t)$ as $n\to 0$ is concerned.* So we require

$$\lim_{n\to 0} n\, N(n, t) \to 0, \quad \lim_{n\to\infty} N(n, t) \to 0,$$

and

$$\lim_{n\to 0} n^2 \frac{\partial N}{\partial n} \to 0.$$

We can now proceed to check the conservation of the total number of defects. This can be easily checked by calculating $f(t)$. Here it is important to remember that the contribution to $n=1$ comes from the equation for N_2. (See (II. 4)). Thus when we integrate (2), we should include the contribution from N_2 term in the integration. Then we have

$$\frac{df}{dt} = x,\ N_1^2 + A_1 \int_0^\infty n \frac{\partial (nN)}{\partial n}\, dn + 2B_1 \int_0^\infty n \frac{\partial N}{\partial n}\, dn$$

$$+ B_1 \int_0^\infty n^2 \frac{\partial^2 N}{\partial n^2}\, dn,$$

where $A_1=x_1(x_2-N_1)$ and $B_1=x_1(x_2+N_1)/2$. Here the first term is the contribution to the integral from the equation for N_2. Using the above boundary conditions on $N(n, t)$, we have

$$\frac{df}{dt} = x_1 N_1{}^2 - A_1 f(t) + B_1 \int_0^\infty n \frac{\partial N}{\partial n}\, dn. \tag{11}$$

*It is important to note that we have set $N(0, t)=0$ for the unphysical point $n=0$. This requirement is common for all the cases considered.

This equation should be consistent with the equation for (written in the continuum limit)

$$\frac{-dN_1}{dt} = x_1N_1^2 + x_1N_1 \int_0^\infty (nN)dn - x_1x_2 \int_0^\infty (nN)dn.$$

This is possible if the last term in (11) were absent. (It may be worthwhile to point out that (2) does not conserve the total number of vacancies even with the boundary condition dictated by the solution of the parent model.) This means that we should modify the differential equation appropriately to suit the boundary condition on $N(n, t)$. Then the modified differential equation reads,

$$\frac{\partial N}{\partial t} = A_1 \frac{\partial}{\partial n}(nN) + B_1 n \frac{\partial^2 N}{\partial n^2} + B_1 \frac{\partial N}{\partial n}. \tag{12}$$

It may be recalled that we have remarked at the end of paper II that using an appropriate choice of the number of absorption and emission sites, it is possible to overcome the peaked unphysical nature of the distribution. In fact, the above equation corresponds to a slightly different choice of $\psi(n)$ and $\bar{\psi}(n)$. If we use

$$\psi(n) = n - \tfrac{1}{2} \text{ and } \bar{\psi}(n) = n + \tfrac{1}{2}$$

and go through the usual procedure of truncating the Taylor series at the second order, we would get the above equation. The solution of (12) can be obtained typically the same way as the solution of (3) and is (see Appendix A of paper IV, Ananthakrishna 1978c)

$$N(n, t) = \frac{\bar{K}A}{B(1-\phi)} \exp\left[-\frac{(n+\phi)A}{B(1-\phi)}\right] I_0\left(\frac{A\sqrt{n\phi}}{B(1-\phi)}\right). \tag{13}$$

where $\bar{K}$ is a normalisation constant to be determined. The method of obtaining the solution is presented in the next paper. Here we note that the leading term designated by $N_L(n, t)$ is given by

$$N_L(n, t) = \frac{\text{const}}{(1-\phi)} \times \exp\left[-\frac{nA}{B(1-\phi)}\right]. \tag{14}$$

If we wish to write the distribution in terms of the radius of the loop (or the edge length of the tetrahedra) we see that

$$\tilde{N}_L(r, t) = 2a(r/a^2)\, N_L(ar^2/a^2, t)$$

$$= \text{const} \times \frac{2ar}{a^2(1-\phi)} \exp\left[-\frac{Ar^2}{a^2B(1-\phi)}\right]. \tag{15}$$

in the r-space has the peak at a non-zero value of n. (The relation $n=\alpha r^2/a^2$ has been used, where α is a geometrical factor.) We also note that $N_L(\alpha r^2/a^2, t)$ is a Gaussian in n.

Consider equation (11) without the last term, i.e.,

$$\frac{df}{dt} = -Af + x_1 x_2^2. \tag{16}$$

This equation describes the growth of the total number of vacancies in clusters of all sizes. Strictly speaking $f(t)$ is independent of t since we have used the asymptotic value of N_1. (This of course would be true only as $t\to\infty$.) But N_1 has a very short time constant and N_1 attains its asymptotic value in a very short time of the order of a second. We can therefore use the asymptotic value of N_1 and regard $f(t)$ as a weak function of t. (Physically, this is equivalent to introducing all the vacancies initially and allowing only a redistribution of vacancies with a slow variation in $N(n, t)$. Alternatively, we could regard the total number of vacancies to be strictly constant after N_1 has reached equilibrium with the rest of the clusters. This implies that we allow only a strict redistribution of vacancies among the various clusters. This also implies that the dynamical variable of interest is $p(n, t)$ rather than $N(n, t)$. We shall elaborate this point later.) This procedure would offset $\bar{N}$ very little since, by about a second, the term

$$\tilde{N} \simeq \frac{x_2 N_0}{N_0+x_2} + \frac{N_0}{N_0+x_2} \exp -x_1(x_2+N_0)$$

and the last term is of the order of the first. Then the solution of (16) is

$$f(t) = \bar{a} \exp -At + (x_1 x_2^2/A).$$

At $t=0, f(t)=0$, so

$$f(t) = (x_1 x_2^2/A)\,(1-\exp -At). \tag{17}$$

$$\langle n\rangle = \frac{N_0+x_2}{\bar{N}}\left[1 - \left(\exp - \frac{x_1 x_2^2 t}{(N_0+x_2)}\right)\right]. \tag{18}$$

(Note that $\bar{N}$ should be independent of time. Physically it is clear that $\bar{N}(t)$ should reach its steady state much faster than $\langle n\rangle$.) This is the result that one would get if (14) is used. From (14) it is clear that $\bar{N}$ is strictly normalised. (This is what is implied in the above statement.) So the slow growth of the average size can be obtained from (17) itself. In the following we shall see how (18) helps us to identify a smallness parameter in the r-space.

3. Identification of smallness parameter and the connection with Langevin equation

There are several points in the above analysis which suggest that it should be possible to identify a parameter to terminate the Taylor series expansion at the second order.

This parameter may be easily identifiable in an appropriately transformed space as is the case in our problem. The clue that there is such a parameter is at least three-fold. First, the parent equations for deriving the continuum model were modelled as a Markoffian process. Secondly, the leading form of the solution of (12) is Gaussian in r suggests that it may be possible case that leading contribution into a Markoffian form, although (12) may not describe a Markoffian situation (due to the continuum approximation we have made). In this connection it may be important to observe few points. An equation of the type (12) is to be regarded as an equation for the distribution function, not necessarily a Fokker-Planck equation. In the present situation this statement is more relevant for yet another reason namely $N(n, t)$ is not a probability distribution. However, in the approximation we use namely using the asymptotic value of N_1 soon after the initial nucleation period, i.e., when N_1 has *almost* reached its asymptotic value, $\bar{N}$ is regarded as strictly constant. The above restriction concerning $N(n, t)$ is therefore not physically relevant. These points suggest a strong possibility of writing a Langevin equation for the random variable r. Consider an equation for r

$$\frac{dr}{dt} = -\frac{A}{2} r + \bar{\zeta}(t),$$

where $\bar{\zeta}(t)$ is the noise term which can arise due to several reasons. Indeed, the diffusive motion of vacancies, which is the main cause for the growth of clusters, is random. There can be other sources like the presence of the motion of dislocations (which are always present in the system), etc. With the usual assumptions about $\bar{\zeta}(t)$ being a stationary, Gaussian white noise and with the initial condition $\langle r \rangle = 0$ at $t = 0$, we have (see Wang and Uhlenbeck 1945)

$$\langle r^2 \rangle = \exp(-At) \int_0^t \int_0^t \exp\left(\frac{A}{2}(x+y)\right) \langle \bar{\zeta}(x)\, \bar{\zeta}(y) \rangle \, dx\, dy.$$

Using $\quad \langle \bar{\zeta}(x)\, \bar{\zeta}(y) \rangle = 2D\, \delta(x-y),$

we have $\quad \langle r^2 \rangle = (2D/A)\,[1 - (\exp - At)]. \qquad (19)$

Multiplying (19) by a/a^2 and comparing with (18) we get

$$2D = a^2 x_1 x_2^2 / a\bar{N}. \qquad (20)$$

(Here $\bar{N}$ is independent of t and is determined by comparing the solution of the Fokker-Planck equation with (14).) Thus it is clear that the smallness parameter is a, the lattice parameter in the r-space. The associated Fokker-Planck equation in r-space is

$$\frac{\partial N_L(r, t)}{\partial t} = \frac{A}{2} \frac{\partial}{\partial r} [r N_L(r, t)] + \frac{a^2 x_1 x_2^2}{2a\bar{N}} \frac{\partial^2}{\partial r^2} N_L(r, t). \qquad (21)$$

It is clear from the above connection with the Langevin equation that the continuum model we have constructed based on the earlier presented discrete model has built-in internal consistency.

We shall make a few more remarks on some aspects of the model. It may be recalled that the slow growth of the clusters after an initial transient during which N_1 rapidly decays increasing the concentration of N_n rapidly (during that interval) reaching a quasiequilibrium is what we have described by (12). This point has been amply brought out by showing the connection of the slow change of $f(t)$ (after the initial transient) with the Langevin equation. It may also be recalled that we have mentioned that it is possible to regard the concentration of vacancy units in the clusters to be constant right from the period after the initial transient and allow only a strict redistribution of vacancy units. Such a description should be expected to be consistent with our earlier description where $\bar{N}(t)$ rather than $f(t)$ was regarded as constant (and $f(t)$ varied slowly due to slow flux of vacancies to N_n). Hence df/dt is strictly zero and the dynamical variable which should be of interest is obviously $p(n, t)$, the number of vacancy units in the cluster. In this description we regard that p_1 has already attained equilibrium with $p(n, t)$ in a short time. The value of $p_1(\infty)$ to be used is taken from our earlier knowledge. Since this happens in a very short time, we assume that we have introduced all the vacancies into $p(n, t)$ right at the start. The starting point is a slightly altered equation for $p_n(t)$ in comparison with (II. 5) (or equivalently (I. 9) with (I. 17) and (I. 18)).

$$dp_n/dt = n\, p_1\, p_{n-1}\, x_1 - (n+1)\, p_1\, p_n\, x_1$$

$$+ n\, p_{n+1}\, x_1\, x_2 - (n-1)\, x_1\, x_2\, p_n. \tag{22}$$

This equation corresponds to a slightly different choice of $\psi(n)$ and $\bar{\psi}(n)$. Going through the Taylor series expansion for $p_{n\pm1}$ upto second order we get

$$\frac{\partial p}{\partial t} = A\frac{\partial (np)}{\partial n} + B\, n\frac{\partial^2 p}{\partial n^2}. \tag{23}$$

Again, introducing

$$\xi\,(s, t) = \int_0^\infty \exp(-sn)\, p(n, t)\, dn \tag{24}$$

where the contribution p_1 is not included. $p_1 \neq p(1, t) = 0$ and the contribution from $n=2$ is included in the same sense as in the earlier case while dealing with (2) and (12). One can easily check that df/dt is strictly zero if we assume

$$\lim_{n\to 0} p(n, t) \to 0 \;:\; \lim_{n\to 0} n\frac{\partial p}{\partial n} \to 0, \text{ and } \lim_{n\to\infty} p(n, t) \to 0. \tag{25}$$

These conditions are consistent* with the conditions imposed on $N(n, t)$ in obtaining (12). Going through steps similar to that for obtaining the solution of (12), the

*It is important to note that we have set $N(0, t) = 0$ for the unphysical point $n=0$. This requirement is common for all the cases considered.

solution of (23) can be obtained. The details of the method of obtaining the solution is given in Appendix B and the solution is

$$p(n, t) = \frac{p_1(0)\, x_2^2\, n}{(1-\phi)^2\,(N_0+x_2)^2}\left[\exp - \frac{x_2\,(n+\phi)}{(N_0+x_2)\,(1-\phi)}\right] \times \frac{I_1\left(\sqrt{n\phi}\,\dfrac{x_2}{(N_0+x_2)\,(1-\phi)}\right)}{\sqrt{n\phi}\,\dfrac{x_2}{(N_0+x_2)\,(1-\phi)}}. \tag{26}$$

Clearly the leading behaviour of $p(n, t)/n$ is exactly the same as $N(n, t)$ that we have obtained earlier except for the additional time-dependent factor of $1/(1-\phi)$. Thus we have shown that we could either regard the total number of vacancies to be constant (from the time when N_1 has reached equilibrium with the clusters) or regard $\bar{N}$ to be constant (which implies $f(t)$ varies slowly). Both these approaches give the same result as far as $\langle n \rangle$ is concerned as we have shown in paper IV (Ananthakrishna 1979c). In both cases N_1 has been taken to be already in equilibrium with the rest of the clusters.

4. Summary and conclusions

The basic problem that we have pursued in this paper is to build a continuum model for the problem of clustering, more specifically the problem of the growth of clusters after nucleation. To do this we have strongly made use of the discrete model that we proposed in paper I and relied using some properties of its solution obtained in paper II. The feature that is useful in the parent model is that the equation for the growth of clusters could be decoupled from the equation for the decay of the concentration of single vacancy units and thus leading to closed form solution for $(N_1(t))$. The decoupling can be achieved by regarding x_2 to be independent of n. Although this at the first sight appears as a gross simplification is actually exploited since x_2 is directly related to $\langle n \rangle$. Thus a quantity which was initially a function of n, in the final analysis should be regarded as a function of average n. However, this approximation probably leads to a singular distribution and the non-evolution of the peak in the r space. To overcome these two problems, we have resorted to building a continuum model retaining the good features of the parent model. A simple truncation of the Taylor series expansion leads to a partial differential equation for the growth of clusters. Here it is assumed that $N_1(\infty)$ obtained from earlier work can be used. Alternatively it is sufficient to assume that N_1 approaches its steady state value very fast. The amount of vacancies in clusters of all sizes can be estimated as equal to the total number of quenched-in vacancies minus their number in the steady state. This can always be found in general, either by knowing average size and density or is approximated as equal to the number of quenched-in vacancies. The solution of this equation is reasonably consistent with the solution of the parent model. To overcome the two difficulties, we note that the total number of vacancies is not conserved for this equation derived if we impose a nice behaviour for the distribution function for small value of n. This leads us to consider a slightly altered differential

equation. The solution of this revised differential equation has the nice behaviour for small r as well (which is the space used for experiments). Thus the peaked nature of the parent is removed. The leading behaviour of this distribution is a Gaussian in and is shown to be related to writing an appropriate Langevin equation for r. This also helps identify the smallness parameter. The description of the growth process via the differential equation for $N(n, t)$ involves keeping $\bar{N}$ constant from the start of the growth process. The decoupling of the equation for the growth is done at the time when the second term in $N_1(t)$ is of the same order as the first. It is the contribution from the second term in N_1 ofter the decoupling that supplies the slow influx of vacancies which contributes to the slow variation of $f(t)$. This slow change of $f(t)$ is essential in this description which implies that $\langle n \rangle$ changes slowly. The slow influx of vacancies which we have taken to be entirely contributing to $\langle n \rangle$ and not $\bar{N}$, is such that it would affect the magnitude of $\bar{N}$ very little even if we allow the influx of vacancies to affect $\bar{N}$ over the entire interval of time. These points imply that only a quasiequilibrium has been assumed to be prevailing between $N_1(t)$ and $N(n, t)$. Only as $t \to \infty$, a strict equilibrium is attained. It should be noted that we have used $N(0, t)=0$ for the unphysical point $n=0$ in order to obtain the solution for (12). In addition we have required a physically reasonable behaviour for $N(n, t)$ for small n. It is this that leads to (12). *Thus as for the continuum model, we should regard (II. 3) for the single vacancy units along with (12) for the growth of the clusters to be the starting point.* It should be noted that these two equations are consistent for all times, i.e., one can start with these equations and proceed to get the solution for $f(t)$ and hence $N_1(t)$. One can then use the asymptotic value of N_1 in (12) and obtain a solution of $N(n, t)$. The only point that should be borne in mind is that while integrating (12) after multiplying by n to get an equation for $f(t)$, we should write down the contribution to the term N_1^2 from $N(2, t)$, as we did while constructing (12). The alternate picture is to regard $p(n, t)$ to be dynamical variable rather than $N(n,t)$. In this picture $f(t)$ is strictly zero from the start of the growth process, i.e., after N_1 has attained its asymptotic value, which we assume has been attained in a very short time. Only a strict redistribution is allowed. Both these approaches give the same time development for $\langle n \rangle$ as we have shown in the paper IV. However, the time development of the distribution function for the cluster sizes is different. It is this factor which can be used to distinguish the two methods and identify the suitablity of the method for a particular situation. The actual physical situation is probably somewhere between the two approaches. Only an experimental situation can decide which approach is suitable. Thus starting out from the discrete constant binding energy model (which we cannot expect to give correct representation of the single vacancy concentration, the nucleation barrier and hence the nucleation time; in other words the short time behaviour, but is intended to give just sufficient information for us to solve the problem of growth) we have made use of the results on the decay of N_1 namely short time constant and the asymptotic value, in solving the equation for $N(n, t)$. The equation for the growth itself has been evolved in such a way that it is consistent with equation for N_1 and is based on the discrete model. We have evolved two possible ways of solving the growth problem, one via keeping $\bar{N}(t)$ constant and another keeping $f(t)$ constant. It is expected that these two methods approximate different physical situations. In the next paper (paper IV) we shall apply this model for the case of formation of stacking fault tetrahedra and faulted vacancy loops.

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Appendix A

Consider equation (6). The subsidiary system of equation we have to solve are

$$\frac{dt}{1} = \frac{ds}{s(A+Bs)} = \frac{dx}{-sAx}.$$

The characteristic solutions are

$$\frac{s}{s+\frac{A}{B}} \exp -At = C_1 = \frac{s}{s+\frac{A}{B}} \phi(t), \tag{A.1}$$

and

$$\left(s+\frac{A}{B}\right)^{A/B} \chi = b_1. \tag{A.2}$$

Eliminating C_1 and b_1 from the above two equations we get

$$\chi(s, t) = \left(s+\frac{A}{B}\right)^{-A/B} \mathcal{F}\left[\frac{s}{s+\frac{A}{B}} \phi(t)\right], \tag{A.3}$$

where $\mathcal{F}(y)$ is an arbitrary function of its arguments to be determined from the initial conditions. The initial condition is dictated by the fact that at $t=0$ all the vacancies are in the form of single vacancy units, which implies

$$\lim_{t \to 0} N(n, t) \to \delta(n-1).$$

Therefore,

$$\lim_{t \to 0} \xi(s, t) \to \exp -s,$$

and

$$\mathcal{F}\left(\frac{s}{s+\frac{A}{B}}\right) = \left(s+\frac{A}{B}\right)^{A/B} \exp(-s). \tag{A.4}$$

Then

$$\mathcal{F}\left(\frac{s}{s+\frac{A}{B}}\right) = \left[\exp\left\{-\frac{A}{B}\frac{s\phi}{\left(s+\frac{A}{B}-s\phi\right)}\right\}\right]\left[\frac{A}{B}\frac{(s+A/B)}{\left(s+\frac{A}{B}-s\phi\right)}\right]^{A/B}, \tag{A.5}$$

Using (A.5) in (A.3) we get

$$\chi(s, t) = \left\{\frac{A}{B}\frac{1}{\left[s(1-\phi)+\frac{A}{B}\right]}\right\}^{A/B} \exp\left\{-\frac{A}{B}\frac{s\phi}{\left[s(1-\phi)+\frac{A}{B}\right]}\right\} \quad \text{(A.6)}$$

which is the solution of equation (6). The inversion of this equation is very similar to the inversion of the solution of equation (12) in the transformed space. The details have been given in Appendix 1 of the next paper (paper IV, Ananthakrishna 1979c).

Appendix B

In this Appendix we shall outline the method of obtaining the solution of the equation for $p(n, t)$ described by (23). Using (24) and (25) in (23) we get a differential equation for

$$\frac{\partial \xi(s, t)}{\partial t} = -As\frac{\partial \xi}{\partial s} - s^2 B\frac{\partial \xi}{\partial s} - 2Bs\,\xi. \quad \text{(B.1)}$$

The subsidiary system of equation to be solved are

$$\frac{dt}{1} = \frac{ds}{s(A+Bs)} = -\frac{d\xi}{2Bs\,\xi}. \quad \text{(B.2)}$$

The characteristic solutions are

$$\xi\left(\frac{A}{B}+s\right)^2 = C_1. \quad \text{(B.3)}$$

and

$$\frac{s}{\left\{s+\frac{A}{B}\right\}}\exp -At = \frac{s}{\left[s+\frac{A}{B}\right]}\phi(t) = C_2. \quad \text{(B.4)}$$

Eliminating C_1 and C_2 from (B.3) and (B.4) we have

$$\xi(s, t) = \left(s+\frac{A}{B}\right)^{-2}\psi\left[\frac{s\phi}{s+A/B}\right], \quad \text{(B.5)}$$

where $\psi(y)$ is an arbitrary function of its arguments to be determined from the initial condition on ξ. The initial condition in this problem dictates that as $t \to 0$, $p(n, t) \to p_1(0)\,\delta(n-1)$. Using this we have

$$\lim_{t \to 0} \xi(s, t) \to p_1(0) \exp -s. \quad \text{(B.6)}$$

Here $p_1(0)$ corresponds to the amount of vacancies introduced at the beginning of the growth and is equal to

$$p_1(0) \simeq N_0 - \frac{N_0 x_2}{N_0 + x_2}.$$

Thus
$$\psi\left(\frac{s}{s+A/B}\right) = (\exp -s)\left(s + \frac{A}{B}\right)^2 p_1(0) \tag{B.7}$$

Then
$$\xi(s, t) = p_1(0) \exp\left[-\frac{A s \phi}{B[s(1-\phi) + (A/B)]}\right]$$

$$\times \left(\frac{A}{B}\right)^2 \left[\frac{A}{B} + s(1-\phi)\right]^{-2}. \tag{B.8}$$

The method of inverting (2.8) and obtaining $p(n_1 t)$ is the same as inverting $\chi(s, t)$ and has been outlined in Appendix 1 of paper IV.

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